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3 STANDARD FIELD CHEMISTY TEST

Standard Field Chemistry Tests

The most common field test parameters for water sampling are pH, conductivity, temperature and dissolved oxygen. Other parameters may include oxidation/reduction potential (ORP), total dissolved solids, specific ions and turbidity. Parameters chosen will depend on the survey objectives.

Dissolved oxygen is a useful parameter in an environmental emergency or spill situation. It can help determine if the presence of a particular substance caused depletion of dissolved oxygen and why a fish kill may have occurred.

3.1 SINGLE AND MULTIPARAMETER METERS

Single and multiparameter instruments for immediate, on-site measurement of water quality are available from several manufacturers. Typically, these instruments will measure temperature, pH, conductivity, oxidation/reduction potential, dissolved oxygen, turbidity and depth. Additional probes are available for ammonia, nitrate, chloride, chlorophyll, blue-green algae and dyes like Rhodamine. These instruments come in a waterproof housing and can be immersed in natural watercourses and reasonably slow-moving effluent streams to collect real time measurements. Some units provide global positioning (GPS) capability and data logging and computer interface and can be left unattended to operate. There are also mapping programs which can produce site maps in real time which can aid in source detection and follow up sampling planning. Most have electrochemical sensors that are specific to each parameter and these sensors must, of course, be individually calibrated against reference solutions.

Consult the manufacturer's manual for applicable operating procedures, calibration and upkeep for each instrument.

FIGURE 3.1:
Single and multiparameter meters can monitor pH, dissolved oxygen, conductivity, salinity, temperature and other criteria depending on the number and types of probes. (Courtesy of Canada – DOE)

3.2 FIELD MEASUREMENT OF PH

Field measurement of pH is very important since many chemicals change behaviour depending on pH and should be measured at each water site if possible. For example, dissolved metals are more biologically available and therefor more toxic at lower pH than at higher pH. Information concerning pH is therefore very important for experts who examine the sample analytical results and provide reports on toxicity and environmental impact. pH values can change over time, therefore field measurement provides the optimum results. Subsequent laboratory measurements can provide supporting information. The field measurements can be compared with those obtained in the laboratory to determine if any significant changes or unacceptable deterioration in samples has occurred during transport.

There are many types of pH papers which operate on a colorimetric spectrum and pH meters. pH paper is the lowest cost option and easiest to use; it does not require calibration but has less sensitivity. When using pH paper, it is recommended that the relevant pH buffer standards, usually pH 4.0, pH 7.0 and pH 10.0 are purchased and routinely used to test the paper.

pH meters all have similar operating principles. Using the pH meter is a two-stage operation: the meter is calibrated against a buffer solution of known pH value at a standard temperature and then the sample's pH is checked. In many pen-type pH meters, the pen tip is susceptible to drying out. If the tip dries, the meter will not respond. Check to see if your pH meter tip needs to be kept immersed in solution or high humidity environment and monitor this regularly.

FIGURE 3.2:
Single use pH paper or single parameter pH meters. (Courtesy of United States - EPA/Canada - DOE)

To calibrate a pH meter, follow the manufacturer's recommendations. However the general procedure is as follows:

1. Obtain the relevant pH buffer standards, usually pH 4.0, pH 7.0 and pH 10.0. Some meters will calibrate over this range, other meters will require the pH buffer solution closest to the measurements expected at the field site.
2. Obtain pH paper which covers the range expected at the field site.
3. Obtain distilled or de-ionized (DI) water for rinse purposes.
4. Allow all solutions and the meter to reach room temperature. If the meter does not automatically adjust to temperature, check the temperature of both solutions with a thermometer and record the results.
5. Follow the manufacturer's recommended procedure for calibrating at each buffer solution pH. The pH buffer solution may only be used once for calibration and should be discarded since there is flow through and liquid exchange between the pH probe and the buffer solution. Buffer solutions have a limited shelf life. Remember to check the expiry date before taking the buffer solution into the field. All buffer solutions and pH paper must be stored in a clean, dry environment.
6. Remember to rinse the probe with DI water after checking the pH with each buffer solution.

3.3 FIELD MEASUREMENT OF TEMPERATURE

Field measurement of temperature is very important since oxygen and other gases have varying solubility at different temperatures. High temperature may result in low dissolved oxygen and can contribute to the death of aquatic organisms. High temperature may also directly kill aquatic organisms or cause many organisms to avoid the utilization of temperature affected habitat. Temperature may be measured by electronic probes or glass thermometers.

FIGURE 3.3:
Temperature probes range from glass thermometers in a stainless steel casing to single measure or multiple measure probes which can record data. (Courtesy of United States and EPA/Canada - DOE)

3.3.1 USING GLASS THERMOMETERS

1. Use only calibrated thermometers and avoid using mercury thermometers as they are susceptible to causing mercury contamination if they break. A glass thermometer should be contained inside a cylindrical metal casing to prevent breakage. It may take longer for the casing and the thermometer to reach temperature equilibrium.
2. It is preferable to stand the thermometer in the sample in situ, ensuring that the top of the liquid is level with the thermometer immersion line. Allow the thermometer to equilibrate for at least 3 minutes.
3. If a sample is to be taken from the site, the container should be allowed to reach temperature equilibrium with the water before it is taken from the stream. The smaller the size of the container, the faster that ambient temperatures will cause a change in temperature of the liquid. Therefore, collect the water sample in at least a 125 mL wide-mouth bottle.
4. Stand the thermometer in the sample container, ensuring that the top of the liquid is level with the thermometer immersion line. Allow the thermometer to equilibrate for at least 3 minutes. Read the water temperature by holding the bottle and the thermometer at eye level and keeping the bulb of the thermometer submersed in the sample. Record the temperature to the nearest 0.5 °C.

3.3.2 USING ELECTRONIC THERMOMETERS

1. Make sure the instrument is properly calibrated according to the manufacturer's recommendations and specifications.
2. Rinse the sample container and the probe at least 3 times with the sample water until it is equilibrated with the temperature of the liquid.
3. Make sure the probe does not touch the sides or bottom of the sample container.
4. Take the reading, then repeat the procedure with fresh samples until reproducible readings are obtained that are within +/- 5% of each other.

3.4 FIELD MEASUREMENT OF DISSOLVED OXYGEN

Dissolved oxygen can be measured either by chemical titration or by the more commonly used oxygen-sensitive membrane electrode. Dissolved oxygen is particularly sensitive to changes in elevation where atmospheric pressure changes between sites may cause dissolved oxygen to increase in saturation at low elevations or decrease in saturation at high elevations. If the equipment does not have automatic re-calibration due to changes in barometric pressure and/or elevation changes, then manual re-calibration after significant elevation changes may be required.

3.4.1 DISSOLVED OXYGEN BY CHEMICAL TITRATION

Chemical titration may be done using field kits or at the laboratory commonly using a manganese/alkali-iodide-azide method. Follow the field kit or laboratory procedures. Chemical titration is susceptible to error caused by changes in elevation. Therefore, the test must be done quickly if the sample is moved from a site that has a significant difference from the location where the analysis is done.

Dissolved oxygen concentration may be "fixed" in the field by adding the following reagents, which have been formulated by the support laboratory to the correct concentration to a 1.0 L sample of water:

1. Add 1.0 mL manganese (II) sulphate*.
2. Plus, add 1.0 mL alkali-iodide-azide solution*.
3. Close the sample so as to exclude air.
4. Shake the sample to ensure mixing of the fixative reagents.
5 Conduct the titration at the laboratory using the approved reagents. See TABLE 2.9.3.20

*As specified in the latest edition of standard methods for the Examination of Water and Wastewater (American Public Health Association).

3.4.2 DISSOLVED OXYGEN BY ELECTRONIC PROBE

Ensure the probe is calibrated and equilibrated to the site elevation and water salinity before each reading is taken. Therefore, if the probe is calibrated at the laboratory, it may require a field calibration if there has been a significant change in elevation between the two sites. Water turbulence can increase dissolved oxygen which may mask overall low dissolved oxygen concentrations. Therefore, if possible, select a sample site with steady even flow.

Follow the manufacturer's instructions for transportation, storage, calibration and measurement of the dissolved oxygen meter and probe. The membrane must be changed if the automatic system check indicates a problem or if deterioration is noticed and readings become unstable. Watch for trapped air bubbles under the membrane and discoloration of the internal white electrode.

3.5 FIELD MEASUREMENT OF CONDUCTIVITY

Electrical conductivity of water is a critical indicator of chemical pollution and generally efficient and inexpensive to use. Clean fresh water has very low conductivity as there are very few dissolved charged particles or atoms to conduct electric current. Conductivity will increase due to dissolved salts or dissolved metals in the water. Therefore, high conductivity may indicate that salt has entered fresh water.

Salt may enter a system by:

- Saltwater intrusion from the ocean
- Industrial operations
- Dissolved from rocks at a mining operation or waste landfill

Metals can also cause a rise in conductivity. Metals may enter a system by:

- Dissolved from broken rocks at mine tailings
- From mineral processing plants or industrial operations, such as metal smelting and foundry waste or metal plating operations
- Municipal waste landfills

Electrical conductivity is commonly measured in milli (mS) or micro Siemens (µS). TABLE 3.1 illustrates the common ranges of conductivity. Therefore, if conductivity is outside these ranges, a pollution source should be suspected.

Table 3.1 | Electrical Conductivity of Water from Various Sources

TYPE OF SOLUTION	AVERAGE CONDUCTIVITY
Distilled water	0.5 to 3.0 µS
Melted snow	2 to 42 µS
Drinking water	30 to 1500 µS
Freshwater streams	100 to 2000 µS
Brackish water in estuaries	2000 to 19,000 µS
Salt water in seas and oceans	19,000 to > 50,000 µS

Conductivity probes can be used to very quickly and inexpensively search for or map out salt or metallic pollution sources from outfalls or in groundwater by mapping out areas of low or high conductivity. When investigating a site, conductivity probes can be lowered into the water at various locations and depths starting at a background site and moving towards a suspected source or at a source and moving away towards a background site. This flexibility allows the potential or actual source to be detected and a potential zone of impact mapped out. To detect contaminated upwelling groundwater, the probes can be lowered from a bridge or boat so that the probe is just at the sediment/water interface. A change in conductivity (and often temperature and dissolved oxygen) may indicate a source of contamination and further sampling and tests can be done to confirm whether pollution is present.

A conductivity probe may be a single probe or included in a multimeter with dissolved oxygen and pH probes. To calibrate a conductivity meter, follow the manufacturer's recommendations. However, the general

procedure is as follows:

1. Do not use the same sample that has been used to measure pH because the pH electrode changes the conductivity of the sample.
2. Obtain the relevant conductivity standards, within the range expected at the field site.
3. Obtain distilled or de-ionized (DI) water for rinse purposes.
4. Allow all solutions and the meter to reach room temperature. If the meter does not automatically adjust to temperature, check the temperature of both solutions with a thermometer and record the results. Conductivity probes are less sensitive to changes in elevation than dissolved oxygen probes, so calibration is easier.
5. Follow the manufacturer's recommended procedure for calibrating at each conductivity.
6. Remember to rinse the probe with DI water after checking conductivity with each conductivity solution.
7. Conductivity solutions have a limited shelf life. Remember to check the expiry date before taking the conductivity solution into the field. All conductivity solutions must be stored in a clean, dry environment.

3.6 FIELD MEASUREMENT OF AMMONIA

Ammonia is a common pollutant originating from many industrial operations, mining (where ammonium nitrate is used as a blasting chemical), fish and meat processing operations, animal barns and feedlots. Ammonia can be highly toxic to both terrestrial and aquatic organisms.

3.6.1 COLLECTING AND TESTING AMMONIA IN WATER SAMPLES

Ammonia in water can be detected using field kits that use reagents to cause a color reaction in the sample. These can be purchased from suppliers and used in the field to obtain reasonably accurate estimates of dissolved ammonia. If ammonia is detected in a field test, a water sample that is collected must be collected so that there is very little gas space in the sample jar, called the "head space". This prevents dissolved ammonia from flashing into the head space and being lost. The sample must be kept cool (4°C) and transported to the laboratory as soon as possible for analysis.

FIGURE 3.4:
Portable ammonia test kits are valuable for field measurements as ammonia is volatile and should be measured as soon as possible. (Courtesy of Canada – DOE)

3.6.2 COLLECTING AND TESTING AMMONIA IN AIR SAMPLES

The sampling and testing of ammonia in air often requires specialized equipment that captures the vapours or exhaust from an industrial operation and analyses it in a detector. Some devices use intake nozzles to extract a portion of the air flow into a detector. These methods can be complex and cause disturbance of the operation being investigated. Gas detection tubes use a chemical substance inside a glass tube which reacts and changes color when in contact with ammonia. These can be hand-held units which consist of a small pump that holds the glass tube. The ends of the tube are broken open and inserted into the holder which then pumps the suspected contaminated air through the tube. A color change specific to ammonia indicates its presence or absence. Open space optical ammonia detectors use a light source in the ultra violet (UV) or infra-red (IR) range beamed through an open space to a detector. The detector can be up to 750 m away. This method causes very little disturbance of the operation being investigated.

Photo-acoustic detectors operate by passing gas through a detection tube through which light of a specific wavelength is shone. As the light is absorbed at different concentrations the brightness of the light hitting the detector is converted to an audio signal. The intensity of the audio sound indicates the concentration of ammonia.

There are many other ammonia detection systems which use similar combinations of detection. For field use, gas detection tubes are the most common and generally the lowest cost.

3.7 FIELD MEASUREMENT OF WATER CLARITY

Water clarity can be an important environmental factor. The degree of clarity gives an indication of the ability of light to penetrate the water column and allow organisms to see or carry out photosynthesis. The greatest impact on water clarity is by suspended solids and colloidal suspensions and surface films which may degrade the water quality when discharged from pollution sources. In the field, water clarity is usually measured with a Secchi disk, which is a circular disk that has two opposing white quadrants and two opposing black quadrants and is usually 20 cm to 30 cm in diameter, or a "Triton Turbidity Wedge" or by photo-meters.

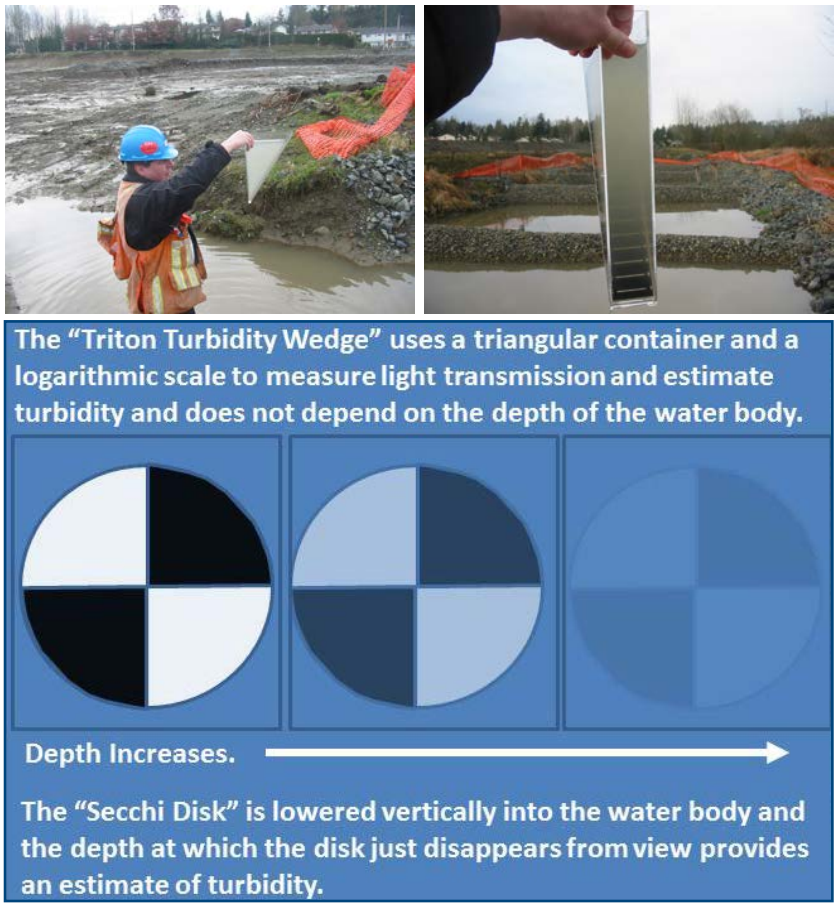


FIGURE 3.5:
Simple field methods of measuring turbidity. (Courtesy of Genesis Environmental Sciences Ltd. and Triton Environmental Consultants Ltd)

SUGGESTED PROCEDURE

The use of the Secchi disk has inherent variability due to the different visual acuity of the user, and differing light intensities due to seasonal and weather conditions. Therefore, steps should be taken to minimize the variability.

- Avoid taking readings during high wave conditions and at dawn or dusk.
- The same person should take all the readings at a site and should record if they are wearing polarized glasses to reduce the impact of reflected glare.
- The readings should be taken between 09:00 and 15:00 if possible.

- The readings should be taken from the shady side of the boat to reduce impact of reflected glare.

1. Lower the Secchi disk into the water to the depth where the pattern is no longer visible. Record the depth.
2. Raise the Secchi disk till the pattern becomes visible.
3. Repeat the raising and lowering and record the depths at least three times. The average of the depths becomes the "extinction depth" to the nearest 0.1 m.
4. Record the date, time, atmospheric and water conditions in your notebook.

3.8 MISCELLANEOUS FIELD TEST KITS

Accidents and spills often involve unknown hazardous or toxic substances. In planning an early and efficient response to the emergency, one necessary first step is to determine what compounds or chemicals you are dealing with. Hazardous chemical categorization kits use various reagents and tests to determine what the spilled product might be. These kits have improved over the years and are now more user friendly. They do tend to be very expensive and require some maintenance.

Chemical categorization strips often use a chemical on paper (such as pH test strips) which react to produce a color change. These are inexpensive, disposable and often have a two-year shelf life.

They can be used to determine if the product:

- is acid or alkaline.
- is an oxidizer.
- contains fluorides, iodine, chlorine or bromine.
- involves organic solvents.

Kits also exist to determine the presence of PCBs in transformer oil or soil. These kits are relatively inexpensive and easy to use. They are disposable and have a two-year shelf life.
All of these kits should be used as screening tools to determine the presence or absence of an environmental contaminant. If the contaminant is suspected or confirmed then a sample should be collected in a proper container according to the recommended protocol in SECTION 2.9

3.9 DYE TESTS

Dyes may be suitable for detection or demarcation of pollution in either salt or fresh water, depending on their solubility. For most environmental inspection and investigation purposes, dyes are used (**1**) to verify or locate the final discharge point of spills or effluents that go through a closed or otherwise unobservable path (e.g. culverts, storm drains, drainage tiles, piping or groundwater) before discharging to the environment and (**2**) to delineate a zone of impact. The dyes used have very low environmental toxicity and generally are simple and low cost to use. They are often brilliant green, orange or red.

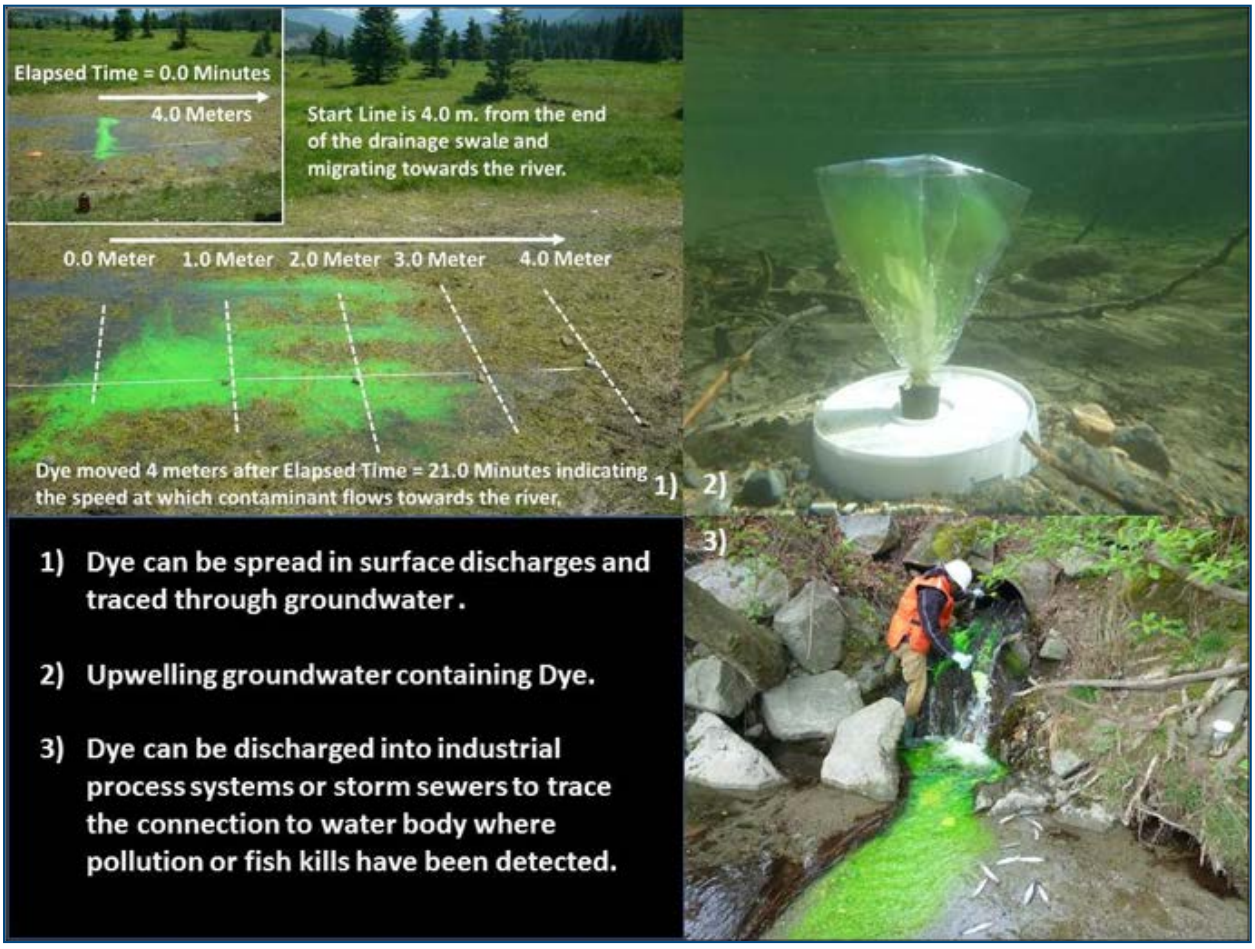


FIGURE 3.6:
Sequence of Fluorescein dye to estimate seepage flow and connection to industrial discharges and sewers. (Courtesy of Canada – DOE)

The dyes may be measured by visually observing the colour in the water after the dye is released. The dyes are visible in the part per billion range at very specific light wavelengths and may be measured by visual observation or using a spectrophotometer. The specificity of the wavelengths makes them good for legal investigations.

When using dyes, remember:

- Once wet, dye will stain everything it touches and is extremely difficult to remove from clothing, hands, equipment, etc.
- Only conduct dye testing after obtaining all other samples.
- Inform emergency response agencies and local water authorities

that you are conducting dye tests, as the resulting brightly coloured fluorescent waters will lead to many enquiries.
- Any equipment used to handle the dye will have to be bagged and disposed of since cleaning it is almost impossible.
- Low concentrations of Fluorescein dye exposed to sunlight will be visible for an hour or more.

3.9.1 TYPES OF DYES AND DYE MEASUREMENT

Two of the most common tracer dyes are Intracid Rhodamine WT and Fluorescein (xanthene dyes), which are water-soluble dyes commercially available for dye testing.

- Intracid Rhodamine WT is available as a dark red liquid, in a 20% solution. It turns water a bright, fluorescent orange colour. Intracid Rhodamine WT is less susceptible to ultraviolet light (UV) degradation than Fluorescein, less readily absorbed by fine particulate matter and is less toxic, which makes Intracid Rhodamine WT the dye of choice for determining effluent flows using fluorescence.
- Rhodamine WT will absorb light in the 567 to 579 nanometre wavelength for use with spectrophotometers.
- Fish toxicity of Intracid Rhodamine WT (determined by 96h LC50 rainbow trout) is 320,000 ppb making it about 10 times less toxic than Fluorescein.
- Fluorescein (an orange crystalline powder) turns water a fluorescent yellow-green colour. Fluorescein is the dye of choice for tracing enclosed piping, as it is rapidly destroyed by ultraviolet (UV) light.
- Fluorescein is visible to the trained eye in clear water at 10 ppb and to the untrained eye at 100 ppb; therefore aim for a concentration of 1 000 ppb or more. This is based on commercial dye strength of 35% - 37% dye/powder.
- Fluorescein will absorb light in the 515 to 519 nanometre wavelength for use with spectrophotometers.
- Fish toxicity of Fluorescein (determined by 96h LC50 rainbow trout) is 1,372 to 3,433 ppb.

3.9.2 DESIGNING A DYE TEST

Dye tests can be done by visual observation or by spectrophotometer.

3.9.2.1 Dye Tests Using Visual Observation

For a simple test, the dye can be mixed so that it remains visible to the eye from the point of release to the point of discharge if it is used to confirm the route of a piping system.

1. Position personnel at observation points along the piping system or watercourse to record the progress of the dye slug. This includes removing manhole covers and inspection grates to allow visual inspection.
2. Introduce the dye directly into the watercourse, gently flushing it in with a stream of water.

3. Record the time at which the dye was introduced and the times at which it appears at the observation points. If possible photograph the dye as it appears at each point.

Note: If the dye becomes too dilute or the water is too high in turbidity, this type of test may not work well. It may also not work well to trace contaminated groundwater as the dilution may be too great to visually see the dye, therefore a spectrophotometer may be required.

CALCULATION OF THE VOLUME OF DYE TO BE USED IN A VISUAL OBSERVATION TEST

To calculate the amount of dye to be added, use the following formula. You will have to estimate the variables.

Vd = (QL/V) Cp

Vd = volume (mL) of dye
Q = discharge rate (m^3/s)
L = length of flow path (km)
V = velocity (m/s)
Cp = concentration (ppb) at terminal site

3.9.2.2 Dye Tests Using a Spectrophotometer

In the low part per billion ranges or in highly turbid water or dispersed in groundwater, the dyes may be visible using a spectrophotometer. Dyes will absorb light at very specific wavelengths, which provides an efficient and very low cost method of detecting them. A spectrophotometer uses a specific wavelength of light and shines it through a sample of water in a glass vial. The concentration of dye in the water is proportional to the amount of light absorbed and therefore a light detector on the other side of the vial can provide a signal which is measured on the meter.

3.9.3 CREATING OPTICAL MIXTURES OF DYE

Solutions of dye can be made at specific concentrations so that concentrations of pollutants can be estimated very inexpensively by co-relating the dispersion of the dye to a known pollutant concentration.

The general procedure for making standard dye solutions is as follows:

1. Mix #1 - Mix the dye at known concentrations by weighing 1.0 gram into a 1.0 litre volumetric flask and filling with DW or DI water = 1,000,000 µg/L
2. Mix #2 - Take exactly 50 ml of Mix #1 and pour into a 1.0 L volumetric flask and fill it with DW or DI water = 50,000 µg/L
3. Mix #3 - Take exactly 50 ml of Mix #2 and pour into a 1.0 L volumetric flask and fill it with DW or DI water = 2,500 µg/L
4. Mix #4- Take exactly 50 ml of Mix #3 and pour into a 1.0 L volumetric flask and filling with DW or DI water = 125 µg/L
5. Mix #5- Take exactly 50 ml of Mix #4 and pour into a 1.0 L volumetric flask and filling with DW or DI water = 6.25 µg/L

(This process can be repeated to make lower concentrations, or dilution volumes can be altered to vary the concentration.)

6. Start with the lowest concentration to the highest concentration and pour a sample of each mixture into the spectrophotometer glass vial and measure the absorbance. Rinse the sample holder between samples with DW or DI water and clean with an optical paper.

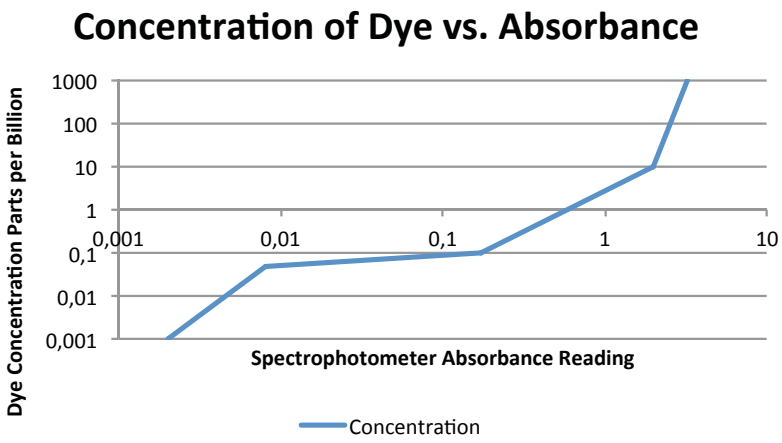


FIGURE 3.7
Plot dye concentration vs. absorbance (logarithmic scale) for use in the field to estimate pollutant concentrations and confirm sewer connections. (Courtesy of Canada – DOE)

7. Plot the absorbance on the "X" axis and the concentration on the "Y" axis of a graph. This will generate a curve (often a straight line) where the higher the absorbance the higher the dye concentration.

3.9.4 CONDUCTING THE SPECTROPHOTOMETER DYE TEST IN SURFACE WATER OR A PIPING SYSTEM

1. Position personnel at observation points along the piping system or water course to record the progress of the dye slug. This includes removing manhole covers and inspection grates to allow visual inspection.
2. Trace the dye by injecting the highest concentration mix using an injection pump at a constant rate into the watercourse or piping system at the starting location of the test.
3. Collect samples at various times at each sampling point. Test samples by taking water samples and placing them in the spectrophotometer. Record the time at which the dye was introduced, the time at which it appeared at each sampling point, the time each sample was collected, and the absorbance at each observation point.
4. Use the graph to estimate the concentration of the dye and the dilution rates.

For example, assume an outfall pipe discharges a pollutant at 100 parts per million and the dye is injected at the discharge point and subsequently sampled at a downstream point. If the dye concentration at the downstream point is 1/10th the original concentration, then the pollutant is also likely to be 1/10th the original discharge concentration. Since the dye can be measured immediately on site using a spectrophotometer, the investigator can quickly determine the spread and potential impact of the pollutant at a very low cost.

3.9.5 CONDUCTING THE SPECTROPHOTOMETER DYE TEST IN GROUNDWATER

The dye can be injected into up-gradient groundwater well(s) and allowed to percolate with the groundwater towards downstream wells or surface water bodies. Samples can be collected from downstream wells or from upwelling groundwater and measured with a spectrophotometer.
Absorption media (usually activated carbon in a mesh bag) can also be planted by suspension in the downstream wells or implanted into the bank/bottom sediment of the water body. The absorption packets are collected after an exposure period (usually several days or weeks depending on the known or suspected rate of groundwater flow) and the dye is extracted using solvents and the concentration of the extract is measured by spectrophotometry.

3.10 INFRA-RED AND RADIOACTIVE SCANNING TESTS

Hand-held field equipment which uses infra-red or radioactive scanning can provide field screening analytical results in very short time frames. These may be more than $50,000 for a typical unit and are cost effective where large quantities of materials or large sites must be examined.

Hand-held Fourier Transform Infrared (FTIR) Spectroscopes can qualitatively analyse multiple chemical components such as ammonia, boron trichloride, phosgene, nitric acid, sulfur dioxide, arsine, boron trifluoride, carbon disulfide and hydrogen cyanide, and is especially useful for safety screening and sample screening at contaminated sites and chemical hazard situations.

FIGURE 3.8:
Hand-held X-ray fluorescent (XRF) analysers have the capability to quantify or qualify nearly any element from magnesium to uranium, depending on specific instrument configurations. These are particularly useful for heavy metals contaminated sites. (Courtesy of United States - EPA)

4 COMMON FIELD SAMPLING EQUIPMENT

Common Field Sampling Equipment

Field sampling equipment must be specific to the required task and the conditions under which the sampling is undertaken. Unique situations usually require the acquisition of specialty equipment and/or expertise. The following list comprises the equipment that is useful for the majority of situations an environmental enforcement officer is likely to experience

4.1 FIELD EQUIPMENT CARE AND GENERAL MAINTENANCE

Field instruments are usually battery powered and may require special batteries not easily available in remote locations. Rechargeable nickel-cadmium (Ni-Cad) batteries may be affected by prolonged storage periods. Ni-Cad batteries can develop a memory loss if not cycled occasionally. During storage, you should try to discharge and recharge these batteries occasionally to keep them in good condition. Also, some pH meters may continue to use battery power to maintain their calibration even though the power is off, so it is a good idea to remove the batteries from such units during extended storage periods. Never change batteries under explosive conditions. Dispose of Ni-Cad batteries as hazardous waste or at a recycling operation.

Before leaving on your sampling trip, make sure that you understand the field equipment's operation and maintenance requirements and that you have included any necessary spare parts, calibration standards, and batteries. Meters should be calibrated prior to departure for the field as this will ensure that the meters are operating properly.

IN THE FIELD

Ensure that equipment has been properly calibrated or standardized according to the manufacturer's recommendations. The frequency of calibration or standardization will vary. Document your calibrations including expiration dates of buffer solutions and any meter adjustments made. Ensure that equipment is safe for field conditions. Protect equipment from temperature extremes. If equipment is left in a vehicle, solutions may freeze in the cold or deteriorate from excess heat. Protect equipment from physical damage and be aware of the proper care and handling of each instrument.

In certain situations, samplers may be required to conduct air monitoring to determine if combustible vapours or specific air contaminants are

present, particularly during environmental emergencies. Equipment for this includes explosimeters and various portable analysers and detectors. Since this type of field equipment is quite variable and specialized, its use will not be covered in this manual. The manufacturer's instructions should be consulted.

4.2 AUTO SAMPLERS

Automated samplers, or auto samplers, can be used in various applications, most often in sampling industrial locations, sewers or similar locations where a representative sample over a fixed time period (e.g. 24 hours) is required. Auto samplers must be mechanically and electrically suited to the environment in which they will serve and should be easily accessible for routine inspection and maintenance. The three most important characteristics of an automated sampler are its ability to obtain a representative sample, its material composition, and its temperature stability.

FIGURE 4.1:
An auto sampler which can be programmed to collect single or composite samples on a regular or irregular time basis or triggered by water quality (pH, temperature, dissolved oxygen, conductivity, flow, etc.) (Courtesy of Canada – DOE)

There are various manufacturers of auto samplers. Many of these units have a digital programming capability and are versatile enough to be used in a variety of situations. Some features include:

- Battery or AC power capability
- Rugged construction and ability to function in adverse conditions
- The ability to control sample temperature (generally an insulated base for adding ice)
- Easy-to-use controls and programming functions
- Ease of maintenance and cleaning
- The ability to collect composite or individual samples
- A purge function (flushes the intake line between samples)
- Multiplex feature (ability to distribute one sample over several bottles or more than one sample per bottle)

- Minimal contact of sample with materials in the sampler
- The ability when used with flow measuring equipment to allow for flow-proportional sampling
- Screened and weighted intake line
- Portability and versatility (for different locations)
- High-speed peristaltic pump capable of lifting a static head of about 6 m (20 ft)

Follow the manufacturer's recommendation for setting up the auto sampler. The sampler should produce sufficient volume at the end of the desired sampling period (usually 24 hours).

In setting up an auto sampler, take the following into consideration:

- Install the sampler as close as possible to sample a free-flowing location, preferably at a point of thorough mixing.
- If using the purge function, keep the sampler above the discharge point of the tubing to ensure that the purge cycle will completely drain the intake line.
- Depending on the analytes of interest, use a stainless steel, Teflon or plastic intake screen to avoid plugging the sampling line with suspended solids. The intake should be weighted to hold it in place in the effluent stream. During sampling, it may be necessary to clean the screens periodically (depending on the size of solids in the sampling medium).
- The sample receiving bottle should be plastic, glass or Teflon, depending on the analyte of interest.
- For preservation after sampling, maintain the sample temperature at 4°C using ice or a refrigeration unit. Also keep the sample in darkness to reduce any photo-degradation of the analytes of interest.
- For some samples, preservatives, such as nitric acid for metal analysis, may be added directly to the receiving bottle before you start sampling.
- Use minimal lengths of intake tubing to reduce contamination of the sample by the intake line. Replace the tubing with new line for each sampling site to minimize cross contamination.
- Monitor the temperature of the sample periodically during the sampling period, particularly if the sampling area is warm.
- In very cold weather, use heating cables to ensure that samples do not freeze; consider wind chill when installing the equipment.
- Keep an individual maintenance log book for each auto sampler.

After samples have been collected in an auto sampler, transferring samples from carboys to bottles is a potential source of error. Mix the sample in the carboy, thoroughly stirring with a clean stainless steel, Teflon coated bar, magnetic stirrer, solvent rinsed glass rod, or by swirling the carboy itself to ensure that results are representative. Partially fill (about 1/3) each of the sample bottles in turn, mixing the carboy contents as frequently as possible. Just before pouring, back-swirl the carboy to

stop the liquid from rotating and churn it up thoroughly, since suspended solids will tend to centrifuge towards the carboy walls. Repeat this process until all bottles are filled.

4.3 DRUM SAMPLERS

Sampling from drums, barrels and tanks can be accomplished with specialised plastic, glass, or Teflon tubes, with or without closure mechanisms.

FIGURE 4.2:
Glass composite liquid waste sampler "COLIWASA" or tube sampler. External glass tube contains the sample and the internal glass tube has a stopper which prevents sample from leaking out.
(Courtesy of United States - EPA)

4.3.1 TUBE SAMPLER (SAMPLE THIEF)

This sampler is basically a hollow glass or rigid plastic tube that can be of any length but is generally about 1.0 m long. The plastic sampler can be used for metals, strong alkalis and hydrofluoric acid sampling, and the glass sampler for organics.

SUGGESTED PROCEDURE

1. Insert the sampler into the material to be sampled to the desired depth.
2. Place your gloved thumb securely over the open end, pressing down

firmly to seal the tube and carefully withdraw the sampler.

3. Carefully place the lower end of the tube near the open end of the sample jar taking care not to touch the sides. Ease up on the pressure of the thumb or gently rotate the tube so as to break the seal and allow the contents to drain into the sample jar.
4. To stop the flow from the tube, increase pressure with the thumb.

4.3.2 COMPOSITE LIQUID WASTE SAMPLER (COLIWASA)

The COLIWASA is one of the most important samplers for liquid hazardous wastes and can sample larger containers. It allows representative sampling of multiphase wastes of a wide range of viscosity, volatility and solids content. Its simple design makes it easy to use and allows for the rapid collection of samples, minimizing the sample collector's exposure to potential hazards. Samples collected by a COLIWASA are depth-integrated which means if there are layers of different chemicals in a drum or tank, the COLIWASA will collect a sample from each layer. COLIWASA and similar tube or drum samplers are available in plastic, glass or Teflon. With some, the sampling tubes may be coupled together to extend their reach. The plastic types may be disposable and are used to sample most containerized liquid wastes except wastes that contain ketones, nitrobenzene, dimethylformamide, mesityl oxide and tetrahydrofuran. The glass or Teflon types use borosilicate glass or Teflon for the sampling tube, with Teflon parts. Glass however, is incompatible with strong alkalis or hydrofluoric acid solutions.

The main parts of the COLIWASA are the sampling tube, the closure-locking mechanism and the closure system. The sampling tube typically holds up to 1 L of liquid depending on its length and diameter, and consists of a translucent pipe 1.52 m long and 4.1 cm inside diameter, usually made of polyvinyl chloride (PVC) or borosilicate glass plumbing tube. The closure locking system consists of a sharply tapered fritted glass or neoprene stopper, attached to a 0.95 cm outside diameter stopper rod of either PVC or Teflon. The upper end of the stopper rod is connected to the swivel of a channeled aluminum bar. The aluminum bar serves both as a T-handle and loop for the sampler's closure system.

SUGGESTED PROCEDURE

1. Put the sampler in the open position.
2. Slowly lower the sampler into the liquid so that the liquid level inside and outside the tube is the same. If the level inside the sampler tube is lower than that outside, the sampling rate will be too fast, resulting in a sample that is unrepresentative.
3. When the sampler stopper hits the bottom of the waste container, close the shut-off valve at the bottom of the sampler. Slowly withdraw the sampler from the container.
4. Place a suitable container under the sampling tube and slowly discharge the sample into the container.

4.4 DEPTH SAMPLERS

4.4.1 SHORT, MEDIUM AND LONG EXTENDED POLES WITH CLAMP

Depth or extended pole samplers are used to collect liquid waste samples from disposal ponds, pits, lagoons and effluent streams. Their purpose is to allow extended reach and isolate you from possible danger. The sampler consists of an extendable pole with an adjustable clamp (to hold a sample container). Commercial extended pole samplers are available with a variety of clamping systems to hold the sample container and also manipulate the container to various angles. Improvised sampler holders can be made from:

- A golf ball retriever
- A 2- or 3-piece telescoping aluminum or fibreglass paint or broom tube

Whatever the handle is, it should be convenient to use and be easy to decontaminate. Telescoping tubes or paint roller extension poles are often available at hardware or swimming pool supply stores. Aluminum poles are lighter and will conduct electricity which can create an electrical shock hazard. Fiberglass poles are heavier but provide a degree of protection against electrical shock.

There are extended pole samplers that have a steel spring that attaches the pole to the container holder. These often present a serious disadvantage when sampling as the spring will swivel making it impossible to control the position of the opening of the sample container. This prevents the option of selecting a surface film sample or collecting a sample at a specific depth and is not recommended for common use.

SUGGESTED PROCEDURE

1. Assemble the sampler. Ensure all parts are solidly secured.
2. Rinse sampling clamp and container three times with water from the sample source.
3. Slowly submerge the container with minimal surface disturbance.
4. Allow sample stream to flow gently into container with minimal splashing.
5. Repeat collection if necessary. When container is filled, cap tightly.
6. Remove container and store sampler head (clamp) in plastic bags for subsequent decontamination or decontaminate on site before using it at a subsequent site.

4.4.2 WEIGHTED BOTTLE SAMPLER

The weighted bottle sampler consists of a weighted container holder attached to a length of cable made of rope, chain or wire and can be used to sample liquids in storage tanks, wells, sumps or other reservoirs that cannot be adequately sampled with another device.

FIGURE 4.3 :
Weighted bottle sampler being used.
(Courtesy of Canada – DOE)

The weighted bottle sampler can either be fabricated or purchased. Decontamination of the cable and the sampler is of concern and therefore non rusting chain or cable is preferred. However, safety in terms of non-sparking materials is also an issue especially in relation to flammable or explosive organic chemicals and petroleum products. Therefore, the cable and the container holder should be made of non-sparking materials, usually consisting of a lead or aluminum weight and container holder. The outside of the bottle is exposed to the waste and must therefore be properly decontaminated after use.

The bottle sampler may be used without a stopper if a continuous depth sample is required. If a specific depth sample is required, then a separate line and stopper release mechanism is required.

SUGGESTED PROCEDURE (SPECIFIC DEPTH SAMPLE)

1. Lower the sampling device to the required predetermined depth.
2. Pull out the bottle stopper with a sharp jerk on the sampler line and allow the bottle to fill completely.
3. Retrieve sampler.
4. Transfer sample into laboratory cleaned sample bottles.
5. Clean the sampler and line carefully.

4.4.3 DEEP WATER SAMPLERS AND DEEP PORE WATER SAMPLERS

Deep water samplers come in several forms, hollow tube, peristaltic, drive point, dredge and remotely operated vehicles.

4.4.3.1 Hollow Tube Samplers

Hollow tube trip mechanism samplers consist of a hollow tube attached to a weighted cable. The ends of the tube are open and the sealing lids are held back by a spring or elastic tube mechanism. The spring or elastic tube runs through the center of the sample tube. The sample tube may be mounted in a vertical or horizontal position. The tube is lowered to the desired depth by a cable. Therefore the inside of the tube is exposed to the entire water column as it is being lowered. A trip mechanism, usually a lead or steel messenger is sent down the cable and trips the release on the sealing lids which then close and trap a sample of water. The sampler is then lifted to the surface and the contents emptied into a prepared sample container.

FIGURE 4.4:
Hollow tube type water samplers with trip mechanisms.
(Courtesy of Brazil – Federal Police)

4.4.3.2 Peristaltic Samplers

Intermittent or continuous flow samples can be obtained by attaching proper tubing (usually polyethylene or Teflon) by a weighted mechanism into the water column and using a pump. Usually, a peristaltic pump can extract up to 6 metres of lift to collect a sample from the water column.

There are several commercially available samplers that allow collection of water samples at the epibenthic layer (the layer of water just above the bottom sediment) and sub benthic layer called the hyporheic zone. The hyporheic zone is the critical habitat zone where upwelling groundwater mixes with overlying stream, river, lake or ocean water. This is critical habitat and subject to pollution especially from upwelling contaminated groundwater.

BICKERTON DRIVE POINT SAMPLER

The Environment Canada - Bickerton drive point sampler is a short tube sampler with a drive point that can sample shallow zone. It is hand-held by wading or from a small boat usually to less than 2.0 meters of overlying water. The power source to drive the mechanism into the hyporheic zone

is usually a pneumatic hammer. This sampler has very limited water depth and current speed capability. Its lighter weight generally allows in excess of 8 sample sites per day.

K-INTERSTITIAL (KIST) WATER/GROUNDWATER/SEDIMENT SAMPLER

The Environment Canada KIST water/groundwater/sediment sampler is a very highly portable sampler that can connect to a peristaltic pump and be lowered to depths of at least 30 metres. The depth of water depends largely on the length of connective cable for an optional camera attachment that allows the water column and sediment bottom to be observed during deployment and operation. Video can be live streamed and stored on a laptop for later examination. The sampler can collect samples from the water column and the epibenthic layer (layer of water just above the sediment). Using a manual slide hammer percussion mechanism, it can drive a shallow piezometer or split spoon sampler up to a metre into the bottom sediment depending on the structure of the sediment substrate. Water samples are extracted by a peristaltic pump using tubing connected from the surface to the drive point mechanism inserted into the bottom sediment. Sediment samples can be collected using a split spoon attachment.

The high portability of the KIST sampler allows it to be used in remote areas on small boats with a 2 person crew or on large vessels in areas of high current up to 2.0 metres/second. Its lighter weight generally allows up to 8 sample sites per day.

FIGURE 4.5:
Hyporheic water and sediment core sampling features of the KIST sampler.
(Courtesy of Canada - DOE)

NEPTUNE TRIDENT WATER AND GROUNDWATER SAMPLER

The Neptune Trident water and groundwater sampler is a much larger and heavier sampler and generally uses a much larger winch mechanism to collect the same types of samples as the KIST sampler or the Bickerton sampler. It can operate to the same depth and current conditions as the KIST sampler except it requires a larger boat platform due to its larger weight, a larger crew, and heavier winch mechanism requirements. This means it has less portability relative to the other two samplers. The KIST and Bickerton samplers can be deployed from a 3 metre Zodiac-style or larger boat. The sediment penetration mechanism is hydraulic, requiring a power unit (generally pneumatic) to operate. The hydraulic power system of the penetration unit requires less manual power generation than the KIST or Bickerton samplers and typically allows up to 4 sample sites per day.

FIGURE 4.6:
Hyporheic water and sediment core sampling features of the Neptune sampler.
(Courtesy of Coastal Monitoring Associates – USA)

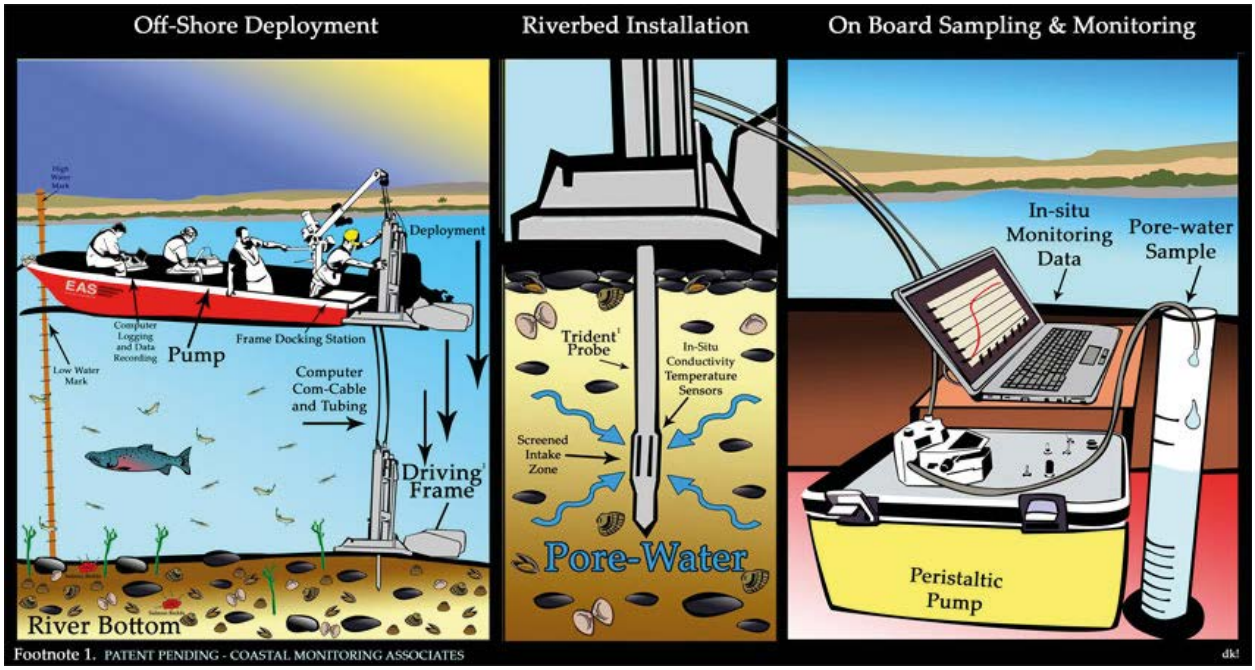


FIGURE 4.7:
Neptune hyporheic water sampler.
(Courtesy of Coastal Monitoring Associates – USA)

HEALTH AND SAFETY:

Each of these three samplers carries inherent health and safety risks which increase with the sampler weight. Since the samplers penetrate the sediment bottom, they can be susceptible to capsizing and sinking the support vessel should they be used in high current areas. For this reason, a safety support crew may be required for the KIST and the Neptune sampler, but especially for the Neptune as it requires a steel cable which is difficult to cut in an emergency. The lower mass of the KIST sampler allows a poly fiber to be used which is much easier to cut and jettison in an emergency. The KIST sampler is also a much lower cost so that its loss presents a much smaller financial burden.

4.4.3.3 Vacuum Samplers

The vacuum sampler system is a liquid waste sampling device that uses a sample tube attached to a vacuum pump. When the pump is operated, the sample is transferred from its original container to a sample container. Vacuums are particularly useful for sampling hazardous liquid wastes.

HEALTH AND SAFETY:

Care must be taken when using electronic pumps. Ensure that there are no fire or explosion hazards as motors and sparks can ignite flammable vapours.

SUGGESTED PROCEDURE

1. Assemble vacuum sampler, attaching tubing to pump and submerse suction end into the liquid.
2. Pump desired volume directly from container into laboratory cleaned sample bottle. Take care not to touch the outer or inner rim of the sample container with the tubing.

4.4.3.4 Remotely Operated Vehicle (ROV) Samplers

Remotely operated vehicles (ROVs) come in many sizes and depth capacities, and in general use an umbilical cable to control. Thus, depth of operation depends largely on pressure capacity and the length of the cable. Most can sample the water column using either a pump or a hollow tube trip mechanism. Cost and risk of operation are dependent on the size, depth capability, and the corresponding boat and crew requirements. Safety issues are similar to the other deep water samplers.

FIGURE 4.8:
Photo of peristaltic pump being used to extract groundwater from a shallow piezometer.
(Courtesy of Canada – DOE)

4.5 DREDGE/GRAB SAMPLERS

Dredge/grab samplers are used to sample shallow sludge and sediment, from silts to granular materials. Maximum penetration depth is 8 cm - 10 cm. Samples cannot be collected undisturbed. The dredge is a clamshell-type scoop activated by a counter-lever system. It has a screened or open top, allowing water to flow through freely when the dredge is in the open position during descent. Dredges are usually constructed of galvanized steel, brass or stainless steel. Various sizes are available. Larger versions may require a winch.

HEALTH AND SAFETY:

Take care in operating the dredge. Once the sampler is latched open, its jaws can snap shut like a bear trap with enough force to cause serious physical injury.

SUGGESTED PROCEDURE

1. Attach the dredge to the required length of sample line.
2. Secure the free end of the sample line to prevent accidental loss of the sampler.
3. Open the sampler jaws until they are latched. Support the sampler by its lift line or the sampler will be tripped and the jaws will close.
4. Slowly lower the sampler to the bottom and allow the sample line to slacken. When the line slackens, the latch releases, allowing the clamshell to close when the sampler is retrieved.
5. Slowly raise the sampler clear of the surface and open the clamshell into a sample tray.
6. Thoroughly decontaminate the sampler with water and appropriate solvent before next use.

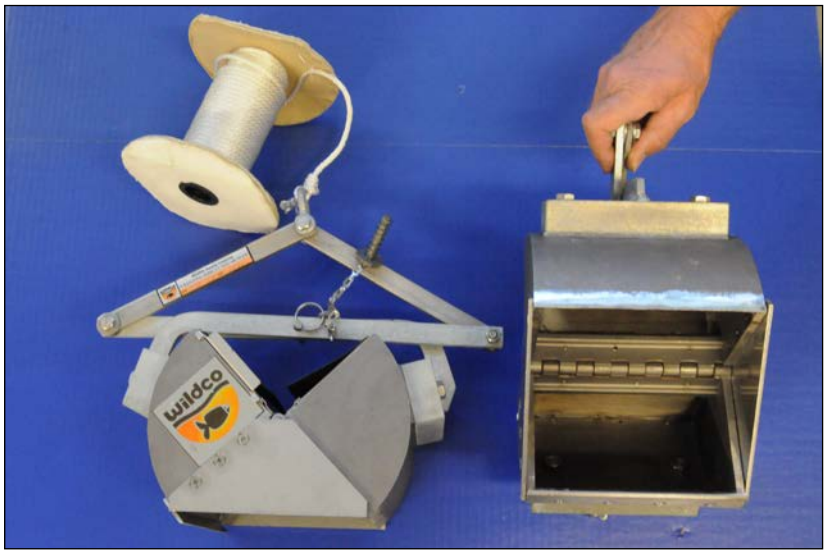


FIGURE 4.9:
Typical dredge for collecting surface sediment samples. (Courtesy of United States – EPA/ Canada - DOE)

4.6 SOIL SAMPLERS

4.6.1 SCOOPS, TROWELS AND SHOVELS

Soils can be sampled at or below the surface, depending on the type of information required. There are several different types of samplers that can be used to collect a soil sample. Scoops and trowels come in different sizes and makes. Many are coated with chrome paint which may peel off and contaminate the sample. Stainless steel blades are preferred. A trowel and shovel can be bought from a hardware store; the scoop can be bought from laboratory supply houses. An alternative sampler for small samples is a stainless steel tablespoon. Shovels are generally small, collapsible models. Include a dustpan for gathering loose or particulate solids with this equipment.

SUGGESTED PROCEDURE

1. Collect small, equal portions of sample from the surface or near the surface at specified intervals.
2. Transfer sample into laboratory cleaned sample bottles. For organic analyses, cover the mouth of the container with aluminum foil before capping tightly.
3. No preservative is generally required. Keep samples at 4°C or lower.

4.6.2 HAND PUSH TRIER

Sampling triers are similar to liquid triers and are used to sample moist or sticky compressed solids or soil. A typical sampling trier is a tube about 61 cm - 102 cm long and 1.27 cm - 2.54 cm in diameter, with a slot that extends almost its entire length. The tip and edges of the tube slot are sharpened to allow the trier to cut a core when rotated in a solid material. Sampling triers are usually made of stainless steel with wooden handles. The trier is pushed or hammered into the solid or soil to depth and then turned in a circular rotation to cut a cylinder of the solid or soil. Due to friction, extracting the sampler from the soil may require a jack mechanism.

FIGURE 4.10:
Typical reusable stainless steel and disposable plastic sample scoops
(Courtesy of United States – EPA/Canada - DOE)

SUGGESTED PROCEDURE

1. Insert the trier into the solid material at an angle up to 45º from the horizontal to minimize spillage from the sampler. Tilt the sample container if necessary.
2. Rotate the trier once or twice to cut a core of material.
3. Slowly withdraw the trier, making sure that the slot is facing upward.
4. Transfer the sample into a suitable container using a spatula or brush.

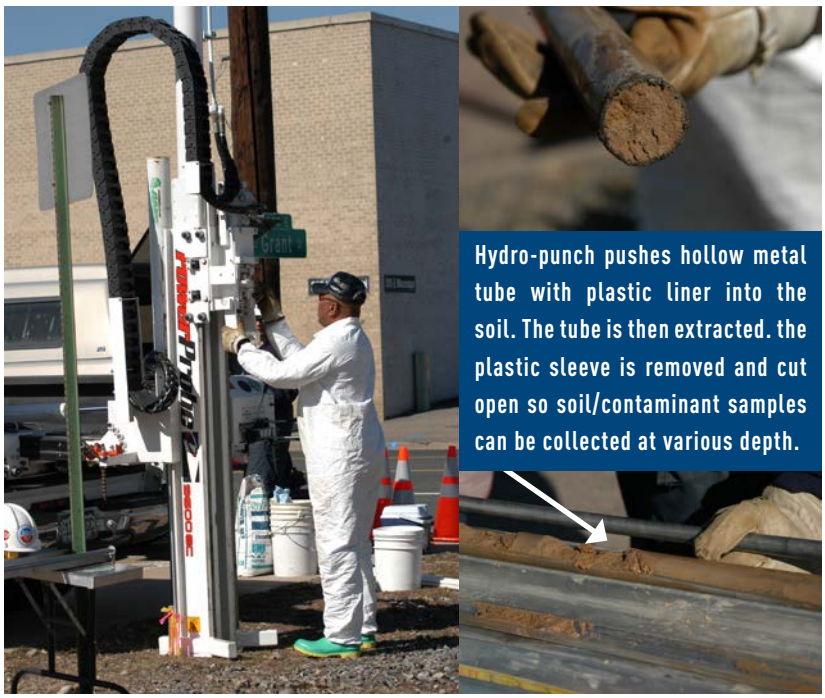
FIGURE 4.11:
Soil sampling trier.
(Courtesy of United States – EPA)

4.6.3 HYDRAULIC DIRECT PUSH SOIL SAMPLER

Direct push soil samplers refer generally to hollow tubes that are mounted in a hydraulic ram that can push the tube vertically or at a limited angle directly into the soil. There is no drill bit so the soil sample is collected as a column with the center of the sample undisturbed. The exterior of the core may be subject to smearing due to the motion of the tube penetrating the soil. The tube wall is generally thin and the end has a tapered edge to facilitate cutting into the soil. This type of sampler can be used where rocks and boulders are absent from the soil.

Thin-walled corers or Shelby Tubes can be used manually or with power equipment to obtain undisturbed soil profiles or sediment and sludge samples. They can also be used to collect samples through shallow overlying liquids. Samples may be extruded from the tubes for examination. Alternatively, if tube liners are used, the samples may be sealed and sent directly to the laboratory in the tube liner.

Push tubes used manually are straight tubes that are generally 5.1 cm or less in diameter and 1 to 3 metres in length. Larger diameter push tubes require the use of power equipment. A tapered nosepiece acts as the cutting edge of the tube. These samplers are generally constructed of chrome-plated or stainless steel and most can be adapted to hold brass or polycarbonate plastic liners. Some thin-walled corers have a handle to make it easier to drive the corer into the matrix. Corers may also have a check valve on top to prevent wash-out during retrieval through an overlying water layer. Samples from greater depths can be obtained by first auguring a hole to the desired depth and then attaching a push tube to a sampling head connected to the correct length of push rod extension.



Hydro-punch pushes hollow metal tube with plastic liner into the soil. The tube is then extracted. the plastic sleeve is removed and cut open so soil/contaminant samples can be collected at various depth.

FIGURE 4.12:
Portable hydraulic push type soil sampler mounted on truck. (Courtesy of United States – EPA)

SUGGESTED PROCEDURE

1. Push the corer into the material to be sampled with a smooth continuous motion until the tube is full.
2. Use the hydraulic ram to withdraw the tube from the soil.
3. Remove the nosepiece (if removable) and push the sample into the container or tray.
4. The solid core sample may be cut in half using a clean wire pulled length wise through the center to split the core.
5. The split core may be examined to determine stratified features and zones where contamination is believed to exist.
6. The outer edges of the core should not be used for samples if possible.
7. The samples should be collected from the center of the core where there is the minimum chance of cross contamination. Usually a pre-cleaned stainless steel spoon is used to gouge out a sample and place it into the appropriate wide mouth sampling jar. If organics are a concern then the sample should be collected as quickly as possible to minimize vapour loss and the jar should be covered with aluminum foil and then sealed with a lid.
8. Thoroughly decontaminate the sampler by washing with water and appropriate solvent.

4.7 GRAIN TYPE SAMPLER

The grain sampler is used for sampling powder, granular waste, grains contaminated with pesticides or other chemicals, or materials in bags, fiber drums, sacks or similar containers. This sampler is most useful when the solids are no greater than 0.6 cm in diameter. This sampler generally consists of two slotted telescoping tubes, usually made of brass or stainless steel. The outer tube has a conical pointed tip that permits the sampler to penetrate the containment bag and the material being sampled. The sampler is opened and closed by rotating the inner tube. Grain samplers are generally 61 cm - 100 cm long and 1.27 cm - 2.54 cm in diameter and are commercially available at laboratory supply houses.

SUGGESTED PROCEDURE

1. With the sampler in the closed position, insert it into the granular or powdered material or waste being sampled. Insert from a point near a top edge or corner, through the centre, to a point diagonally opposite the point of entry.
2. Rotate the inner tube of the sampler into the open position.
3. Rotate the sampler a few times to allow materials to enter the open slots.
4. Close the sampler and withdraw it from the material being sampled.
5. Lay the sampler flat, with the slots facing upward.
6. Rotate the outer tube and slide it free from the inner tube.
7. Transfer sample into sample containers.

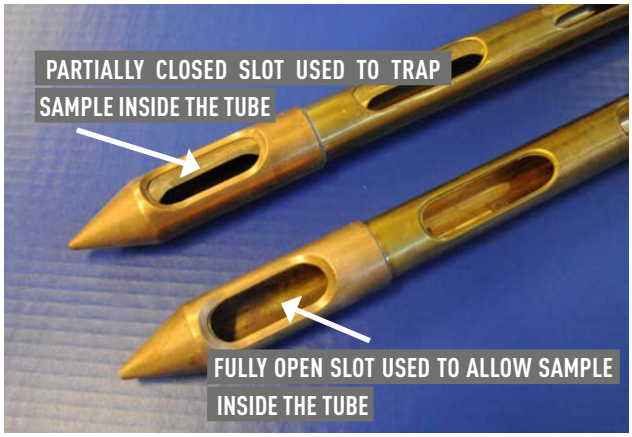


FIGURE 4.13:
Grain sampler for bulk dry materials sampling.
(Courtesy of United States – EPA/ Canada - DOE)

5

BEHAVIOUR OF LIQUIDS, FLOW MEASUREMENT AND MASS DISCHARGED

Behaviour of Liquids, Flow Measurement and Mass Discharged

Liquids such as water and other chemicals have properties of density (weight per unit volume), usually measured as kg/m^3, and this must be taken into consideration when sampling for pollutants.

Sampling should consider the physical conditions at the site and the characteristics of the known or suspected pollutant to determine where the optimum location is to collect a sample when a pollutant is discharged into water. TABLE 5.1 provides an example of how liquids might be found in a barrel of illegally mixed liquid wastes.

Table 5.1 | Density of typical chemicals used to make a "chemical cocktail" to hide illegal wastes in barrels and tanks

LIQUID	DENSITY	LAYER IN THE BARREL
Gasoline	850 kg/m^3	Top
Water	1,000 kg/m^3	Middle top
Salt water	1,025 kg/m^3	Middle bottom
Perchloroethylene (dry cleaning fluid)	1,623 kg/m^3	Bottom

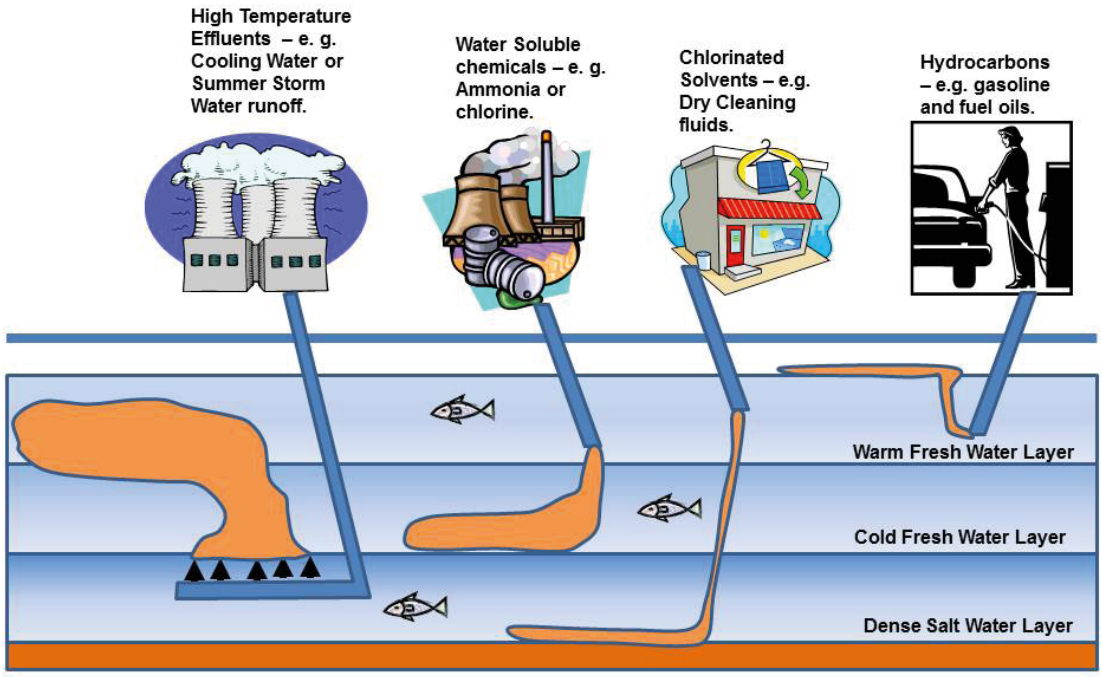
Dissolved components and temperature can further influence the behaviour of liquids and mixtures of liquids. These must all be taken into account when developing and executing a sampling plan. Therefore, just as liquids separate themselves in an illegal barrel of hazardous waste according to density, they will also separate themselves if illegally dumped into a body of water.

5.1 MIXTURES OF WATER OF VARYING DENSITIES

The behaviour of water is dependent on its dissolved content and temperature. These factors should be taken into consideration when collecting samples.

5.1.1 FRESH WATER

Fresh water generally refers to land based water sources that have little or no mineralised salt content, though many natural land based sources may be very high in mineral salts. Therefore, it can be further classified according to its electrical conductivity which is a measure of how much salt it contains (see TABLE 3.1, SECTION 3.5). Pure water has very



The temperature and density of pollutants and the receiving water must be considered when collecting legal evidence as the optimum location can vary depending on the conditions in the environment at the time of sampling.

FIGURE 5.1:
Behaviour of liquids of various density and temperatures. (Courtesy of Genesis Environmental Sciences Ltd.)

low electrical conductivity and a density of 1,000 kg/m^3 at 3.98 °C and free of air*. Deviations from this condition, especially temperature will change its properties, especially its density. Warmer water is less dense and will float on cold water. (*Handbook of Chemistry and Physics, CRC Press, Table F11)

5.1.2 BRACKISH WATER

Brackish water is a transition phase where fresh water, usually from streams, rivers or groundwater, mixes with salt water. Brackish water zones in estuaries are often particularly rich in bio-diversity and critical habitat for migratory fish. Migratory fish must switch liver and kidney functions from living in fresh water to salt water when they migrate out of and back into fresh water. The brackish water zones of estuaries provide the habitat for this to occur. Brackish water has intermediate conductivity (see TABLE 3.1, SECTION 3.5) and density between fresh and salt water.

5.1.3 SALT WATER

Salt water generally refers to water sources which have mineralized salt content, most commonly found in seas and oceans. (**Note:** Certain land areas which were once inland seas may have groundwater that still contains salt water.) Salt water has a very high electrical conductivity (see TABLE 3.1, SECTION 3.5) and a mass of approximately 1,025 kg/m^3 at 3.98 °C when free of air*. (*Handbook of Chemistry and Physics, 61st edition, CRC Press, Table F3)

5.1.4 MIXTURES OF FRESH AND SALT WATER

Many cities and industries are located at river estuaries where fresh water and salt water mix. Fresh water, which has a density of approximately 1,000 kg/m^3, will float on top of salt water, which has a density of approximately 1,025 kg/m^3, and form a separate layer. Therefore, if a pollutant is discharged into the fresh water on the surface, it may stay in the top freshwater layer. If a pollutant is discharged into the underlying saltwater layer, it may stay in the underlying salt water.

5.1.5 MIXTURES OF FRESH WATER OF DIFFERENT TEMPERATURES

Thermal differences in liquids will affect their density. The warmer the liquid, the less dense it will become and it will tend to float. The colder a liquid, the denser it will become and it will tend to sink. Therefore, an effluent pipe discharging cold water into warm water will cause the pollutants to sink to the bottom of the stream. Effluent discharging warm water into a colder stream will cause the effluent to rise to the surface.

5.1.6 MIXTURES OF FRESH WATER CONTAINING DISSOLVED POLLUTANTS

Water effluents containing dissolved pollutants will have a higher density than fresh water. If the temperatures of the effluents are the same as fresh water, the effluents will tend to sink.

5.2 FLOW MEASUREMENT

Flow measurement techniques depend on the setting of the fluid flow but generally are in open or closed channels. Open channels commonly refer to streams and drainage channels contained in concrete, while closed channels commonly refer to enclosed pipes of various shapes and cross sections. It is critical to measure flow in order to calculate loading of pollutants and dilution factors. These are critical to assessing environmental damage and are used in determining clean up orders and assessing penalties on conviction.

5.2.1 OPEN STREAM CHANNEL – ESTIMATE USING FLOATING OBJECTS

Flow measurement of an open stream will depend on the type of bottom, the depth and current speed.

ASSEMBLE EQUIPMENT

Assuming the channel is safe to wade across, the minimum equipment needed to estimate flow is:

- ☐ Life jacket
- ☐ Wading boots
- ☐ Metered measuring stick
- ☐ Measuring tape
- ☐ Stopwatch

☐ Floating object which will partially submerge such as a grapefruit or stick

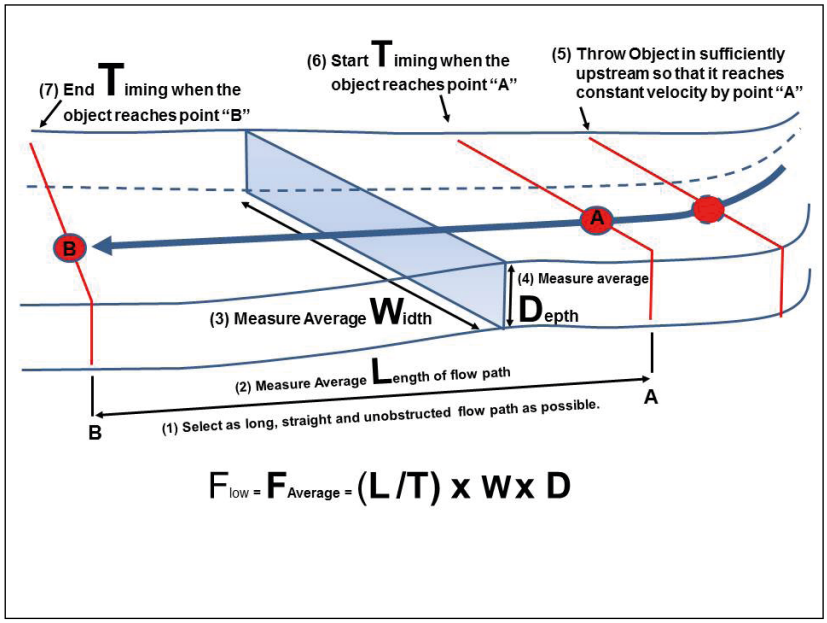


FIGURE 5.2:
Flow measurement of open stream channel, estimate using floating objects.
(Courtesy of Genesis Environmental Sciences Ltd.)

SUGGESTED PROCEDURE

1. Select a section of the stream that is as straight as possible with a fairly uniform bottom structure and a minimum of large obstructions such as rocks and debris.
2. Measure out a consistent distance along the bank, 10 m to 20 m long where (A) = the upstream point and (B) = the downstream point.
3. Only if it is safe to do so, stretch and anchor the measuring tape across the stream. If it not safe, then toss a string with a rock to the other side, retrieve the string and measure the retrieved length or estimate the distance by eye.
4. Only if it is safe to do so, for streams 5 metres or greater, wade across and use the metre stick to measure the stream depth every meter and record the depth. For narrower streams divide the width into 3 or 5 equal portions.
5. Stand upstream of (A) and toss the floating object into the center of the stream, far enough upstream so that it reaches constant velocity by the time it reaches (B)
6. Start the stopwatch, measure and record the time it takes the floating object to travel from (A) to (B).
7. Repeat steps 4 and 5 at least three times and obtain an average time, e.g. 8 seconds.
8. Calculate the average surface velocity of the stream by dividing the distance by the time, e.g. Velocity = 20 m /12 s = 1.7 m/s.
9. Since water flows faster on the surface than it does on the bottom, multiply the Velocity by 80% to obtain average velocity, e.g. V_{avg} = 0.8 x 1.7 m/s = 1.3 m/s.
10. To calculate the volume of water passing a point, multiply the cross sectional area of the stream by the average velocity. The accuracy of the estimate increases with the greater number of cross sectional areas.
    Volume = V_{avg} x Width x Depth = 1.3 m/s x 5 m x 0.9 m = 5.85 m^3/s

5.2.2 OPEN STREAM CHANNEL – ESTIMATE USING HAND-HELD FLOW METER

Stream flow using a hand-held flow meter can increase accuracy of the estimate. Some flow meters will automatically estimate the average water velocity at a point. Most flow meters have a depth scale on the side.

SUGGESTED PROCEDURE

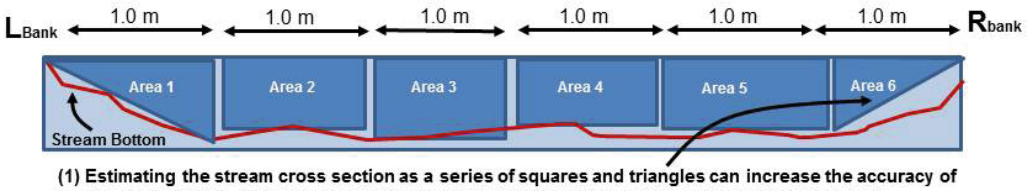
1. Measure out a single point on the bank, D1.
2. Only if it is safe to do so, stretch and anchor the measuring tape across the stream at D1.
3. Only if it is safe to do so, use the flow meter to measure the stream depth every metre and record the depth. For stream 5 m or wider use 1.0 metre increments, for narrower streams divide the width into 3 or 5 equal portions.
4. At the same point where depth is measured, move the flow meter at a constant rate from the surface down to the bottom and back to the surface several times until the average velocity is obtained.
5. Some flow meters will automatically multiply the average velocity by 0.8 to factor in the different speeds at the top and the bottom of the stream.
6. Record the average velocity at each point in the stream.

FIGURE 5.3:
Use of tape measure and portable flow meter to estimate stream flow.
(Courtesy of Canada – DOE)

7. To calculate the volume of water passing a point, multiply the cross sectional area of the stream by the average velocity. The accuracy of the estimate increases with the greater number of cross sectional areas.

FOR EXAMPLE:

The left and right banks can be estimated as triangles and the center portion as squares.



(1) Estimating the stream cross section as a series of squares and triangles can increase the accuracy of the flow calculation. This requires wading across and taking depth measures at regular intervals.

FIGURE 5.4:
Flow measurement of open stream channel, estimate using squares and triangles (Courtesy of Genesis Environmental Sciences Ltd.)

Table 5.2 Typical examples of how to calculate flow area and flow rates in a stream

DISTANCE	AREA 1 = ½ X W X D	AREA 2 = W X D	AREA 3 = W X D	AREA 4 = W X D	AREA 5 = W X D	AREA 6 = ½ X W X D	AVERAGE VALUE
W =WIDTH	1.0 m	1.0 m	1.0 m	1.0 m	1.0 m	1.0 m	1.0 m
D = DEPTH	0.2m	0.17 m	0.2 m	0.16 m	0.17m	0.17	0.20
A = W X D AREA M2	0.1 m^2	0.17 m^2	0.2 m^2	0.16 m^2	0.17 m^2	0.08 m^2	
V = VELOCITY M/S	0.5	1.3	1.4	1.5	1.3	0.6	1.3
VOLUME M3/S = A X V	0.05 m^3/s	0.22 m^3/s	0.28 m^3/s	0.24 m^3/s	0.22 m^3/s	0.05 m^3/s	

The total volume is estimated as the sum of all the area volumes:
Volume = 0.05 m^3/s + 0.22 m^3/s + 0.28 m^3/s + 0.24 m^3/s + 0.22 m^3/s + 0.05 m^3/s = 1.06 m^3/s
Generally, estimates using floating objects and estimated depths will overestimate or underestimate flows. Therefore, whenever possible, a flow meter should be used on as many intervals across the stream as possible.

5.2.3 OPEN CHANNEL – FLUMES AND WEIRS

Hydraulic structures, built into the channel, are the most commonly used ways for measuring the rate of flow in an open channel in large industrial facilities. The structure must be designed so that the rate of flow through or over has a known mathematical relationship with the liquid level. This known mathematical relationship allows the flow rate through the open channel to be derived from a single measurement of the liquid level. There are too many to include in this manual. The field personnel are recommended to collect the literature and manufacturer's information from the facility during their inspection and keep it for reference. The hydraulic structures used to measure flow in open channels are called primary measuring devices. There are two types: weirs (see FIGURE 5.5) and flumes (see FIGURE 5.6).

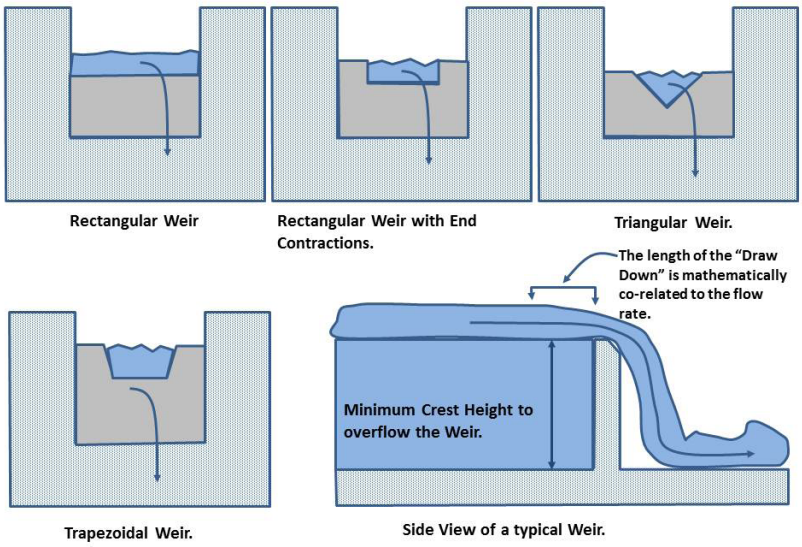


FIGURE 5.5:
General design of a flow measuring weir.
(Courtesy of Genesis Environmental Sciences Ltd.)

Many industrial facilities use weirs, flumes, or both, together with secondary measuring devices that convert liquid height into units such as gallons per day (gal/d) or cubic metres per day (m^3/d). These devices also provide records in the form of strip charts and/or totalizer meters.

A weir is a dam built across an open channel. The liquid flows over the weir, usually through some type of opening or notch. Weirs are usually classified according to the shape of the notch. The most common types are rectangular, trapezoidal (or Cipoletti) and triangular (or V-notch). Each type of weir has an associated equation for determining the flow rate through the weir, based on the liquid height passing over the weir.

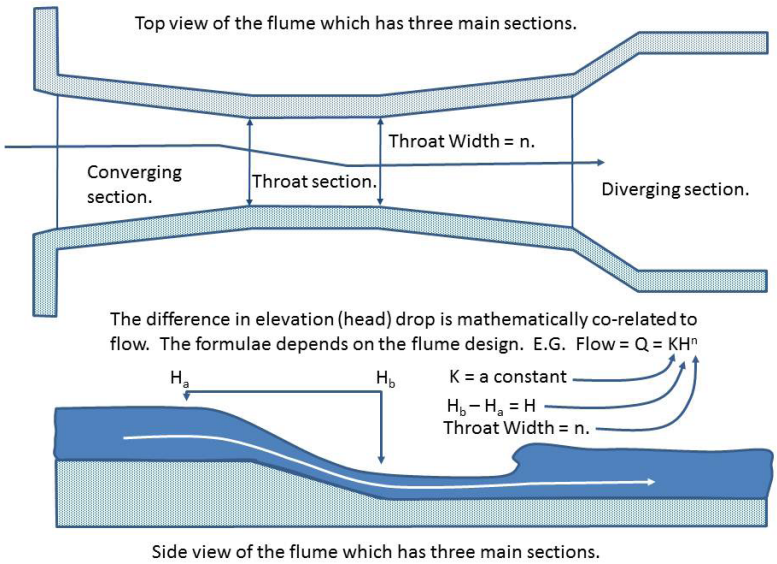


FIGURE 5.6:
General design of a flow measuring flume.
(Courtesy of Genesis Environmental Sciences Ltd.)

A flume is a specially shaped section of an open channel in which the area, or the slope, or both, is/are different from that of the channel. The configuration of a flume causes the liquid to flow faster through the flume. It also changes the liquid level. A flume normally consists of a converging section, a throat section and a diverging section. The flow

rate through the flume is a function of the liquid level at some point or points in the flume. The liquid height is usually measured by some type of sensor. The most commonly used types of flumes are Parshall flumes and Palmer-Bowlus flumes, although there are many other types available.

5.2.4 CLOSED CHANNEL – CALIBRATED BUCKET METHOD

The simplest method for estimating flow from a closed channel discharge pipe is using a calibrated bucket and stopwatch. The end of the pipe or discharge structure should be elevated to allow the free fall of liquid. If there is no free fall of liquid, the measurement will be less accurate.

FIGURE 5.7:
Calibrated bucket flow measurement does not need to capture the entire flow. The volume will be measured as "flow is greater than X litres / second".
(Courtesy of Canada – DOE)

ASSEMBLE EQUIPMENT

- ☐ Life jacket
- ☐ Wading boots
- ☐ Calibrated bucket
- ☐ Stopwatch
- ☐ Measuring tape or stick

SUGGESTED PROCEDURE

1. Only if it is safe to do so, measure out the diameter of the pipe and the depth of the discharge at its center.
2. Set the stop watch to zero and start it as soon as it enters the free falling flow. Note: It is preferable, but not necessary, to capture all the flow in the bucket. If only part of the flow is captured, the end result will be recorded as "greater than X litres per second".
3. Stop the stopwatch as soon as the bucket is filled.
4. Repeat steps 2 and 3 until at least three consistent times are recorded.
5. Calculate the flow rate by dividing the volume of the bucket by the average number of seconds to fill it. See TABLE 5.3

Table 5.3 | Examples of how to calculate flow rates using a calibrated bucket

TRIAL	TRIAL #1	TRIAL #2	TRIAL #3	TRIAL #4	AVERAGE
VOLUME OF BUCKET	10.0 litres	10.0 litres	10.0 litres	10.0 litres	10.0 litres
TIME TO FILL 10 LITRES	4.0	3.7	3.8	3.6	3.8 seconds
FLOW RATE L/S	2.5	2.7	2.6	2.8	2.6 L/s

5.2.5 CLOSED CHANNEL – CALIFORNIA PIPE METHOD

The California pipe method provides a reasonable estimate of flow from an open, nearly horizontal round pipe where the water free falls from the pipe (see FIGURE 5.8). The accuracy decreases if the pipe is greater than three feet (about 1.0 metre) in diameter. There are two critical measurements, diameter (D) and height (H) of the water in the pipe. Changes such as elbows, T-joints or other configurations in the pipe within 6 diameters of the outfall can cause distortions in the result. The horizontal length of undisturbed pipe should therefore be at least 6D. The formula uses feet as a measure so it produces a result in ft^3/s which must be converted to L/s.

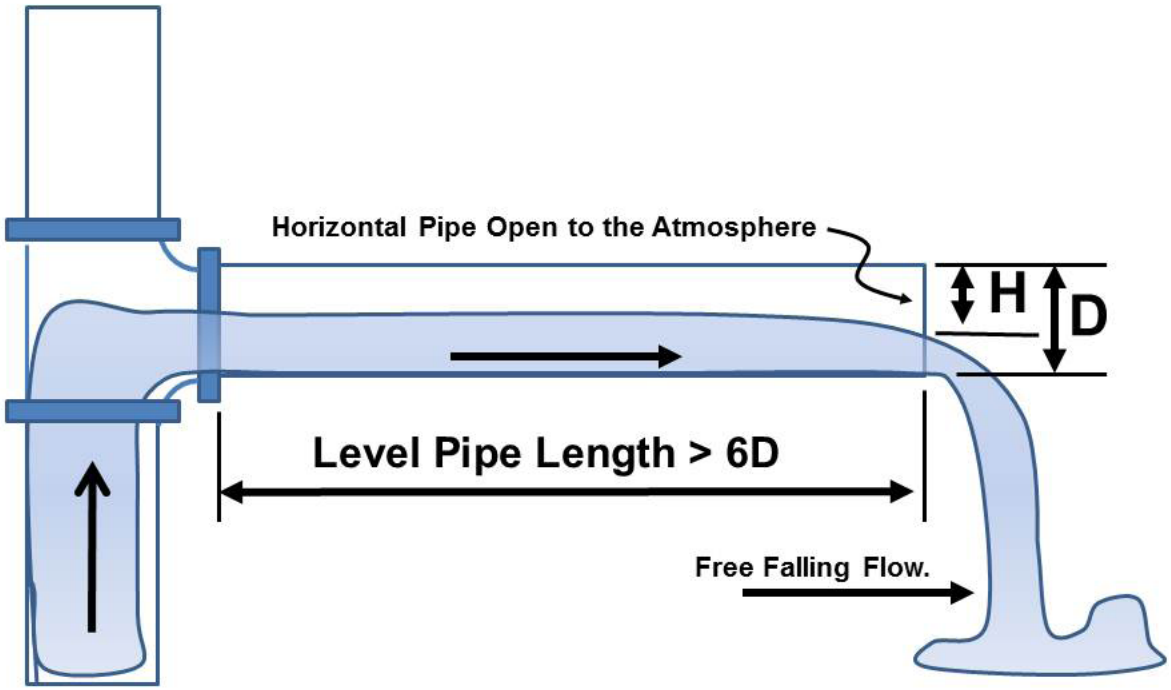


FIGURE 5.8:
Diagram of the California pipe method.
(Courtesy of Genesis Environmental Sciences Ltd.)

ASSEMBLE EQUIPMENT

☐ Measuring tape or stick

SUGGESTED PROTOCOL

1. **Only if it is safe to do so**, measure out the inside diameter of the pipe "D" and the inside depth of the discharge at its center "H".
2. Enter the values into the following formula

$$\text{Flow Rate} = Q = 8.69\left[1 - \frac{(D-H)}{D}\right]^{1.88} \times D^{2.88} = X\ ft^3/s$$

For example, assume the measurements in Figure 5.8 are D = 1.2 ft and H = 0.33 ft.

$$\text{Flow Rate} = Q = 8.69\left[1 - \frac{(1.2-0.33)}{1.2}\right]^{1.88} \times 1.2^{2.88} = 1.3\ ft^3/s$$

Convert Q from ft^3/s to L/s = 1.3 ft^3/s x 28.3 L/ ft^3 = 36.7 L/s.

5.3 FLOW MEASUREMENT AND CALCULATION OF MASS OF POLLUTANT DISCHARGED

Flow measurement ranges from simple field techniques to complex measuring systems used in industrial scale operations. Flow measurement is critical as it allows the environmental investigator to estimate the mass of environmentally hazardous materials discharged in an incident using the following formula:

Mass Discharged = Concentration (kg/m^3) x Flow (m^3/h) x Time (h)

For example: Water with a dissolved copper concentration of at 50 µg/L is discharged at 50 m^3/h for 10 hours from a metal factory.

1. Convert µg/L to kg/m^3
   = 50 µg/L x 0.000001 g/µg x 0.001 g/Kg x 1000 L/m^3
   = 0.00005 kg/m^3
2. Calculate Mass Discharged
   = Concentration (kg/m^3) x Flow (m^3/h) x Time (h)
   = 0.00005 kg/m^3 x 50 m^3/h x 10 h

6 SAMPLING LIQUIDS

Sampling liquids

= 0.025 kg copper was discharged

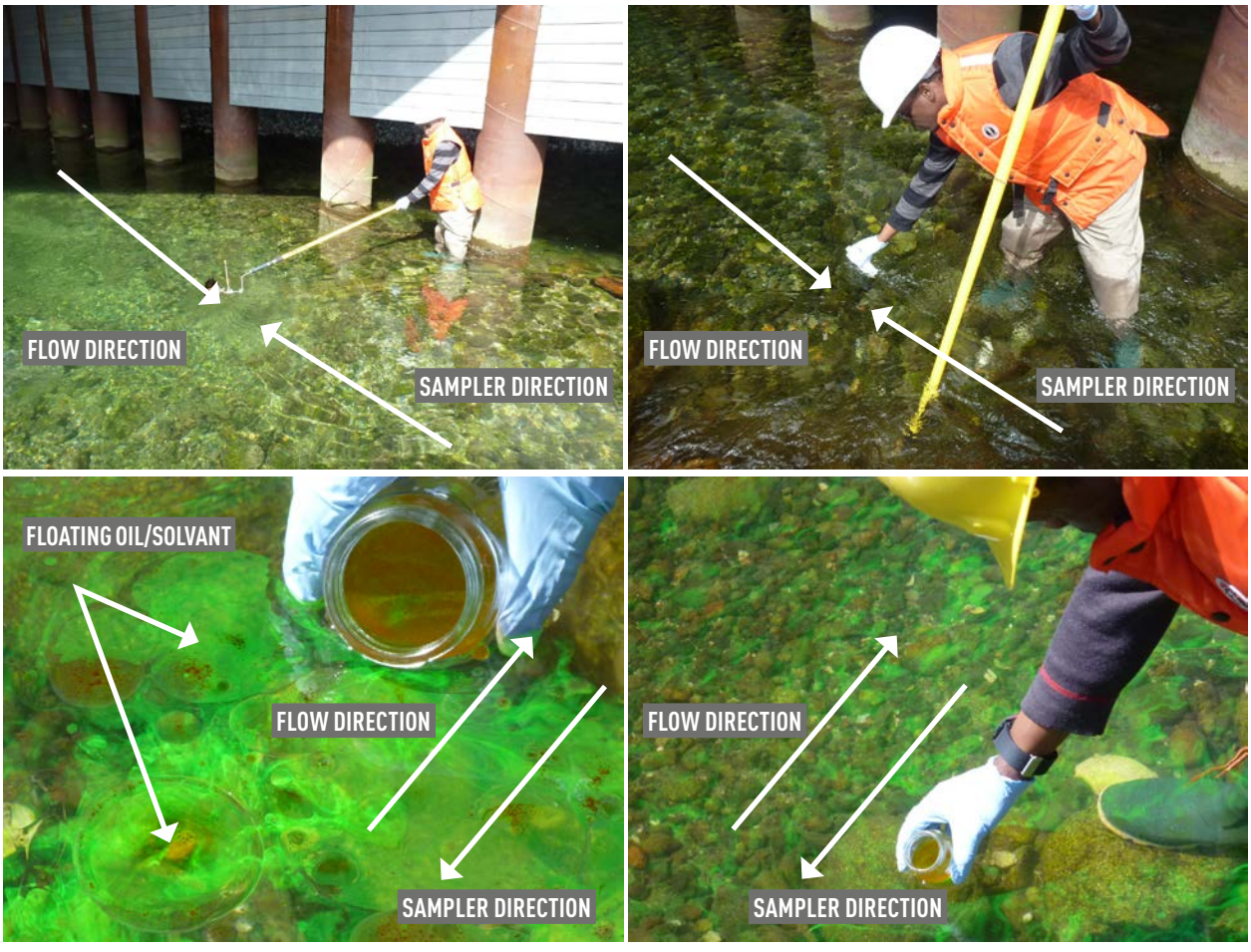
Sampling liquids depends on the physical setting, whether the water is flowing or stagnant, whether wading or taking a boat into the water will stir up sediment, and physical factors such as the contamination from bridges or structures.

6.1 SURFACE SAMPLING OF LIQUIDS BY HAND METHODS

Samples taken from shallow depths (less than 1 to 2 m) can be collected by hand or by using a sampling pole (telescoping if required). When sampling surface water from well-mixed rivers and un-stratified lakes, you may take samples directly into hand-held sample bottles. Collect water from below the surface to avoid skimming the surface film.

Where there is an oil or floating film the sample should be collected just under the surface of the water to maximize collection of pollutant.

FIGURE 6.1:
Surface water grab sample being collected using a hand method and facing upstream, a telescoping pole from shore, bridge or boat.
(Courtesy of Canada – DOE)



ASSEMBLE EQUIPMENT

- ☐ Life jacket, if there is a drowning hazard
- ☐ Wading boots, if required
- ☐ Protective gear such as appropriate gloves depending on the known or suspected pollutant (see SECTION 2.6.5)
- ☐ Sampling pole and attachment for the type of container
- ☐ Select the correct sample bottle and preservative
  See SECTION 2.9.2

SUGGESTED PROCEDURE

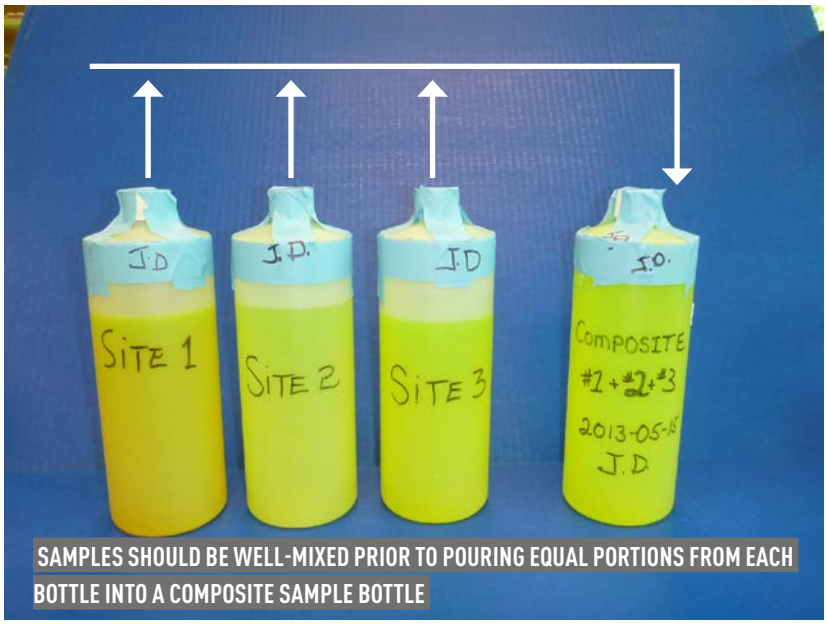
1. Ensure that safety precautions have been implemented.
2. In a river, stand perpendicular to flow facing upstream. In a lake, wade beyond where shore sediment is affected by wave action.
3. Remove the lid ensuring not to touch the inside of lid or mouth of sample container, or use a bucket, ensuring you do not touch the inside of the bucket.
4. Grasp bottle or bucket at the base with one hand and plunge bottle mouth down into the water or effluent.
5. Position the mouth of the bottle or bucket into the current, away from the hand of the collector and the sampling platform or boat making sure that the hand is always downstream.
6. Sampling depth should be 15 to 30 cm (6 to 12 in) below the water surface.
7. If the water is static, an artificial current may be created by moving the bottle or bucket horizontally, in the direction it is pointed, and away from the sampler.
8. For bottles, tip the bottle slightly upwards to allow air to exit and the bottle to fill; or remove the lid of the sample container and fill from the bucket (ensuring not to touch inside of lid or mouth of sample container).
9. After removal of the bottle from the stream, you may need to pour out a small portion of the sample to allow an air space of around 2.5 to 5 cm for proper mixing before analysis. (Note: that if volatile organic compounds (VOCs) are the suspected pollutant, then the bottle should be filled to the top unless space for preservative is required. (See TABLE 2.9.3.35)
10. Seal and label the bottle and place in a cooler.

For bacteriological samples, use same procedure, except use 500 mL sterile bottles.

Once you have taken the sample, if required, transfer it into the appropriate container, cap the container and if necessary, wipe down the outside of the container with a paper towel. To avoid introducing contaminants into the container, never immerse or rinse a sample bottle in water to clean it; use a clean, wet paper towel.

6.2 COMPOSITE WATER SAMPLES – SAMPLING STRATEGIES

Composite samples consist of samples that are taken from the body of water or effluent flow of water at continuous, random or specific intervals and then blended together. The objective is to produce an average sample composition when pollutant concentrations may vary over time and reduce the cost of analysis. Compositing is also useful when individual sample sizes may be too small for analysis. Compositing may help localize areas of high contamination at a reduced cost by grouping sets of samples. If a composite shows an elevated value, the samples in that group, if they have been retained, may then be analysed individually.



SAMPLES SHOULD BE WELL-MIXED PRIOR TO POURING EQUAL PORTIONS FROM EACH BOTTLE INTO A COMPOSITE SAMPLE BOTTLE

FIGURE 6.2:
Multiple water samples and a composite sample collected manually.
(Courtesy of Canada – DOE)

The trade-off is that composite sampling has limitations such as:

- Compositing gives less information on variance (between samples or over time) and may therefore mask real differences.
- Information regarding analyte relationships in individual samples may be lost.
- Compositing may dilute an analyte to a level below the detection limit, producing a false negative.
- If compositing reduces the number of samples collected below the required statistical need of the data quality objectives (DQOs), then those objectives will be compromised.
- In the field, the sample compositing strategy must reflect the legislative and data requirements. The actual time intervals, volumes collected and sample preservation method can vary according to the situation.

6.2.1 COLLECT SAMPLES INTO A SINGLE COMPOSITE SAMPLE BOTTLE

1. Use a manual sample bottle or an auto sampler programmed to collect a sample and dispense it into a single large container.
2. Mix the large sample container well and dispense a portion into a small bottle and preserve according to the requirements of SECTION 2.9.
3. Where volatile organic compounds (VOCs) are known or suspected, the composite sample should be mixed:
   - using a clean stir stick (such as a clean glass rod) for the shortest time possible to minimize the loss of vapour from the container; or,
   - by filling the composite container completely full, closing it with the maximum exclusion of air possible and gently swirling and inverting the container to obtain maximum mixing.

ADVANTAGE

Simplest technical method and lowest analytical cost.

DISADVANTAGE

Highest risk of false negative results, lowest analytical resolution of the profile of contaminants in the effluent and most difficult to relate to a problem in the industrial process.

6.2.2 COLLECT SINGLE SAMPLES AND SUBSAMPLE INTO A SINGLE COMPOSITE BOTTLE

1. Use a manual sample bottle or an auto sampler programmed to collect an equal volume of sample and dispense it into single sample containers.
2. Mix each small sample container well. Dispense an equal portion into a small bottle using disposable graduated pipettes or a graduated cylinder and preserve according to the requirements of SECTION 2.9.
3. Retain each small sample container for possible future analysis.
4. Where volatile organic compounds (VOCs) are known or suspected, the composite sample should be mixed:
   - using a clean stir stick (such as a clean glass rod) for the shortest time possible to minimize the loss of vapour from the container; or,
   - by filling the composite container completely full, closing it with the maximum exclusion of air possible and gently swirling and inverting the container to obtain maximum mixing.

ADVANTAGE

Simpler technical method and allows for individual samples to be analysed if the composite indicates a positive result.

DISADVANTAGE

Most labour intensive, increased mixing and pouring required, potentially higher analytical cost.

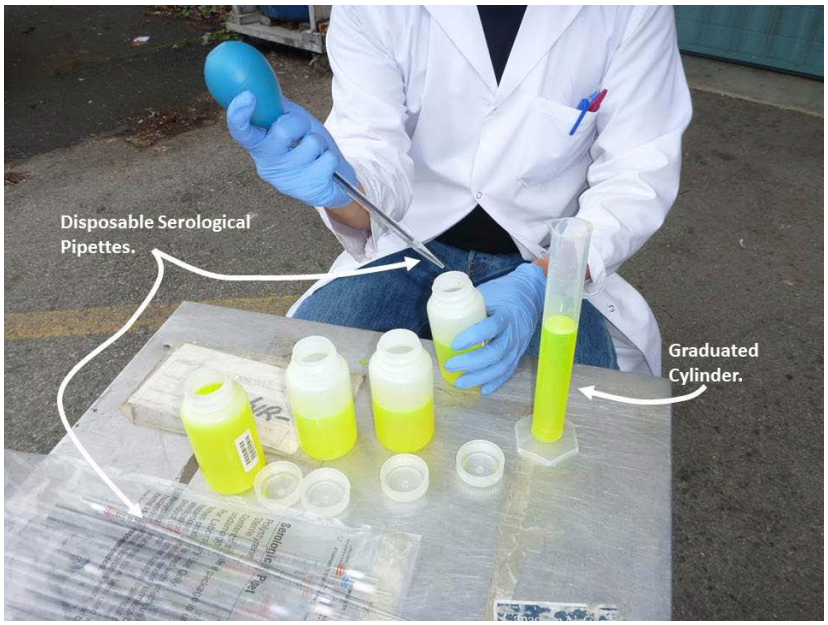


FIGURE 6.3:
Individual samples may be composited by mixing and decanting samples or using disposable graduated serological pipettes or a graduated cylinder to subsample individual samples. (Courtesy of Canada - DOE)

6.2.3 COMPOSITE WATER SAMPLES – AUTOMATED SAMPLING

Composite samples can be collected by using an automated sampler and may be triggered by a time, flow rate, flow volume, pH, conductivity or temperature basis.

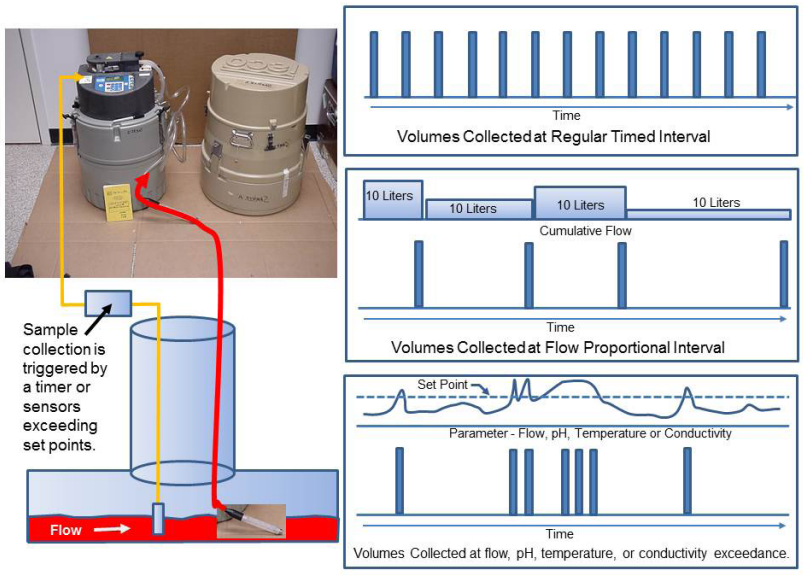


FIGURE 6.4:
Auto sampler connected to or programmed to be triggered by time intervals, proportional flow intervals, or set points of flow, pH, temperature or conductivity. (Courtesy of United States – EPA and Genesis Environmental Sciences Ltd.)

SUGGESTED PROCEDURE

1. Select a well-mixed sample collection site.
2. Set the auto sampler to collect equal volumes of sample based on:
   - regular time intervals;
   - flow proportional basis (each time a certain volume passes the sample point); or,
   - parameter exceeds flow rate, pH, temperature or conductivity settings.
3. Insert multiple composite samples into the sampler for discrete sampling; or,

4. Insert a large composite sample bottle into the sampler for single mix sampling.
5. After the composite sample is collected, stir/mix each sample and quickly pour ½ into the composite sample bottle.
6. Preserve the individual and the composite samples with the appropriate preservative.
7. Store and ship according to normal protocol.
8. Retain the individual samples for later analysis if the composite sample exceeds the regulated limits for the parameter.

6.3 SAMPLING FLOATING LIQUIDS AND PETROLEUM PRODUCTS

Organic solvents with densities less than water and crude, refined petroleum and waste oils will float on water and may contain various contaminants therefore it is wise to treat them as hazardous materials. The main sources from which organic solvents and oil samples may be collected are on water, from shorelines (oil on pebbles and stones, in sand or on debris), from contaminated wildlife and the pure oils or waste oils from storage or dispensing devices.

FIGURE 6.5:
Collecting samples of floating liquids and petroleum products. (Courtesy of Brazil – Federal Police and Canada - DOE)

Conduct a task hazard analysis of the sampling (see SECTION 2.6). Some issues related to sampling floating liquids and petroleum products are:

- ☐ Ensure the area is well ventilated.
- ☐ Test for explosive gases with a calibrated explosimeter.
- ☐ Ensure absorbent materials are on hand in case of spillage.
- ☐ Ensure that the tank or tanker truck roofs are structurally sound to walk on before attempting to take a sample from a top hatch.
- ☐ Ensure the barrel, tanker truck, storage tank and sample container has proper electrical grounding to prevent sparks from static electricity.

- ☐ Wear fire or flash resistant clothing and protective gear as determined by your Task Hazard Analysis and local regulations.
- ☐ Ensure there are no ignition hazards such as:
  - lightning storms
  - electrical motors
  - combustion engines
  - people smoking
- ☐ Wear protective eyewear.
- ☐ Wear protective breathing apparatus as per local regulations.
- ☐ Wear protective gloves at all times. It is advisable for prevention of cross contamination and for health and safety reasons to wear two pairs of disposable gloves when taking samples. The outer pair of gloves is to be changed after each sample and the inner pair of gloves is to be changed any time they become soiled. See SECTION 2.6.5 regarding protective equipment).
- ☐ Solvents and oil on skin should be removed as soon as possible by scrubbing with soap and warm water.
- ☐ If possible do not store petroleum or solvent samples in the passenger compartment of vehicles as leaks may cause release of hazardous vapours and explosive/fire conditions.

6.3.1 SAMPLING FLOATING LIQUIDS AND PETROLEUM PRODUCTS ON WATER

ASSEMBLE EQUIPMENT

- ☐ Life jacket, if there is a drowning hazard
- ☐ Breathing equipment, if there is a vapour hazard
- ☐ Protective clothing and gloves suitable to the product
- ☐ Non-sparking flash lights
- ☐ Sampling pole and attachment for the type of container, or
- ☐ Clean rope and non-sparking bottle holder
- ☐ Select the correct sample bottle. See TABLE 2.9.2.2
- ☐ Select the correct preservation method
  - Store at 4°C, or
  - Add 2 mg sodium thiosulphate to the bottle prior to sampling

SUGGESTED PROCEDURE

Note: At no time should plastic sample collection equipment or sample bottles be used to collect solvents, oil or petroleum samples.

1. Use amber glass bottles, 125 mL - 250 mL, with Teflon-lined lids or heat-treated aluminum foil as a seal between jar and lid.
2. Label the sample bottle before filling.
3. Collect solvents and oil or petroleum samples with as little water as possible. This will help reduce chemical, physical or biological alterations of the oil when in prolonged contact with water between the time of sampling and analysis.
4. Whenever possible, avoid collecting solvents and oil or petroleum samples containing organic material such as marine vegetation, grass, bits of wood, etc.

5. The laboratory requires a minimum oil layer of 3 mm in a 125 mL glass bottle to run the full range of analytical tests.
6. To concentrate the sample to the required thickness, tilt the lip of the sampling bottle just below the water surface and skim off the oily layer. If this yields too thin a layer, cap the bottle and invert it. Allow the oil to rise to the surface; then loosen the cap just enough to let the aqueous under layer run out of the bottle. Tighten the cap, turn the bottle right-side up and repeat the process until enough oil has been collected.

   Note: Filling jars completely with liquid may result in leakage as temperature change of the sample could cause expansion and leakage from the seal or breakage of sample container. Bottles may have to be completely filled to minimize vapour loss from volatile organic compounds (VOCs) therefore it is important to keep the sample at 4°C.
7. For very thin films of solvents and oil or petroleum product on the water surface an absorbent material may be needed to collect a sample. Place an absorbent pad on top of the oil film and slowly turn it in a circular motion to collect the oil layer. Transfer the pad to a clean glass bottle and seal it. Include a piece of unused material in a separate jar for use as a blank.
8. Solvents and oil or petroleum in small dispersed pools, in globules or in difficult to reach areas may require sampling with a disposable glass or plastic pipette and bulb.
9. After sampling, clean the outside of the jar to remove excess solvents and oil or petroleum adhering to the surface by wiping it with absorbents or paper towels. Do not rinse or immerse the jar in water.
10. After sample collection, store in a cool and dark place in order to reduce evaporative changes or microbial degradation of oil samples.

6.3.2 SAMPLING FLOATING LIQUIDS AND PETROLEUM PRODUCTS FROM BARRELS

All low density organic solvents and petroleum products and wastes represent a toxic and explosive hazard especially when contained in any form of container. Appropriate safety equipment must be worn and non-sparking tools must be used to open containers with these materials inside.

ASSEMBLE EQUIPMENT

- ☐ Breathing equipment, if there is a vapour hazard
- ☐ Gas vapour test equipment, if there is a vapour hazard
- ☐ Protective clothing, eyewear and gloves suitable to the product
- ☐ Drum Sampler
  - Sample Thief, or
  - COLIWASA (see SECTION 4.3)
- ☐ Explosion proof peristaltic pump or hand pump and appropriate tubing, or
- ☐ Clean rope and non-sparking bottle holder
- ☐ Non-sparking flash lights
- ☐ Select the correct sample bottle. See TABLE 2.9.2.2

FIGURE 6.6:
Using a gas vapour analyser and a glass COLIWASA sampler to collect a sample of unknown substance from a barrel. (Courtesy of United States – EPA)

SUGGESTED PROCEDURE

1. Label the sample bottle before filling.
2. If the barrel is equipped with a dispensing valve, use a wire with two clamps to electrically ground the barrel to the sample container before opening the valve. This reduces the risk of an electric charge creating a spark and igniting fumes or fuel. Collect a sample in an amber glass jar. See TABLE 2.9.2.2
3. If the barrel is not equipped with a dispensing valve, open the container with non-sparking tools (usually made of aluminum alloy).
4. If a consistent product throughout the barrel is known, use a tube sampler (Sample Thief), COLIWASA, or non-sparking hand pump to extract a sample and dispense into an amber glass jar.
5. If layers of liquid (such as illegally disguised organic wastes) are known or suspected, use a tube sampler (Sample Thief) or COLIWASA to extract a sample and dispense into an amber glass jar.

6.3.3 SAMPLING FLOATING LIQUIDS AND PETROLEUM PRODUCTS FROM LARGE TANKS AND TANKER TRUCKS

If access is required to the top of a tank or tanker truck, the health and safety plan must ensure that the structure of the tank is strong enough to support the weight of the sampling team and that precautions are taken to use non-sparking equipment and pumps to collect the sample. See FIGURES 6.7 AND 6.8

FIGURE 6.7:
Sample collected from a bulk tank using a peristaltic pump. Note : if hazardous vapours are present, respirators would be required.
(Courtesy of the Netherlands – NFI)

ASSEMBLE EQUIPMENT

- ☐ Breathing equipment, if there is a vapour hazard
- ☐ Protective clothing, eyewear and gloves suitable to the product
- ☐ Drum Sampler
  - Sample Thief, or
  - COLIWASA (see SECTION 4.3)
- ☐ Explosion proof peristaltic pump or hand pump and appropriate tubing
- ☐ Electrical grounding cable with metal clamps on each end
- ☐ Clean rope and non-sparking bottle holder
- ☐ Non-sparking flash lights
- ☐ Select the correct sample bottle. See TABLE 2.9.2.2

SUGGESTED PROCEDURE

1. Label the sample bottle before filling.
2. If the large tank or tanker truck is equipped with a dispensing valve, use a wire with two clamps to electrically ground the tanker to the sample container before opening the valve. This reduces the risk of an electric charge creating a spark and igniting fumes or fuel. Collect a sample in an amber glass jar.

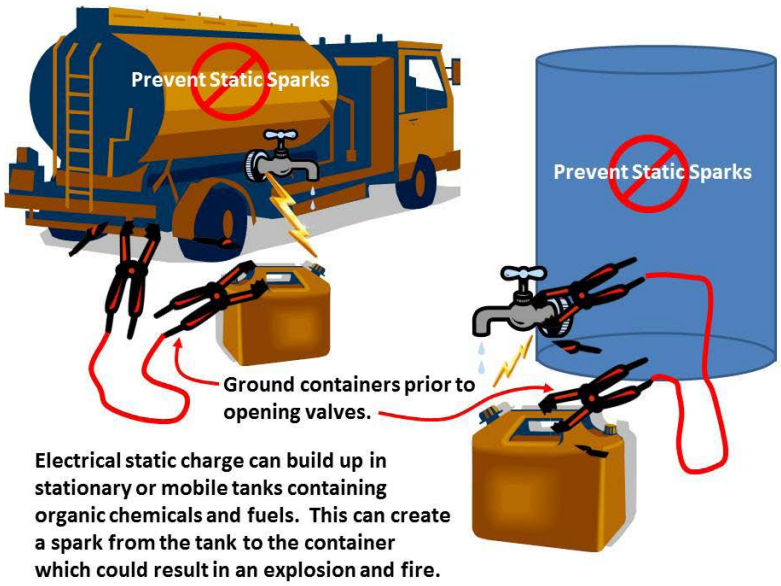


FIGURE 6.8:
Grounding wire attached to a tank or tanker truck valve. (Courtesy of Genesis Environmental Sciences Ltd.)

3. If the large tank or tanker truck is not equipped with a dispensing valve, open the container with non-sparking tools (usually made of aluminum alloy).
4. If a consistent product throughout the large tank or tanker truck is known, use a tube sampler (Sample Thief) or COLIWASA or non-sparking hand pump. If the large tank or tanker truck must be sampled from a top hatch it may be better to use an amber glass bottle in a non-sparking sample bottle holder made of lead or aluminum and a disposable rope. **Note:** stainless steel ropes or chains can create a spark and explosion hazard. Lower the amber glass bottle to extract a sample and dispense into an amber glass jar.
5. If layers of liquid (such as illegally disguised organic wastes) are known or suspected, use a tube sampler (Sample Thief) or COLIWASA or a weighted sample bottle holder and sample the layers and dispense into an amber glass jar.

6.3.4 SAMPLING FLOATING LIQUIDS AND PETROLEUM PRODUCTS ON SURFACES, SOLIDS AND WILDLIFE

Floating liquids (usually organic solvents) and petroleum products will float and subsequently adhere to solid surfaces such as sands, gravels, beach sediment and debris, and wildlife.

ASSEMBLE EQUIPMENT

- ☐ Breathing equipment, if there is a vapour hazard
- ☐ Protective clothing, eyewear and gloves suitable to the product
- ☐ Sampling swab
- ☐ Clean knife or spatula for scraping
- ☐ Sterile knife, scalpel or scissors to cut fur, feathers or tissue or tar balls
- ☐ Select the correct sample bottle. See SECTION 2.9.2
- ☐ Clean aluminum foil
- ☐ Clean plastic bags

SUGGESTED PROCEDURE

1. Photograph the site and if present, the impacted animal before and after the sampling is conducted especially so that the species of animal can be identified.
2. For oil on sand and fine gravel, use a pre-cleaned stainless steel spoon to scoop up a surface sample and place in a wide mouth glass jar which has an aluminum foil or Teflon lined lid. Close the lid, seal and store in a dark place (such as a cooler) at 4°C and submit for hydrocarbon identification analysis.
3. For oil in the form of tar balls, collect the entire tar ball in a jar or cut the ball and using a spatula to scoop out the center of the tar ball which has been subject to less weathering. In either technique, specify the analysis of the center of the tar ball which may provide a better link to the source of the oil.
4. For oil on a solid surface, gently sweep the surface with a piece of oil-absorbent material or cotton swab and place material (or cotton swab) into a sample jar which has an aluminum foil or Teflon lined lid. Close the lid and seal and store in a dark place (such as a cooler) at 4°C and submit for hydrocarbon identification analysis. Include a piece of unused material in a separate jar for use as a blank.
5. For oil on wildlife such as birds or sea mammals it depends on whether the animal is alive or dead. For live animals, only approach and capture the animal if you are trained in capture techniques. Restrain the live animal so as to minimize injury to the sampler and the animal according to the prescribed technique. Gently sweep the surface with a piece of oil-absorbent material or cotton swab and place material into a sample jar which has an aluminum foil or Teflon lined lid. Close the lid, seal and store in a dark place (such as a cooler) at 4°C and submit for hydrocarbon identification analysis. Include a piece of unused material in a separate jar for use as a blank.
6. For oil on wildlife such as birds or sea mammals which are dead and too large to place in a bag or jar, there are several options:
   - Gently sweep the surface with a piece of oil-absorbent material or cotton swab and place material into a sample jar which has an aluminum foil or Teflon lined lid, or
   - Use a sterile knife, scalpel, or scissor to cut a portion of contaminated fur, feathers, or skin and place material into a sample jar which has an aluminum foil or Teflon lined lid.
   - Close the lid and seal and store in a dark place (cooler) at 4°C and submit for hydrocarbon identification analysis. Include a piece of unused material in a separate jar for use as a blank.

6.4 ESTIMATING THE VOLUME OF OIL CONTAINED IN AN OIL SLICK ON WATER

A general estimate of the volume of an oil slick on water can be made following this general rule of observations.

Table 6.1 | Estimating the Volume of an Oil Slick on Water

STANDARD TERM	APPEARANCE	OIL (L/km²)
BARELY VISIBLE	barely visible under most light conditions	44
SILVERY	visible as a silvery sheen on surface water	88
SLIGHTLY COLOURED	first traces of colour visible	175
BRIGHTLY COLOURED	bright bands of colour visible	330
DULL	colours begin to turn dull brown	1 170
DARK	much darker brown	2 337

Note : Each 2.54 cm thickness of oil equals 21.42 L/m² or approximately 30 500 000 L/km².

6.5 SAMPLING MEDIUM DENSITY LIQUIDS

Medium density liquids may have a density which causes them to float or disperse midway in the water column. This can occur when there is an underlying saltwater wedge, such as in an estuary, when salts or metals have been dissolved in water, or when the temperature of the water is such that its density causes it to disperse in the middle depth of the water column. Medium density liquids may be detected by using temperature or conductivity sensors, or if the water is clear enough, by visually looking into the water column.

ASSEMBLE EQUIPMENT

- ☐ Breathing equipment, if there is a vapour hazard
- ☐ Protective clothing, eyewear and gloves suitable to the product
- ☐ Multimeter probe capable of testing temperature, pH, conductivity and dissolved oxygen
- ☐ Sampler
  - Sample Thief, or
  - COLIWASA, or
  - Explosion proof peristaltic pump or hand pump and appropriate tubing, or
  - Clean rope and non-sparking bottle holder
- ☐ Select the correct sample bottle. See SECTION 2.9.2

SUGGESTED PROCEDURE

1. Using a probe, test the water for pH, temperature and conductivity to determine if there is a defined difference in the water column which

would indicate that medium density liquids are present.
2. Use a sampling pole or other extension device with the appropriate sample container attached and collect a sample.
3. Collect and preserve the sample according to the recommended procedure. See TABLE 2.9

6.6 SAMPLING HIGH DENSITY LIQUIDS

High density liquids are found in places such as electrical equipment (notably transformers and capacitors containing polychlorinated biphenyls, PCBs), sewers and water bodies where chlorinated solvents such as cleaning agents have been illegally disposed.

6.6.1 SAMPLING ELECTRICAL EQUIPMENT FOR PCBS

When sampling electrical equipment, you should determine if the oil contains PCBs. When in doubt, assume that it does and follow the procedures given for PCB sampling in this manual.

SUGGESTED PROCEDURE

1. Prepare and use all prescribe safety equipment for handling PCBs. Generally this includes eye protection, inhalation protection, PCB resistant gloves and coveralls.
2. Electrical equipment must be de-energized by a person trained to do so prior to any attempt to enter into a sampling area. Failure to de-energize can result in fires, electrical shock and burns which can result in damage to electrical systems and industrial processes and very severe injuries or death of the sampler and possible bystanders.
3. All sampling equipment and a spill containment kit consisting of plastic tarps, absorbent, equipment such as shovels or scoops and contaminated containment vessels should be prepared prior to entry into and initiation of sampling.

6.6.2 SAMPLING FROM ELECTRICAL CAPACITORS FOR PCBS

Electrical capacitors are sealed units and may not be labelled to identify that they contain PCBs. If there is no identifying label, it should be assumed that they contain PCBs and then sampled according to the following procedure.

ASSEMBLE EQUIPMENT

The following equipment should be prepared for sampling a de-energized sealed unit:

- ☐ Two component epoxy resin to use as a sealant after the sampling
- ☐ Clean 6 mm (¼ inch) diameter steel drill bit and drill
- ☐ Polyethylene sheet to lay under the capacitor and sampling equipment, or
- ☐ Stainless steel tray capable of hold the capacitor
- ☐ Glass pipette and rubber bulb capable of entering a 6 mm (¼ inch) hole in the capacitor

- ☐ Appropriate sized glass sample bottle and lid. See SECTION 2.9.2
- ☐ Hexane solvent for cleanup of equipment
- ☐ Plastic bags to dispose of contaminated materials
- ☐ Large metal washer and rubber washer and screw capable of threading into the 6 mm (¼ inch) steel hole
- ☐ Disposable PCB test kit (commercial kits are available.)
- ☐ Assemble appropriate protective gear, goggles/eye glasses, disposable coveralls, rubber boots and gloves. See SECTION 2.6

SUGGESTED PROCEDURE

1. **Warning: severe shock and injury or death could result from failure to de-energize the capacitor.** Consult with a qualified electrician to ensure that the electrical capacitor is disconnected from the electrical system and that the capacitor has been de-energized and that any stored electrical charge has been depleted.
2. Wear appropriate protective gear, goggles/eye glasses, disposable coveralls, rubber boots and gloves. See SECTION 2.6
3. Examine the label and determine if it says that the capacitor contains PCBs or contains a trade mark name such as Askarel, Pyranol or Inerteen which are known PCB liquids. Trade names of PCB liquids may be different in other countries.
   See also: US EPA Compliance Monitoring, Polychlorinated Biphenyl Inspection Manual
   http://www.epa.gov/compliance/resources/publications/monitoring/tsca/manuals/pcbinspect/index.html
4. Record the information on the label(s) in the field notes and/or photograph it.
5. Lay out the polyethylene on a stable surface and lay the capacitor securely on the polyethylene surface.
6. Drill a 6mm (¼ inch) hole into the top surface of the capacitor.
7. Insert the glass pipette into the hole and attach the rubber bulb and extract a sample of the liquid.
8. Repeat the pipette insertion until sufficient liquid is in the sample container. For concentrated PCB liquids, this is usually only a few millilitres.
9. If possible, conduct a field screening test following the instructions on the disposable PCB test kit.
10. Seal the sample and store according to the requirements of TABLE 2.9.2.2.
11. Assemble the screw with metallic washer followed by a rubber washer.
12. Mix a small amount of two component 5 minute epoxy resin according to the instructions. Place a small amount of the resin onto the surfaces of the metallic and rubber washer and insert the screw into the 6mm (¼ inch) hole and screw the hole shut. Cover the screw with 5 minute epoxy resin and allow time for the resin to harden.
13. Ensure the capacitor is stored according to the regulatory requirements.
14. Carefully dispose of all potentially contaminated sampling materials into a waste container and label the container according to regulatory requirements.

6.6.3 SAMPLING FROM ELECTRICAL TRANSFORMERS FOR PCBS

Electrical transformers are usually non-sealed units which may or may not be labelled to identify that they contain PCBs. The volumes of PCB liquid or PCB contaminated liquid as insulating/cooling liquid can be very large from a few litres to a thousand litres or larger. Normally, a transformer will be equipped with an access hatch for servicing and adding new liquid and a drain spigot for collection of samples or for complete draining to replace the liquid if necessary. The risk in transformer sampling is that frequently the drain spigot from which a sample is to be collected is old and can fail during any attempt to open it. This can result in very large spills, therefore precautions need to be taken to contain any spill. If there is no identifying label, it should be assumed that they contain PCBs and then sampled according to the following procedure.

FIGURE 6.9:
Sampling electrical transformer for PCB liquid.
(Courtesy of the Netherlands – ILT and Canada – DOE)

ASSEMBLE EQUIPMENT

The following equipment should be prepared for sampling a de-energized electrical transformer unit.

- ☐ Assemble appropriate protective gear, goggles/eye glasses, disposable coveralls, rubber boots and gloves. See SECTION 2.6
- ☐ Stainless steel tray capable of placing under a spigot from the transformer to contain leakage, or
- ☐ Polyethylene sheet to lay under the transformer and sampling equipment
- ☐ Glass pipette and rubber bulb or disposable flexible plastic bulb-pipette capable of drawing a 10 ml sample of oil
- ☐ Appropriate sized glass sample bottle and lid. See TABLE 2.9.2.2
- ☐ Hexane solvent for cleanup of equipment
- ☐ Plastic bags to dispose of contaminated materials
- ☐ Sand or absorbent (such as pet litter)
- ☐ Tools to open the access port of the transformer and/or the drain spigot.
- ☐ Explosion proof peristaltic pump and disposable tubing
- ☐ Disposable PCB test kit

SUGGESTED PROCEDURE

1. Wear appropriate protective gear, goggles/eye glasses, disposable coveralls, rubber boots and gloves. See SECTION 2.6
2. **Warning: severe shock and injury or death could result from failure to de-energize the transformer.** Consult with a qualified electrician to ensure that the electrical transformer is disconnected from the electrical system and that the transformer has been de-energized.
3. Examine the label and determine if it says that the capacitor contains PCBs or contains a trade mark name such as Askarel, Pyranol or Inerteen which are known PCB liquids. Trade names of PCB liquids may be different in other countries.
   See also: US EPA Compliance Monitoring, Polychlorinated Biphenyl Inspection Manual
   http://www.epa.gov/compliance/resources/publications/monitoring/tsca/manuals/pcbinspect/index.html
4. Record the information on the label in the field notes and/or photograph it.

ACCESS VIA THE ACCESS PORT OF THE TRANSFORMER

1. Open the access port and obtain a sample by;
   - using the glass pipette and rubber bulb or disposable flexible plastic bulb-pipette capable of drawing a 10 ml sample of oil, or
   - using a peristaltic pump with disposable tubing, to suck sufficient sample into an appropriate glass sample bottle. See FIGURE 6.7 AND TABLE 2.9.2.2
2. Use a disposable PCB test kit to determine if the oil contains PCBs above the regulated limit.
3. If it contains PCB above the regulated limit, submit the sample for laboratory analysis.

ACCESS VIA THE DRAIN PORT OF THE TRANSFORMER

1. Lay out the polyethylene on a stable surface at the drain spigot of the transformer. If it is very large, build up a berm by laying out a ring of sand or sandbags/pet litter bags around the area to be sampled.
2. Open the drain valve a small amount and collect the initial sample in a separate jar to flush out the spigot. Then close the spigot.
3. Open the drain valve a small amount and collect the primary sample in a separate jar. Then close the spigot.
4. If possible, conduct a field screening test following the instructions on the disposable PCB test kit.
5. Seal the sample and store according to the requirements of TABLE 2.9.2.2.
6. Ensure the transformer is stored according to the regulatory requirements.
7. Carefully dispose of all potentially contaminated sampling materials into a waste container and label the container according to regulatory requirements.

6.6.4 SAMPLING SURFACES FOR PCBS

Take wipe samples of any smooth surface that is considered relatively

nonporous (e.g., metal, glass or enameled wood). Take destructive samples of hard porous surfaces (e.g., cement, brick, asphalt or bare wood).

ASSEMBLE EQUIPMENT

- ☐ Personal Protective Equipment: Disposable PCB-resistant gloves (one pair per sample), disposable coveralls, footwear covers and safety goggles
- ☐ Gauze pads (10 cm x 10 cm cotton, pharmaceutical grade)
- ☐ 40 mL glass vials with tetrafluouroethylene (TFE) lined caps
- ☐ Stainless steel forceps
- ☐ Container of reagent grade hexane (e.g. eyedropper bottle)
- ☐ Stainless steel template or disposable cardboard template (10 cm x 10 cm)
- ☐ Plastic disposal bags
- ☐ Secondary sample container bags, officials seals, and custody forms
- ☐ Sample labels and indelible pens

SITE SELECTION

If the area of suspected contamination is small, take three co-located but equidistant samples from the center of area. If it is a large spill site, See SECTION 2.4.3.

SUGGESTED PROCEDURE

1. Use the PPE listed above.
2. Identify in the field logbook the size and location of the areas to be sampled.
3. Photograph the area, from at least four directions and an elevated view, if possible.
4. Moisten gauze pad with hexane using a squeeze bottle or with an eyedropper.
5. Lay down the 10 cm x 10 cm template onto the sample area.
6. Using stainless steel forceps to hold the gauze pad, thoroughly swab a 100 cm^2 sample area as identified with the template. Swab in a

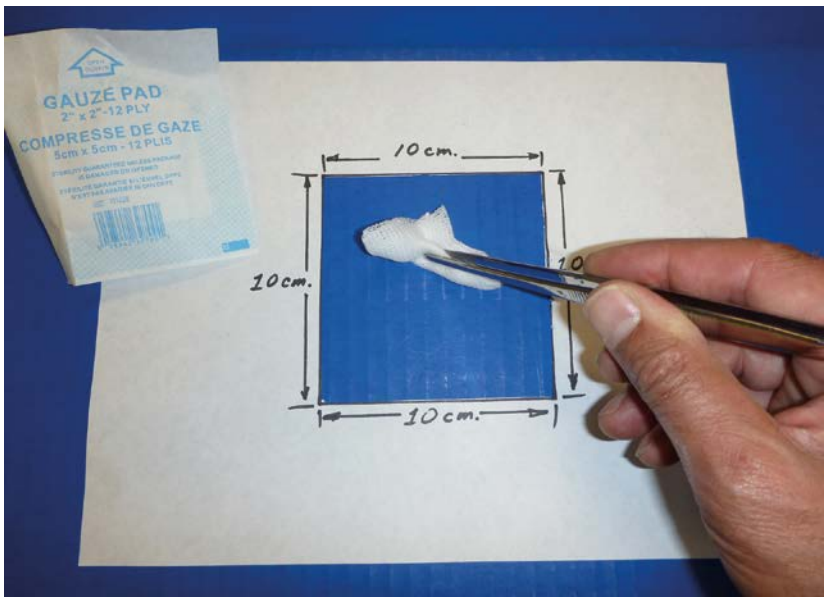


FIGURE 6.10:
Use a hexane swab and wipe a 10 cm x 10 cm area. (Courtesy of Genesis Environmental Sciences Ltd.)

horizontal direction with one side of the swabbing material and repeat in the vertical direction with the other side.

7. Place the pad in a clean sample container. Cap the container.
8. Identify, officially seal, and log samples. Place samples in a cooler.
9. Place contaminated equipment into a plastic bag for disposal or decontamination.
10. Using a clean forceps and swab prepare a control blank by going through the entire procedure without swabbing the surface.
11. Placing samples in a cooler is recommended when dealing with PCBs.

Additional details can be found at: US EPA Compliance Monitoring, Polychlorinated Biphenyl Inspection Manual
http://www.epa.gov/compliance/resources/publications/monitoring/tsca/manuals/pcbinspect/index.html

6.7 SAMPLING GROUNDWATER

Groundwater sampling consists of sampling water from shallow surface seeps which may be aboveground or upwelling into the bottoms of streams, lakes, rivers or the ocean. A sample may be taken from shallow piezometers pushed a metre into the ground or from wells drilled to hundreds or thousands of feet below the ground surface.

6.7.1 SHALLOW GROUNDWATER SEEPAGE METER – ESTIMATING CONTAMINANT LOAD TO STREAMS

Shallow groundwater will seep up into surface water bodies such as the foreshore areas of streams, rivers, lakes and oceans. A simple and effective low cost method to collect the groundwater before it completely mixes with the overlying body of water is to use a seepage meter. The seepage meter also provides a method by which groundwater flux into the overlying body of water can be calculated. See WATER 7 AND FIGURES 6.11 AND 6.12

ASSEMBLE THE MATERIALS TO MAKE THE SEEPAGE METER

- ☐ Select the container to use as a seepage meter. This can be a 4-litre or 10-litre plastic bucket (which may be obtained from a hardware or paint supply store) or as large as a 200 L steel drum
- ☐ 0.5 to 10 litre plastic bags with no sealing rims
- ☐ 2.0 cm or larger diameter rubber bungs
- ☐ 0.7 to 1.0 cm diameter rigid plastic tubing
- ☐ Elastic bands
- ☐ Drill and drill bits at least 3mm (1/8 inch) smaller in diameter than the rubber bungs and slightly smaller than the plastic tubing
- ☐ Shovel
- ☐ Graduated cylinder
- ☐ At least two sample jars and appropriate preservative. See SECTION 2.9.2

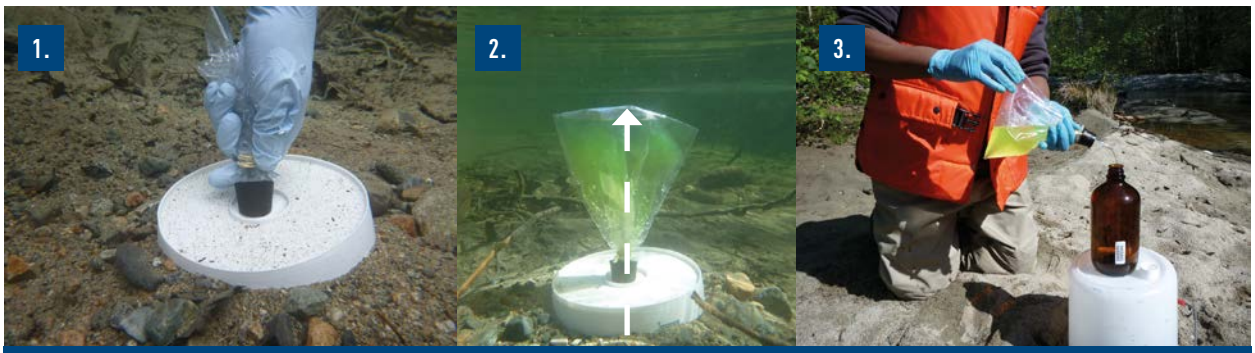
1. Drill the bottom of the bucket to accept the rubber bung (shown with tube and plastic baggie).
2. Insert the seepage meter bucket into the substrate.
3. Squeeze the air out of the baggie prior to insertion into the seepage meter.

FIGURE 6.11:
Construction and installation of a seepage meter.
(Courtesy of Canada - DOE)

SUGGESTED PROCEDURE

1. Drill a hole in the center of the bottom of the bucket which allows a tight fit of the rubber bung.
2. Drill a hole in the center of the rubber bung which allows a tight fit of the tubing.
3. Cut the tube into approximately 6 cm length and insert into the rubber bung so that at least 3 to 4 cm extends out the top (wide end) of the rubber bung.
4. Push the seepage meter into the soil/sediment in the area of suspected groundwater upwelling until the bottom of the bucket comes to rest on the substrate. The top of the bucket should be at least 6 cm below the surface of the water body. If the substrate is too difficult to push into, use a shovel to dig a hole capable of containing the bucket. Place all the material from the hole into the bucket, quickly flip the bucket and place it in the hole so that the material is retained inside the bucket.

FIGURE 6.12:
Insertion, groundwater filling, and sampling of the seepage meter bag.
(Courtesy of Canada - DOE)



1. Deflate the bag as the rubber bung is inserted into the hole in the bucket.
2. Water pressure from upwelling groundwater will force water into the bag.
3. Pour the sample from the bag into a sample jar.

5. Pack any remaining substrate around the bucket to form as natural a seal as possible.
6. If possible, allow the bucket and the groundwater flow to equilibrate for 24 hours.
7. Attach the open end of the plastic bag to the plastic pipe using the elastic band to secure the bag to the pipe. Ensure that any liquid

entering the bottom of the bung will only pass into the pipe and subsequently into the plastic bag.

8. Deflate the bag and keep it deflated as the rubber bung is inserted into the hole in the bucket.
9. Record the time at which the rubber bung was inserted.
10. Collection of a sample from the seepage meter: Water pressure from upwelling groundwater will force water into the inverted open end of the bucket and up through the pipe to inflate the plastic bag. It may take several minutes to several days to inflate the bag depending on the flow of groundwater. The sample should be collected by removing the entire bung/bag assembly taking care that ambient water from the stream does not enter the rubber bung.
11. Record the time at which the bag was removed from the seepage meter.
12. Pour the sample from the bag into a sample jar according to the type of analysis required. See SECTION 2.9

ESTIMATE THE RATE OF GROUNDWATER FLUX (VOLUME PER UNIT AREA OF STREAM BOTTOM)

To estimate the rate of groundwater flux into the bag, pour the water from the bag into the graduated cylinder and record the volume.

Calculate the groundwater flux using the following formula:

$$\text{Groundwater Flux} \left(\frac{\text{litres}}{\text{area x time}}\right) = F = \frac{V}{T} \times \frac{1}{A}$$

V = Volume of water (litres) collected in the bag
T = Time (hours or minutes) to collect the volume
A = Area of the bottom of the bucket (m^2)

ESTIMATE THE LOADING OF CONTAMINANTS TO THE BODY OF WATER

Calculate the loading of contaminants to the body of water using the formula:

$$\text{Groundwater Contaminant Loading} \left(\frac{\text{Load}}{\text{time}}\right) = L = \frac{V}{T} \times \frac{1}{A} \times C \times A_s$$

V = Volume of water collected (litres)
T = Time (hours) to collect the Volume
A = Area of the bottom of the bucket (m^2)
A_s = Area of the impacted stream (m^2)
C = Concentration (e.g. µg/L)

Example: Assume 2 litres of liquid were collected in the seepage meter baggie over 6.5 hours from a bucket with a base of 0.1 m2 and the concentration was 32 µg/L selenium and the impacted area of the stream was estimated to be 15 m^2.

$$\text{Groundwater Contaminant Loading} \left(\frac{\text{Load}}{\text{time}}\right) = L = \frac{2}{6.5} \times \frac{1}{0.1} \times 32 \times 15 = 1{,}470\ \mu g\ \text{selenium/h}$$

6.7.2 SHALLOW GROUNDWATER – PIEZOMETERS

Samples of shallow groundwater may be collected by using piezometers which may be tubes of plastic (usually polyvinyl chloride, PVC) or stainless steel with slots cut into the pipe, or with well point tips that have slots or screened holes that allow water to enter the tip after it is driven into the ground. The type of material used to make the piezometer will depend on the type of analysis, soil type, depth to groundwater, and method of insertion into the soil. The best material is stainless steel due to strength, resistance to corrosion and ease of decontamination.

FIGURE 6.13:
Installation of shallow piezometers using a slide hammer, and measurement of groundwater elevation. (Courtesy of Canada – DOE)

The method to collect the water sample from the piezometer will depend on the diameter of the piezometer's outer tube and the construction of the piezometer tip. The most common are piezometer tips with a nipple to which a pumping tube of 3 to 10 mm inside diameter can be attached. The pumping tube runs inside the piezometer tube to the surface and exits via an exit port or from the top of the piezometer tube. A peristaltic pump can be attached to the pumping tube and most pumps can extract up to 6 metres of lift.

FIGURE 6.14:
Grab sample being collected from a shallow piezometer using a peristaltic pump.
(Courtesy of Canada - DOE)

ASSEMBLE EQUIPMENT

- ☐ Piezometer tubes
- ☐ Couplings
- ☐ Tubing bypass
- ☐ Piezometer tips
- ☐ Hammer or slide hammer and percussion pad
- ☐ Peristaltic pump
- ☐ Correct pumping tube
- ☐ Bottles and preservatives. See SECTION 2.9.2
- ☐ Multimeter probe capable of testing temperature, pH, conductivity and dissolved oxygen, or test kits
- ☐ Container to store contaminated purge water

SUGGESTED PROCEDURE

1. Thread the pumping tube and attach it to the piezometer tip and thread the pipe(s) onto the tip.
2. Pound the assembled piezometer into the soil or foreshore sediment to the desired depth to reach groundwater.
3. Attach the peristaltic pump and pump out the initially disturbed groundwater from the piezometer. Calculate the volume in the tube and if possible (depending on the rate of groundwater flow into the piezometer) purge at least 3 times that volume from the tube.
4. Check that the purge liquid is relatively free of suspended solids.
5. Check that pH, temperature and conductivity have stabilized.
6. Allow the piezometer to equilibrate for 4 to 24 hours.
7. Collect a sample of groundwater. Attach the peristaltic pump or use a bailer, collect a sample and preserve it according to the requirements for the type of analysis. See SECTION 2.9

6.7.3 DEEP GROUNDWATER SAMPLING

Deep groundwater wells are generally significantly more complex to install and operate than shallow hand driven wells and therefore installation of deep wells will not be covered in this manual. Deep wells generally require a powered drilling rig and specialty tools to drill and install a casing to form the outside pipe. Alternatively, they may consist of an outside pipe to form a wall and an inside pipe to form the water extraction conduit. The wells may require screens and sealing units at various depths so as to intersect ground structures that are capable of conveying groundwater and any contaminants they contain. Sampling from these wells generally consist of two types of samplers – passive (non-pump) methods and pump methods.

6.7.4 DEEP GROUNDWATER – DIFFUSION SAMPLERS AND CHECK VALVE SAMPLERS

Passive non-pump methods collect groundwater contaminants either by diffusion or by an expandable sleeve with check valves. The advantage of the non-pump methods are that the well does not have to be purged before collecting a sample. This eliminates the cost of the operator and equipment to purge and store contaminated groundwater and ultimately costs to properly dispose of contaminated purge water. For all pumping methods, the passive sampler or the tubing for electric pumps should be dedicated to a single well to prevent cross contamination of other wells.

ASSEMBLE EQUIPMENT

- ☐ Correct pumping tube (usually polyethylene for metals or salts, or Teflon for organics)
- ☐ Bottles and preservatives. See SECTION 2.9.2
- ☐ Multimeter probe capable of testing temperature, pH, conductivity and dissolved oxygen, or test kits
- ☐ Container to store contaminated purge water
- ☐ Sampler
  - diffusion sampler, or
  - check valve sampler, or
  - check valve pump, or
  - peristaltic pump, or
  - down hole positive displacement pump

SUGGESTED PROCEDURE – DIFFUSION SAMPLERS

Diffusion samplers consist of a longitudinal bag that has a narrow diameter so that it can be lowered into the well. It is usually about 25 to 50 mm in diameter and filled with distilled or de-ionized water.

1. The water-filled diffusion sampler is suspended on a string or rope and lowered to the predetermined depth adjacent to the desired well screen.
2. The higher concentration of contaminants in the well water results in a concentration gradient which causes the contaminants to diffuse from the well water into the bag until the concentration inside and outside the bags are equal.

3. After a pre-determined time (see the manufacturer's suggested instructions) the bag is withdrawn from the well, punctured, and the water is poured into the recommended sample container and preserved. See SECTION 2.9

SUGGESTED PROCEDURE – CHECK VALVE SAMPLERS

Check valve samplers consist of a longitudinal bag that has a narrow diameter so that it can be lowered into the well. It has a closed end on the bottom to which a weight (usually stainless steel) is attached. The top end of the bag has a one way check valve that allows water into the bag when it is rapidly pulled up.

1. The check valve sampler is suspended on a string or rope and lowered to the predetermined depth just at or below the desired well screen.
2. The check valve sampler is then pulled up which causes the check valve to open and allow water to enter the sampler until it is full. If it is a pump type valve, the check valve is raised and lowered in multiple strokes where the down stroke allows water in and the upstroke forces the check ball against the seat and pumps the water up the tube.

6.7.5 DEEP GROUNDWATER – ACTIVE PUMP SAMPLERS

Active pump samplers come in three general forms, a hand-held and hand-operated positive displacement (check valve) pump, an electric peristaltic pump, and an electric centrifugal pump. Each type of pump requires the purging of the well by pumping a certain volume (usually three times the well volume) prior to collecting a sample. This requires the collection and proper disposal of contaminated groundwater.

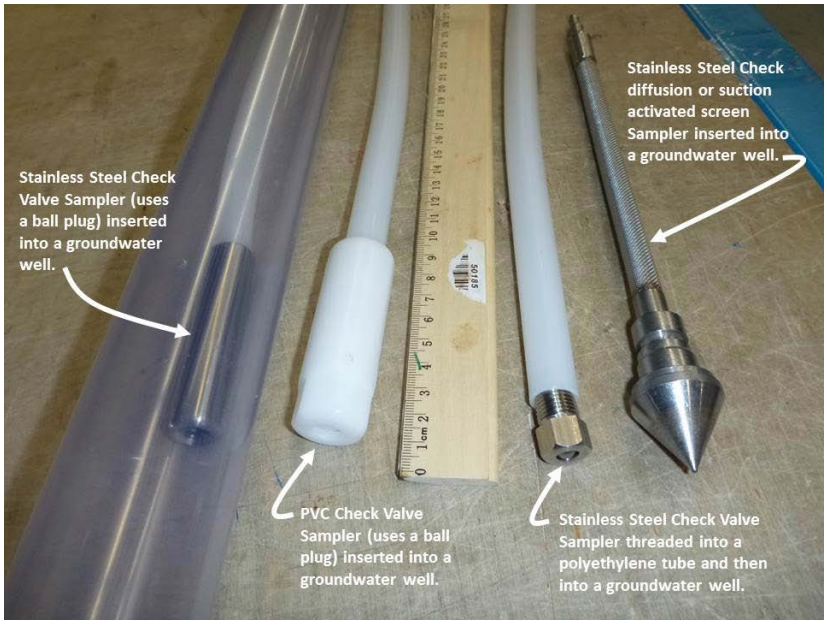


FIGURE 6.15:
Check valve pumps and suction screen which can be used to extract groundwater from piezometers.
(Courtesy of Canada - DOE and Pine Environmental)

SUGGESTED PROCEDURE – CHECK-VALVE PUMP

1. Check valve pumps have a small check valve that is connected to a length of tubing (usually polyethylene or Teflon).

2. The pump is lowered to the desired well screen and repeatedly lifted and lowered. The check valve allows water into the bottom of the tube when it is lowered and lifts it when raised.
3. Repetition of lowering and raising will cause the water to rise to the surface where it is pumped into the proper container and preserved. See SECTION 2.9

SUGGESTED PROCEDURE – ELECTRIC PERISTALTIC PUMPS

Peristaltic pumps have a flexible tube that is connected to a length of tubing (usually polyethylene or Teflon).

1. The tube is lowered to the desired well screen and the pump is turned on. The pump works via suction at the surface and is usually limited to about 6 metres of lift.
2. Pumping continues to raise the water in the tube to the surface where it is pumped into the proper container and preserved.
3. The pumps can be reused at multiple wells however the tubing should be dedicated to a single well. Therefore it must be disconnected and replaced at the next well.

SUGGESTED PROCEDURE – ELECTRIC POSITIVE DISPLACEMENT PUMPS

Electric positive displacement pumps have a tube connected to them.

1. The pump with a power cable and tubing attached is lowered into the well to the desired well screen depth.
2. The pump is turned on and the water is pumped to the surface. Because they operate by positive displacement, they can be used in deeper wells.
3. Pumping continues to raise the water in the tube to the surface where it is pumped into the proper container and preserved.

6.7.6 SEDIMENT PORE WATER (SHALLOW WATER ZONES)

Sediment pore water refers to the water that fills the spaces in the pores between the particles of sediment. Sampling of this water before it mixes with overlying water can be achieved using a pore water sampler. The design of the sampler depends on the depth of the overlying water. This section refers to shallow water zones that can be sampled by wading or from a boat in shallow water. Pore water can be sampled for any chemical compound which may contaminate it, commonly heavy metals, organic solvents and volatile organic compounds (VOCs).

A shallow zone pore water sampler generally consists of a stainless steel tube with a piezometer tip on the end. Some designs include a central push rod which is inserted into the stainless steel tube. The push rod is used to insert the sampler into the bottom sediment. After insertion, the push rod is extracted and the sampler tube is connected to a pumping tube and pump or a syringe.

6.7.7 VOLATILE ORGANIC COMPOUNDS IN SEDIMENT PORE WATER

ASSEMBLE THE EQUIPMENT

- ☐ Appropriate safety equipment to protect against VOCs
- ☐ Pore water sampler (properly cleaned for organic compounds)
- ☐ Flange or sampling platform
- ☐ Peristaltic pump or syringe
- ☐ Tubing for peristaltic pump or syringe
- ☐ Sample container with seal (40 mL glass vials with Teflon septa) and sealer tool

INSTALLATION AND SAMPLING PROCEDURE

1. In order to reduce or prevent surface water from entering the sample ports, a flange can be laid on the sediment through which the sampler penetrates. The flange should be as tight fitting as possible.
2. Insert the pore water sampler using the push rod. Extract the push rod when the desired depth has been reached.
3. Attach the hose to the sampler and to the peristaltic pump.
4. Purge enough pore water to clear any entrained surface water.
5. Collect the sample into the 40 mL glass vials until completely full with a surface meniscus. Seal with the Teflon septa to ensure there is no head space in the vial.
6. Invert the vial and tap to ensure there are no entrained water bubbles.
7. Store the sample in a cool dark container and ship for analysis.

An alternative to the peristaltic pump is to use a syringe attached to the sample hose to extract the sample.

6.7.8 HEAVY METALS AND NON-VOLATILE CHEMICALS IN SEDIMENT PORE WATER

ASSEMBLE THE EQUIPMENT

- ☐ Appropriate safety equipment to protect against heavy metals
- ☐ Pore water sampler properly cleaned for metallic or organic compounds
- ☐ Flange or sampling platform
- ☐ Peristaltic pump or syringe
- ☐ Tubing for peristaltic pump or syringe
- ☐ Vacuum flask with connectors
- ☐ Inline filters which connect to the extraction tubing
- ☐ Sample container with seal (40 mL glass vials with Teflon septa) and sealer tool

INSTALLATION AND SAMPLING PROCEDURE

1. In order to reduce or prevent surface water from entering the sample ports a flange can be laid on the sediment through which the sampler penetrates. The flange should be as tight fitting as possible.
2. Insert the pore water sampler using the push rod. Extract the push rod when the desired depth has been reached.

3. Attach the hose to the sampler.
4. Attach the inline filters to obtain dissolved metals samples.
5. Attach the hose after the filter to a vacuum flask. The vacuum flask will allow the collection of liquid in the flask and prevent contamination of the peristaltic pump hose and pump.
6. Purge enough pore water to clear any entrained surface water and dispose.
7. Attach a clean vacuum flask and collect a sample.
8. Transfer the sample from the vacuum flask to the sample container and preserve according to the requirements. See SECTION 2.9.2
9. Store the sample in a cool dark container (such as a cooler) and ship for analysis.
10. An alternative to the peristaltic pump is to use a syringe attached to the sample hose to extract the sample. The sample is then kept in the syringe or transferred to the appropriate sample bottle. SECTION 6.7.9 and FIGURE 6.16

For further information see "USEPA, SESD Operating Procedure, Pore Water Sampling, SESDPROC-513-R0, Pore Water Sampling_AF.R0.coc, Feb. 05, 2007

FOR PORE WATER FROM SEDIMENT SAMPLES

1. Collect a sediment sample using sediment sampling techniques.
2. Submit the sample for pore water by extraction by centrifuge.

6.7.9 SAMPLING WATER FOR HEAVY METALS – TOTAL, EXTRACTABLE AND DISSOLVED

Heavy metals may be analysed to determine their availability to cause environmental damage. Sampling procedures are conducted to allow tests for total, extractable and dissolved metals.

6.7.9.1 Heavy Metals – Total and Extractable

Total metals include metals which are bound to particles in the water as well as dissolved metals which are electrically charged and floating freely/dissolved in the water. Extractable metals will be analysed by digesting the sample in hot, dilute acid to extract metals which are lightly absorbed to particles in the sample. Total metals will be analysed by completely digesting all particles in the sample solution. Therefore, total and extractable metals samples do not require filtering, whereas dissolved metals sampling require filtering before preservation by the addition of nitric acid.

ASSEMBLE THE EQUIPMENT

- ☐ Sample bottles. See SECTION 2.9.2
- ☐ Nitric acid preservative. See SECTION 2.9.2. To minimize the risk of handling nitric acid, if possible, obtain small vials with the appropriate volume of acid for a single dose to the sampling bottle. These may be obtained from the supporting laboratory.
- ☐ Appropriate protective gear to handle metals contaminated samples and nitric acid preservative (eye protection, gloves, coveralls)
- ☐ pH test paper

SUGGESTED PROCEDURE

Obtain the representative sample using the appropriate technique leaving enough room in the sample bottom for the addition of the nitric acid preservative.

Note: Total metals and extractable metals do not require filtering prior to preserving the sample with nitric acid. When nitric acid is added, this will act to prevent the dissolved metals in the sample from plating out on the insides of the sample container.

Add the specified volume of nitric acid preservative to the sample.

6.7.9.2 Heavy Metals – Dissolved

ASSEMBLE THE EQUIPMENT

- ☐ Sample bottles. See TABLE 2.9.2
- ☐ Nitric acid preservative. See TABLE 2.9.2. To minimize the risk of handling nitric acid, if possible, obtain small vials with the appropriate volume of acid for single dose to the sampling bottle. These may be obtained from the supporting laboratory.
- ☐ Appropriate protective gear to handle metals contaminated samples and nitric acid preservative (eye protection, gloves, coveralls).

  Note: For a small number of samples and/or where electrical power supply is difficult a syringe filtration system may be appropriate.

PORTABLE FILTRATION EQUIPMENT

- ☐ 50 cc (cm^3) plastic syringe capable of attaching a 0.45 micron (µm) syringe filter
- ☐ 0.45 micron (µm) syringe filters

SUGGESTED PROCEDURE – PORTABLE FILTRATION

1. The 50 cc plastic syringe can be filled by attaching the 0.45 micron syringe filter and sucking the water through the filter into the syringe. The filter is then removed and the filtered water is expressed into the appropriate sample container, or
2. The 50 cc plastic syringe can be filled by sucking the water into the syringe first, and then attaching the 0.45 micron syringe filter and pushing the water through the filter into the appropriate sample container.

VACUUM PUMP FILTRATION EQUIPMENT

- ☐ Vacuum pump with water filtration apparatus
- ☐ 0.45 micron vacuum pump disk filters
- ☐ Stainless steel tweezers to hold the disk filters
- ☐ Electrical cords
- ☐ Electrical power supply compatible with the vacuum pump
- ☐ Sufficient volume of distilled or de-ionized water to clean filtration equipment between samples.

  Note: Where possible, use disposable filters to minimize risk of cross contamination
- ☐ Squeeze bottles to contain rinse water
- ☐ Waste containers capable of holding contaminated rinse water

FIGURE 6.16:
Syringe and 0.45 micron Filter to collect dissolved metals water sample.
(Courtesy of Canada - DOE)

SUGGESTED PROCEDURE – VACUUM PUMP FILTRATION

1. Wash and assemble the vacuum filtration apparatus according to manufacturer's instructions.
2. Insert the 0.45 micron vacuum pump disk filters into the holder
3. Collect the sample according to the sampling protocol and ensure it is well mixed before pouring it into the vacuum filter funnel.
4. Filter the sample and pour it into the sample container leaving enough room in the sample bottle for the addition of the nitric acid preservative.
5. Preserve the sample with nitric acid. See SECTION 2.9.2
6. Wash and clean the vacuum filtration equipment prior to filtration of the next sample.

6.8 BIOASSAY SAMPLING

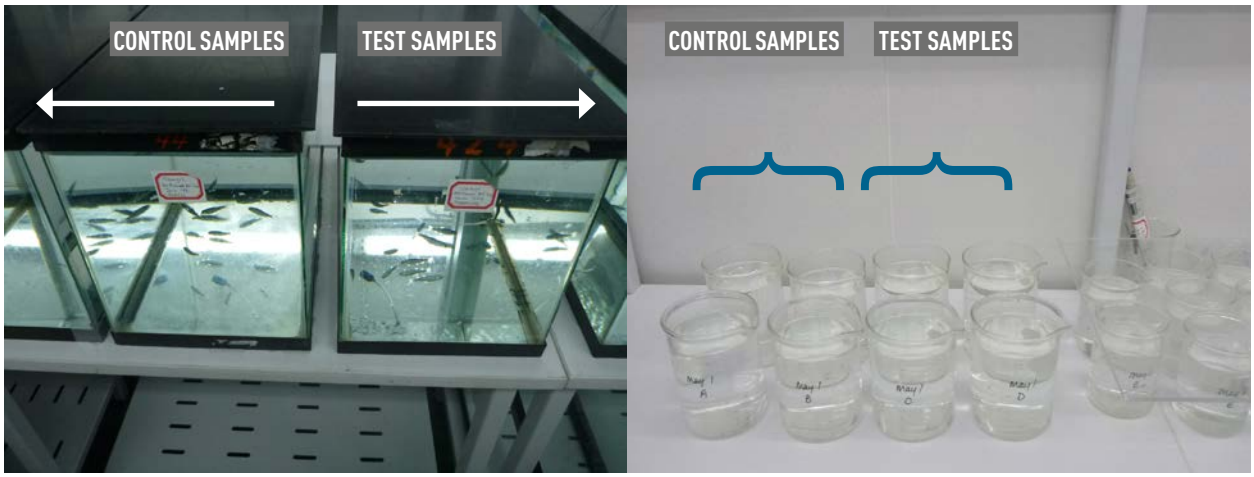
Water samples for bioassays range from less than a litre for tests on small aquatic organisms, such as Daphnia magna (water flea), to 40 litres for minnows, such as rainbow trout, salmon, fat head minnow or other indigenous species.

6.8.1 SAMPLING WATER FOR BIOASSAY OF LIVING ORGANISMS

Bioassays are commonly conducted to verify the impacts of toxic chemicals on living organisms. It is generally easier for the judiciary to understand that a sample killed the organism or caused deformities than it is to understand other chemical or biological information. Therefore, bioassay tests are often key to a legal environmental investigation.

The type of test procedure also depends on the information required, as the end point of the test may be to assess the impact on hatching, growth or survival, both short term and long term. The type of organism depends on the type of toxicant, the availability of the organism, the legislation and the legal precedent for using organisms. Common organisms are juvenile fish, frogs, shellfish, Daphnia magna (water flea) and luminescent bacteria. Generally the test organism is a species which is readily available in the region and can be reared under laboratory conditions. The size of the sample which must be collected depends on the laboratory requirements for the test.

FIGURE 6.17:
Bioassays (96 Hour LT50 or LC50) may use small fish in 40 litre tanks or small water fleas or other organisms in beakers to test the toxicity of effluents or sediments.



6.8.2 ACUTE TOXICITY BIOASSAY – 96 HOUR LT50

The 96 Hour Lethal Time to 50% survival of the test organism (or 96 Hr LT50) test sets out to answer the question: Is the sample acutely toxic? This test is often used as the basic test for fish toxicity and compliance with legal limits. The acute toxicity of a solution at 100 % concentration can be tested by exposing organisms, for example juvenile fish, over a particular time period. The term 96 Hr LT50 means the lethal time it takes for 50% of the organisms to die when exposed to a sample with a maximum exposure time of 96 hours. Depending on the criteria to be tested, the exposure times can vary according to the required legal protocol.

EXAMPLE PROCEDURE OF A 96 HOUR LT50 FISH BIOASSAY PROCEDURE

1. 45 L of sample are collected in a clean plastic container.
2. Conduct the analysis within the prescribed holding period. See TABLE 2.9.2.3
3. A 40 L fish tank is filled with control water.
4. A 40 L fish tank is filled with well mixed sample water.
5. Both tanks are tested for conductivity and pH.
6. Both tanks are aerated to ensure that depletion of oxygen is not a factor.
7. Both tanks are brought to a standard temperature.
8. Ten fish of a particular species and size are placed in each tank under controlled light conditions.
9. The fish are not fed during the test and are monitored at specific intervals and notes of stress signs and/or mortalities are recorded.
10. The control tank test continues for 96 hours.
11. The sample test tank continues for 96 hours or until 50% or more of the fish die.
12. The results are reported as "time for at least 50% of the fish to die".

6.8.3 ACUTE TOXICITY BIOASSAY – 96 HOUR LC50

The 96 Hour LC50 tests sets out to answer the question: At what concentration is the sample acutely toxic, whereas acute toxicity is set as having at least 50% mortality of the test organisms. The acute toxicity of a solution at various concentrations can be tested by exposing an organism, for example juvenile fish, over a particular time period.
The term 96 Hour LC50 means the Lethal Concentration for 50% of the organisms to die when exposed to a specific concentration of the sample, with a maximum exposure time of 96 hours.

This test is more expensive than the 96 hour LT50 as it commonly uses at least four or five concentrations such as 20%, 40%, 60%, 80% and 100% sample concentrations, plus a control. This requires a much larger sample to be collected and correspondingly more bioassay containers, organisms, test space, and analyst time. Normally the results are plotted to determine statistically the estimated concentration at which 50% of the test organisms would survive for 96 hours of exposure. Depending on the criteria to be tested, the exposure times can vary.

EXAMPLE PROCEDURE OF A 96 HOUR LC50 FISH BIOASSAY

1. 90 L of sample are collected in a clean plastic container.
2. A 40 L fish tank is filled with control water.
3. Five 40 L fish tanks are filled with well mixed sample water at say 20%, 40%, 60%, 80% and 100% sample concentration.
4. All tanks are tested for conductivity and pH.
5. All tanks are aerated to ensure depletion of oxygen is not a factor.
6. All tanks are brought to a standard temperature.
7. Ten fish of a particular species and size are placed in each tank under controlled light conditions.

8. The fish are not fed during the test and are monitored at specific intervals and notes of stress signs and/or mortalities are recorded.
9. The control tank test continues for 96 hours.
10. The sample test tanks continues for 96 hours or until 50% or more of the fish die.
11. The results are reported as "the concentration for at least 50% of the fish to die in 96 hours".

6.8.4 EARLY LIFE STAGE BIOASSAYS

Early life stage bioassays set out to answer the question: Will the sample cause an impact on the early life stage development of an organism? Normally, the early life stages of organisms are most susceptible to pollution. Therefore, protocols will be required to expose an organism to a pollutant and to a control sample over a specified period of time.

EXAMPLE PROCEDURE OF AN EARLY LIFE STAGE FISH/FROG/BIRD BIOASSAY

1. If the organism requires the water to flow around it, then a large volume of sample (1000 L or more) is collected in clean plastic containers.
2. Certain early life stage bioassays such as for selenium toxicity to fish/frogs do not require a large volume of the effluent since the selenium is contained in the eggs and only a source of clean water is required to rear the eggs to early life stage end points such as hatching or yolk absorption.
3. All water flows are tested for conductivity and pH.
4. All water flows are aerated to ensure depletion of oxygen is not a factor.
5. All water flows are brought to a standard temperature.
6. A set of 100 newly fertilized fish eggs are placed in incubation trays that are exposed to a flow of control water under controlled light conditions.
7. Five sets of 100 newly fertilized fish eggs are placed in incubation trays that are exposed to a flow of 100% sample concentration.
8. The control tank test continues for 30 days until the eggs hatch and the fish absorb the yolk sacks. Dead eggs and hatched fish/frogs are removed daily.
9. The sample test tanks continues for 30 days until the eggs hatch and the fish/frogs absorb the yolk sacks. Dead eggs and hatched fish/frogs are removed daily.
10. The results are reported as the percent of survival or specific defects such a spinal or cranial deformities depending on the criteria of the test.

Further information on fish bioassays can be found at:

Environment Canada, Wildlife Science and Technology, Biological Test Method Series :

http://www.ec.gc.ca/faunescience-wildlifescience/default.asp?lang=En&n=0BB80E7B-1

US EPA, Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms :
http://water.epa.gov/scitech/methods/cwa/wet/upload/2007_07_10_methods_wet_disk2_atx.pdf

7 SAMPLING SURFACES, SOLIDS, SEDIMENTS AND SOILS

Sampling Surfaces, Solids, Sediments And Soils

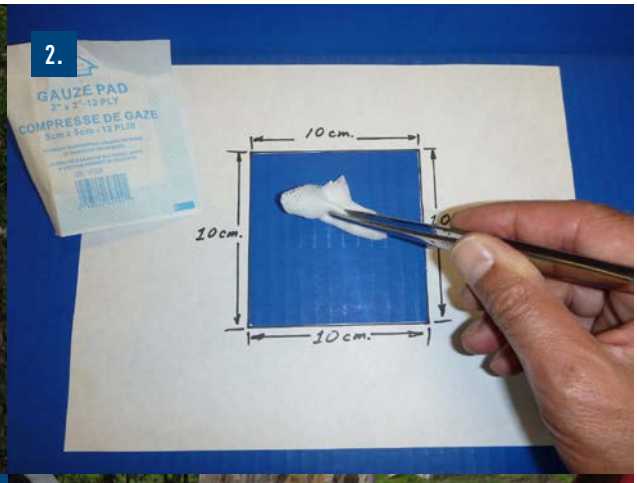
Sampling solid surfaces may be required to measure the degree of fallout from a fire, gas stack emissions, or chemical spills which adhere to or soak into surfaces. The technique used to collect the sample will depend on the type of material deposited or soaked into the surface and the characteristics of the surface.

7.1 SAMPLING SOLID SURFACES

7.1.1 WIPE (SWAB) SAMPLES

Solid surfaces may be sampled by using wipe sampling techniques. Common areas include metal and glass surfaces, window ledges and any structure subject to atmospheric fallout. Sample would be acid digested for metals, or solvent extracted for organics.

FIGURE 7.1:
Swab/wipe sample of fallout, with 100 cm² template and solvent and tweezers. (Courtesy of Genesis Environmental Sciences Ltd.)



1. Fallout from a waste fire can deposit contaminat soot over a wide area.
2. Use a 10 cm x 10 cm cotton swab and a solvent (hexane for organics or nitric acid for metals) and wipe up all the soot in a 10 cm x10 cm area.
3. Place the contaminate swab into a glass sample jar (amber glass for organics, clear glass for metals).

ASSEMBLE THE EQUIPMENT

- ☐ Sample bottles: These depend on the type of contaminant but are usually wide mouth glass jars with foil lined or Teflon lined lids. See SECTION 2.9.2
- ☐ Stainless steel tweezers which have been pre-cleaned and wrapped in aluminum foil.
- ☐ Stainless steel sampling spoons which have been pre-cleaned and wrapped in aluminum foil.
- ☐ Solvent for heavy metals: To collect surface samples containing heavy metals, a dilute solution of analytical grade nitric acid is required. To minimize the risk of handling nitric acid, if possible, obtain a sample in as small a quantity as possible from the supporting laboratory.
- ☐ Solvent for organic compounds: To collect surface samples containing organic (carbon based compounds), analytical grade hexane is required. Due to flammability, obtain a sample in as small a quantity as possible from the supporting laboratory.
- ☐ Solvents for painted or waxed surfaces: Hexane may degrade painted or waxed surfaces extracting paint compounds and contaminating the sample. Therefore, reagent grade propyl alcohol or de-ionized water may have to be used as a substitute.
- ☐ Absorbent pads: Absorbent pads should be made out of analytical grade cotton and of a size which can readily be used for analytical calculation. Common sizes are 10 cm x 10 cm or 25 cm x 25 cm. Obtain such pads from the supporting laboratory or analytical supply companies. **Note:** Sterile pads such as bandages from the health care section of a drug store may be suitable however they should not be made out of synthetic materials, as these will interfere with the extraction and analytical process. It is always recommended to include an uncontaminated pad in a separate glass bottle as a control sample.
- ☐ Appropriate protective gear to handle metals, organics contaminated samples and nitric acid and/or hexane solvents (eye protection, gloves, coveralls)
- ☐ Clean thin cardboard sheets at least 30 cm x 30 cm
- ☐ Scissors or razor knife
- ☐ Tape measure

SUGGESTED PROCEDURE

1. The sampling area may be marked out visually using a tape measure or by using the scissors or razor knife to cut out a square template from the thin cardboard sheet. The square may be any size but it is recommended to be a multiple of the size of the absorbent pad, e.g. for 10 cm x 10 cm pads cut a 10 cm x 10 cm or 20 cm x 20 cm square.
2. Lay the cardboard template onto the surface to be sampled.
3. Use the stainless steel tweezers to hold the absorbent pad.
4. Saturate the pad with the appropriate solvent and store in a sample container as a control sample.

5. Saturate a second pad (and any subsequent pads) with the appropriate solvent.
6. Lay the pad on the surface inside the cardboard template.
7. Use the stainless steel tweezers to stroke the pad across the sample surface, first in one direction. Flip the pad and stroke the surface at right angles to the first direction.
8. If more than one pad is required to remove all visible material from the sample area, place all pads from the same sample site into the same sample container.
9. Record the size of the area sampled at each site in your note book.

7.1.2 CHIP SAMPLES

Chip samples can be collected using a conventional chisel to remove the surface of contaminated material. Commonly this is a steel chisel capable of removing wood or concrete. A specially designed four sided chisel that acts as a punch can be used to either mark out and/or remove a specific square of material. The size of the chisel is commonly 2.5 cm x 2.5 cm or another similar dimension. Care must be taken to only remove the material to the saturated depth.This is often used for PCB contaminated materials.

ASSEMBLE THE EQUIPMENT

- ☐ Sample bottles: These depend on the type of contaminant but are usually wide mouth glass jars with foil lined or Teflon lined lids. See SECTION 2.9.2
- ☐ Decontaminated chisel(s)
- ☐ Decontaminated hammer or electric/pneumatic hammer
- ☐ Clean/new natural bristle brush
- ☐ Clean/new dust collection pan
- ☐ Clean polyethylene sheet (at least 1.0 m x 1.0 m)
- ☐ Appropriate protective gear to handle metals and organics contaminated samples and nitric acid and/or hexane solvents (eye protection, ear protection for loud hammering noises, gloves, coveralls)
- ☐ Optional - Clean thin cardboard sheets at least 30 cm x 30 cm
- ☐ Scissors or razor knife
- ☐ Tape measure
- ☐ Marker

SUGGESTED PROCEDURE

1. Lay out the clean polyethylene ground sheet over the area to be sampled. Cut out an area just larger than the proposed sampling area. Take care not to track contaminants onto the clean upper surface of the ground sheet.
2. The sampling area may be marked out visually using a tape measure/ ruler and then using scissors or a razor knife to cut out a square template from the thin cardboard sheet. The square may be any size but it is recommended to be a multiple of 10 cm x 10 cm to assist in calculations.
3. The area should be chipped out using the hammer and chisel to a

depth of 3 to 6 mm. Record how deep the chips were taken. Take precautions to minimize the spread of the chips. If possible, collect any chips which fall onto the clean polyethylene ground sheet.

4. Collect the chipped pieces including any chips which fall onto the clean polyethylene ground sheet.
5. Dispose of contaminated sampling materials in an appropriate manner.

7.1.3 SWEEP OR VACUUM SAMPLING

Sweep or vacuum sampling may be used for collection of contaminated particulates on solid surfaces which have a rough texture such as pavement, concrete or rough wood.

ASSEMBLE THE EQUIPMENT

- ☐ Appropriate protective gear to handle metals and organics contaminated samples (eye protection, ear protection for the loud vacuum, respiratory protection against dust and vapours, gloves, coveralls)
- ☐ Sample bottles depend on the type of contaminant but are usually wide mouth glass jars with foil lined or Teflon lined lids.
  See SECTION 2.9.2
- ☐ Clean/new natural bristle brush
- ☐ Clean/new dust collection pan
- ☐ Clean/new stainless steel spatula
- ☐ Portable (battery powered) vacuum with a removable dust collection chamber and High-Efficiency Particulate Air (HEPA) filtration system. A HEPA vacuum filter normally removes 99.97% of all particles greater than 0.3 micrometre from the air that passes through the filter.
- ☐ If a portable vacuum is not available, a power source and cords needs to be provided
- ☐ Tape measure
- ☐ Marker

SUGGESTED PROCEDURE

1. Take care not to track contaminants into or out of the contaminated area.
2. The sampling area may be marked out visually using a tape measure or by using the scissors or razor knife cutting out a square template from the thin cardboard sheet or marking out an area using the tape measure and marker. The square may be any size but it is recommended to be a multiple of 10 cm x 10 cm to assist in calculations.

Sweeping technique

1. The marked out area should be swept slowly and carefully so as to minimize the generation or re-suspension of fugitive dust.
2. Collect the sample using the dust collection pan and transfer it into the appropriate sample container.

Vacuum technique

1. The marked out area should be vacuumed to minimize the generation of dust. Care must be taken that the exhaust from the vacuum does not strike the surface and re-suspend the dust. For this reason a HEPA filtration system is required.

2. The HEPA filter should be desiccated dry and pre-weighed prior to use to establish the base line weight before it is used.
3. Insert the HEPA filter and vacuum the pre-marked area.
4. Collect the sample from the vacuum dust collection chamber and transfer it into the appropriate sample container using the stainless steel spatula.
5. Clean the vacuum dust collection chamber using a clean dry brush and add the dust to the appropriate sample container.
7. Replace the HEPA filter according to manufacturer's instructions.

CALCULATE THE DUST DEPOSITION RATES

1. Retain the HEPA filter in an appropriate container, desiccate it, and then weigh it to obtain a dry weight of material caught in the filter. Subtract the clean weight of the filter from the dirty weight of the filter to obtain the mass of dust in the filter.

For example:

Contaminated weight of the filter	= 25.5 g
- Clean Weight of the filter	= 25.0 g
Mass of dust in the filter	= 0.5 g

2. Add the mass collected in the filter to the mass of dust collected in the chamber to obtain the total mass of dust collected over the marked surface.

For example:

Mass of dust in the filter	= 0.5 g
+ Mass of dust in the chamber	= 1.2 g
Total mass of dust collected	= 1.7 g

3. Divide the total mass collected by the total area sampled to obtain the dust deposition rate.

For example:

1.7 g dust/200 cm^2 = 0.0085 g dust/ cm^2

CALCULATE THE CONTAMINANT DEPOSITION RATES

1. Analyse the dust for the desired contaminant (for example a heavy metal such as lead)
2. Multiply the dust deposition by the contaminant concentration and divide by the total area sampled to obtain the contaminant deposition rate.
   E.g. (1.7 g dust x 25 µg Pb/g dust) / 200 cm^2 = 0.21 µg Pb/ cm^2
3. Dispose of contaminated sampling materials in an appropriate manner.

7.2 SEDIMENT SAMPLING

Sediment from surface layers usually reflects recent contamination. For this reason, the top 2 cm is often the layer of most interest. The usual technique is to take surface skim using spoons, shallow core samplers, or for deeper waters, dredges or deep water core samplers are required.

The volume of sediment required depends on the end use. Each chemical and biological test requires a specific amount of sediment. Check with

the lab to determine what volume to collect and what steps to take to preserve the sample. Usually samples are kept at 4°C or frozen.

QUALITY OF SEDIMENT SAMPLES

Sediment samples generally consist of fine particle sizes. The analytical process normally digests the sample in strong acid. Large pebbles and rocks or organic debris such as wood can skew the results by adding a large quantity of material which when digested by the acid will dilute the sediment sample with clean material from inside the pebble or rock.

FIGURE 7.2:
When collecting a sediment sample attempt to collect uniform fine grained material. Remove large rocks or woody debris which cannot be digested. (Courtesy of Canada – DOE)

Contact the laboratory to obtain specifications as to the maximum particle size allowed in the sample. Alternatively, collect the sample and instruct the laboratory to select the correct particle size from the sample and base the analytical results on the selected particle size(s). Submit the sample for analysis and normally specify by dry weight. Since sediment samples can have a wide variation in moisture content it is recommended that the sample contaminant concentrations be specified on a dry weight basis. Dry weight means to dehydrate the sample before analysis so that a consistent basis for measurement can be obtained. This allows comparison between sites and against regulatory standards.

ASSEMBLE THE EQUIPMENT

- ☐ Appropriate protective gear to handle metals and organics contaminated samples (eye protection, respiratory protection against dust and vapours, gloves, coveralls)
- ☐ Appropriate safety equipment including steel toed boots, life vests for working on a boat for deep water and shoreline sampling
- ☐ Sample bottles depend on the type of contaminant but are usually wide mouth glass jars with foil lined or Teflon lined lids. See SECTION 2.9.2
- ☐ Polyethylene drop sheets – minimum 1 m x 1 m
- ☐ Stainless steel trays for sample placement or

- ☐ Plastic trays lined with aluminum foil or polyethylene depending on the type of contaminant
- ☐ Distilled/de-ionized water in wash bottles, if sampling for non-organics
- ☐ Reagent grade acetone/hexane in wash bottles, if sampling for organics
- ☐ Stainless steel tweezers
- ☐ Bristle pipe cleaner brushes for cleaning core sampler tubes

SHALLOW WATER EQUIPMENT

- ☐ Cleaned stainless steel spoons wrapped in aluminum foil
- ☐ Cleaned stainless steel core samplers

DEEP WATER EQUIPMENT

- ☐ Cleaned stainless steel deep water core sampler
- ☐ Cleaned stainless steel dredges, common types are Ponar or Ekman dredge with a maximum 8 cm to 10 cm collection depth
- ☐ Support boat with winch mechanism capable of safely operating the core sampler and/or dredge sampler

7.2.1 SHALLOW WATER SEDIMENT SAMPLING – SAMPLING SPOON

SUGGESTED PROCEDURE

1. Collect a sample using the clean stainless steel spoon by scraping at least the top 2 cm of sediment.
2. Carefully drain off excess liquid while minimizing the quantity of fine sediment lost.
3. Some benthic invertebrates may be included in the sample. Consult with the laboratory as to whether they should be removed. If they are to be removed, then use stainless steel tweezers if possible.
4. Place the sample into the appropriate sample container. Free liquid is usually present.
5. Seal the sample container and submit the sample for analysis and normally specify by dry weight.

7.2.2 SHALLOW WATER SEDIMENT SAMPLING – SPLIT SPOON CORE SAMPLER

A split spoon core sampler is a stainless steel tube which splits into two matching halves. The tube is assembled by fitting the two halves together, fitting a coupling on one end and a hollow coring tip on the other. The length of the tube can be variable and plastic sleeves may be inserted depending on the sampling needs. The split spoon is driven into soils by mechanical- percussion or hydraulic-pressure mechanisms. The split spoon can be driven into off shore sediments by such devices as the KIST sampler. See SECTION 4.4.3.2 AND FIGURE 7.3

FIGURE 7.3:
1) Split spoon assembled prior to sampling. 2) After collection, split spoon is disassembled. 3) Cutting tip is removed. 4) Split spoon is opened and a core sample of sediment is collected. (Courtesy of Canada – DOE)

SUGGESTED PROCEDURE

1. Collect a sample using the clean stainless steel sediment corer by pushing the corer into the appropriate depth to obtain at least the top 2 cm of sediment. Depending on the known or suspected history of the site, deeper samples can be obtained and the reason for deeper sampling should be recorded in your field notebook.
2. Repeat the core sampling until sufficient sample has been collected.
3. Discharge the contents of the core sampler into proper glass or polyethylene containers and seal with Teflon or aluminum foil lined lids.
4. If necessary, allow the sediment to settle in the sample jar and then carefully drain off the supernatant liquid while preventing the loss of fine material. Some free liquid is usually still present.
5. Some benthic invertebrates may be included in the sample. Consult with the laboratory as to whether they should be removed. If they are to be removed then use stainless steel tweezers if possible.
6. If the sample cannot discharge directly into the sample bottle, then discharge it into the stainless steel tray and use a clean stainless steel spoon to transfer the sample into the sample container. Collect a proportionally representative sample if an average value is desired or collect from a specific strata in the core if a specific reason exists for sampling that strata. Document the sampling method in the field notebook.

7. Seal the sample container, store and ship it according to the laboratory specifications (this is normally at 4°C or freezing). Submit the sample for analysis and specify analytical results by dry weight.
8. Clean the equipment between sample sites, by bristle pipe cleaner brushes and then thoroughly rinse the sampler and the utensils with water and organic solvent if the sample is intended for organic analysis.

7.2.3 DEEP WATER SEDIMENT SAMPLING – CORE AND DREDGE SAMPLER SAFETY HAZARDS

Deep water core and dredge samplers are generally larger in size than shallow water samplers and usually require a winch mechanism to lower and raise the sampler and operation from a boat or other floating platform. Additional safety precautions must be employed to operate the floating platform, winch and samplers. This is due to hazards in anchoring boats where currents are strong and underwater hazards can cause emergency situations including sudden swamping and/or flipping of the boat. There are further hazards in handling the ropes and cables which can cause injury or damage by entanglement. Specific task hazard analysis should be conducted with an experienced equipment operator before undertaking deep water sampling.

FIGURE 7.4:
Dredge sample with sediment in stainless steel tray or a tray covered in aluminum foil. Well mixed samples should be placed in amber glass for organics or paper/plastic for metals analysis.
(Courtesy of Canada – DOE)

7.2.4 DEEP WATER SEDIMENT SAMPLING – CORE SAMPLER

Sample collection using a deep water core sampler is essentially the same as a shallow water core sampler except that sediment volumes are generally higher due to the larger size of the core barrel. See SECTION 7.2.2

7.2.5 DEEP WATER SEDIMENT SAMPLING – DREDGE SAMPLER

SUGGESTED PROCEDURE

1. Prepare a clean stainless steel tray capable of holding the sediment brought to the surface by the dredge. Lay out the stainless steel spoons and sample containers on a clean plastic sheet or tin foil. Have distilled or de-ionized water on hand for use for cleaning between samples.

2. Set up the dredge according to the manufacturer's instructions. Use all recommended safety precautions as most dredges are spring loaded and can cause serious injury if the release mechanism is tripped while fingers are between the blades of the dredge.
3. Deploy the dredge until it impacts the sediment and release the trip mechanism to close the jaws. Carefully retrieve the sample to the surface at such a rate that minimizes the loss of fine sediments from the dredge and place the dredge into the clean stainless steel pan. Open the dredge and release the sediments into the stainless steel pan.
4. Use the clean stainless steel spoon to remove a portion of the sediment from the sampler. Collect a proportionally representative sample if an average value is desired or collect from a specific strata in the dredge spoil if a specific reason exists for sampling that strata. Document the sampling method in the field notebook.
5. Seal the sample container and submit the sample for analysis and normally specify by dry weight.
6. Prior to collecting the next sample, clean the dredge and stainless steel tray and sampling spoons by washing with water and wiping with a paper towel to remove any solids, then rinse with water and then distilled or de-ionized water. If sampling for organics, rinse with reagent grade acetone and final rinse with reagent grade hexane. Clean the tray in this manner as required.

7.3 SOIL SAMPLING

Soil sampling generally involves the collection of samples in such a manner that the statistical needs of the sampling program are met and that the sample represents the strata of interest. The deeper into the earth from which the sample is collected the larger the equipment is required to expose and obtain a representative sample and the greater sophistication in safety precautions required to protect the sampler from hazards.

The volume of soil sample required depends on the end use. Each chemical and biological test requires a specific amount of sediment. Check with the lab to determine what volume to collect and what steps to take to preserve the sample. Usually samples are kept at 4°C or frozen.

See SECTION 2.9.2

7.3.1 QUALITY OF SOIL SAMPLES

Soil samples generally consist of fine particle sizes. The analytical process normally digests the sample in strong acid. Large pebbles and rocks or organic debris such as wood can skew the results by adding a large quantity of material which when digested by the acid will dilute the sediment sample with clean material from inside the pebble or rock. Contact the laboratory to obtain specifications as to the maximum particle size allowed in the sample. Alternatively, collect the sample and instruct the laboratory to select the correct particle size from the

sample and base the analytical results on the selected particle size(s). Submit the sample for analysis and normally specify by dry weight. Since soil or sediment samples can have a wide variation in moisture content it is recommended that the sample contaminant concentrations be specified on a dry weight basis. This allows comparison between sites and against regulatory standards.

7.3.2 SOIL SAMPLING STRATEGIES

Soils horizons are generally much more poorly mixed than water columns. Therefore, the use of judgemental, biased and random methods for obtaining samples are required.

7.3.2.1 Judgemental/Biased Soil Sampling

Judgemental or biased sampling involves collecting soil from areas (on the surface or in the vertical soil column) where contamination is suspected based on visual inspection, vapour or other testing methods. For biased sampling, collect samples from obviously contaminated, stained soil or pre-determined sites. This may often be the first approach to determine the potential scope of the situation to be followed by more rigorous methods of choosing a sample spot. Where the enforcement officer has regulatory authority to issue orders, biased sampling usually provides sufficient evidence for the officer to require the regulatee to conduct a more comprehensive sampling program to fully define the contaminated area.

Where hydrocarbons or volatile organics are suspected, sample pre-screening may be achieved by collecting samples and placing them in wide mouth glass jars and sealing the lids with tin foil. Allow the sample to stand for up to an hour. Using a photo-ionization detector, insert the detector nozzle through the aluminum foil and take a head space sample to determine if there are hydrocarbon or organic fumes. Positive results may then be submitted for laboratory analysis.

FIGURE 7.5:
Using a photo-ionization detector, insert the detector nozzle through the aluminum foil and take a head space sample to determine if there are hydrocarbon or organic fumes. (Courtesy of United States - EPA)

7.3.2.2 Systematic Soil Sampling

For systematic samples, the simplest method is to divide the area to be sampled into a grid. The dimensions of the grid can vary in size based on the area to be covered and the history of the incident and the budget for sampling. See SECTION 2.4.3.2

1. It may be necessary to establish an initially large grid composed of large squares (say 1.0 m^2 to 10.0 m^2) to conduct initial analysis and then focus on squares which have positive results by dividing them into smaller squares.
2. Take at least one sample at each intersection in the grid.
3. Make a decision regarding which samples are to be analysed based on site specific factors, risk of false positive or false negative results, time restraints and budget.
4. Based on the sample results, focus additional sampling on those areas with positive results and divide them into smaller grids and re-sample.

   Example: A 5 m x 5 m area is suspected of containing contaminated soil. See FIGURE 2.4
5. Take 30 samples, one from each intersection.
6. Do not mix the individual samples, send all for analysis.

Benefit: Highest precision, least risk of bias, lowest risk of false negative result.

Cost: Highest sampling and analytical cost, longest time to analyse due to the high number of samples.

7.3.2.3 Systematic Soil Sampling: Compositing

To save on analytical costs, several samples may be composited together. Compositing will result in the loss of precision of the initial sampling but may allow for more economic and timely evaluation. Proper compositing will allow the sampler to re-analyse individual samples if they have been retained.

Example: A 5 m x 5 m area is suspected of containing contaminated soil. See FIGURE 2.4

1. Divide the area into 1m x 1m grid results in 30 intersections
2. Label the rows A, B, C, D, E, F.
3. Collect a sample - in this case say 100 mL of soil at each intersection resulting in 30 individual samples.

7.3.2.4 Systematic Soil Sampling: Composite mixing of all samples

Take all 30 samples and mix together and send one sub-sample for analysis.

Benefit: Simple process to mix all 30 samples. Less chance of biasing an individual sample. Shortest time frame to analyse due to lowest number of samples and lowest analytical cost.

Cost: Lowest precision of results with a large probability of a false negative. Will require new sampling if a positive result is obtained.

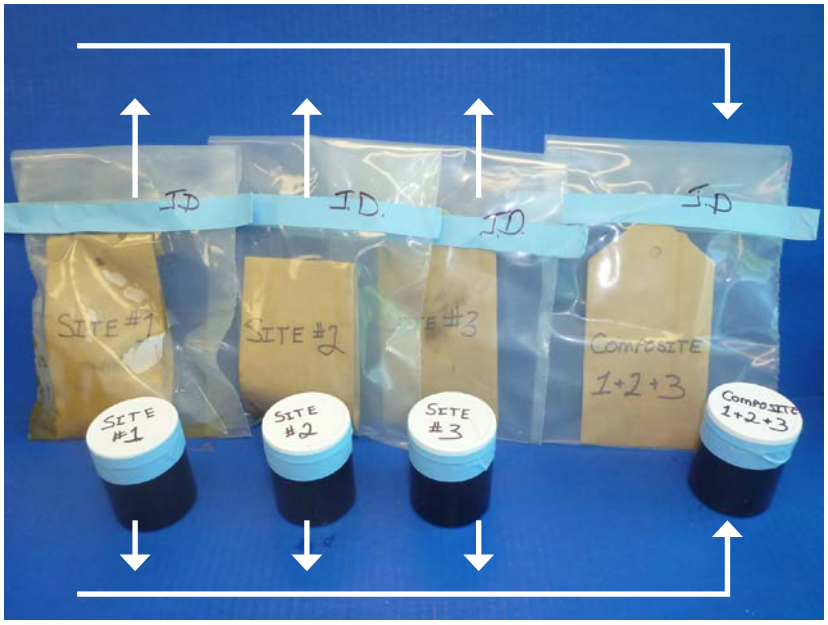


FIGURE 7.6:
Equal portions of individual soil samples are placed into a mixed composite soil sample. Individual samples should be retained for subsequent analysis if the composite tests positive for the contaminant.
(Courtesy of Canada – DOE)

7.3.2.5 Systematic Soil Sampling: Composite mixing of selected samples

Take the samples from each row, mix together and send six samples for analysis.

Benefit: Simple process to mix all six samples. Slightly higher precision, lower risk of false negative result.

Cost: Longer time frame to analyse more samples, relatively low precision of results with a large probability of a false negative. Will require new sampling if a positive result is obtained.

7.3.2.6 Systematic Soil Sampling: Composite mixing, partial retention of samples

1. Mix each sample so that it is homogenous.
2. Take the samples from each row, and remove 1/6 (approximately 15 mL) from each sample and mix together into a single sample for that row. Retain the original samples and send six composite samples for analysis.

Benefit: Slightly higher precision, lower risk of false negative result. Can retest the retained samples individually if a positive result is obtained in the composite sample.

Cost: Relatively low precision of results with a large probability of a false negative. Requires additional work to mix the individual samples.

7.3.2.7 Random Sampling

1. Choose a limited number (say six to ten based on time/budget factors) of sampling locations in the grid using a random numbers table.
2. Take the samples only from each randomly chosen intersection and send for analysis.

Benefit: Lower sampling time and cost, lower analytical cost, and less risk of bias.

Cost: Relatively low precision of results with a large probability of a false negative.

7.3.3 SOIL SAMPLING TECHNIQUES

Surface sampling of soil uses equipment very similar to sediment sampling and usually involves collecting samples at a depth of 0.0 cm to 100 cm depending on soil parameters and the nature of the investigation. One of a wide variety of tools may be used: trowel, scoop, bucket auger, soil coring device, power auger, split spoon sampler, or Shelby tube sampler. For samples at lower depths, a clean bucket auger or power auger may be needed to dig down to the depth of collection. The use of a drill rig and split spoon sampler may be necessary for samples at depths of greater than 1 m.

ASSEMBLE THE EQUIPMENT

- ☐ Appropriate protective gear to handle metals and organics contaminated samples and eye protection, respiratory protection against dust and vapours, gloves and coveralls
- ☐ Appropriate safety equipment including life vests for working near shorelines
- ☐ Sample bottles depend on the type of contaminant but are usually wide mouth glass jars with foil lined or Teflon lined lids. See SECTION 2.9.2
- ☐ Polyethylene drop sheets – minimum 1 m x 1m
- ☐ Stainless steel trays for sample placement, or
- ☐ Plastic trays lined with aluminum foil or polyethylene depending on the type of contaminant
- ☐ Distilled/de-ionized water in wash bottles, if sampling for non-organics
- ☐ Reagent grade acetone/hexane in wash bottles, if sampling for organics
- ☐ Stainless steel tweezers
- ☐ Bristle pipe cleaner brushes for cleaning core sampler tubes
- ☐ Water pump and/or power washer/water supply for cleanup of large excavation tools

Soil Depths of 0.0 m to 1.0 m

- ☐ Cleaned stainless steel spoons wrapped in aluminum foil
- ☐ Cleaned stainless steel core samplers
- ☐ Cleaned stainless steel shovels
- ☐ Small hand-held power augers

Soil Depths of 1.0 m and greater

- ☐ Material to shore up the sides of an excavation. **Note:** Local health and safety legislation will specify the conditions under which precautions such as shoring up the walls of an excavation are required for safe entry. Generally this is required for holes of greater than 1.0 m.
- ☐ Power excavator capable of reaching the prescribed depth
- ☐ Power drill rig capable of reaching the prescribed depth
- ☐ Power sonic or percussion rig capable of reaching the prescribed depth
- ☐ Wire core cutter

7.3.4 SURFACE SOIL SAMPLING USING A SPOON

A stainless steel sampling spoon may be used to collect a soil sample up to a few centimetres in depth from the upper most layer of the soil, to collect sections of a split spoon sample or to scrape from the sides or bottom of an excavated pit, piles of drill spoil, or sonic or percussion drill soil cores.

SUGGESTED PROCEDURE

1. Use the spoon to scrape the top few centimetres of soil. Try to maintain the physical form and chemical composition of the sample as much as possible.
2. Collect the required volume of soil and remove pebbles and stones over a predetermined size and any wood or organic debris using clean stainless steel tweezers or instruct the laboratory to do so.
3. Where organic contaminants are known or suspected, transfer the sample to a container as quickly as possible, with no mixing, to avoid the loss of volatile fractions.

7.3.5 DEEPER SOIL SAMPLING (UP TO 1.0 METER DEEP) USING A SHOVEL AND/OR HAND AUGER

SUGGESTED PROCEDURE

1. The tool (shovel or hand-held auger) used to dig the hole must be uncontaminated and cleaned with water/power washer between sample sites.
2. Lay out a plastic drop sheet to deposit the contaminated soil from the excavation.
3. Using a clean spoon, if possible, scrape the sides of the excavation to expose fresh soil and collect a sample.
4. Collect the required volume of soil and remove pebbles and stones over a predetermined size and any wood or organic debris using clean stainless steel tweezers or instruct the laboratory to do so.
5. Where organic contaminants are known or suspected, transfer the sample to a container as quickly as possible, with no mixing, to avoid the loss of volatile fractions.

7.3.6 DEEPER SOIL SAMPLING BY TEST PITTING AND DRILLING

Excavation and test pitting must consider the health and safety risks of collapse of side walls, fumes and vapour hazards. Steps must be taken

FIGURE 7.7:
Sampling in excavations and test pits must consider safety hazards.
(Courtesy of Canada – DOE)

1. Excavation of the ruptured pipeline.
2. Location of the rupture.
3. Collecting a legal sample. Note: Safety harnesses should be worn and the site should be tested for fumes.

to shore up the sides to prevent a cave-in. The use of extension pole samplers or other equipment can also be used to safely collect a sample.

SUGGESTED PROCEDURE

1. The excavator or drill rig used to dig the hole must be uncontaminated and cleaned with water/power washer between sample sites.
2. Lay out a plastic drop sheet to deposit the contaminated soil from the excavation.
3. Collection of a sample by entering into an excavated hole should only be done when appropriate precautions are made to keep the slopes stable. It may be required to instruct the excavator to bring a scraping of soil to the surface and place the soil on the plastic drop sheet or collect a sample directly from the excavator bucket.
4. Where it is safe to enter the excavation, use a clean spoon and scrape the sides of the excavation to expose fresh soil and collect a sample/samples.
5. Collection of a sample by a drill rig cannot be done by entering into the excavated hole. As the drill reaches critical depths or if the extracted spoil shows contamination characteristics, the drill should be stopped, secured, and when safe to do so, the extracted soil should be sampled. Alternatively, the drill spoils may be placed onto the plastic drop sheet and a sample collected using a clean sampling spoon.
6. Collect the required volume of soil and remove pebbles and stones over a predetermined size and any wood or organic debris using clean stainless steel tweezers or instruct the laboratory to do so.
7. Where organic contaminants are known or suspected, transfer the sample to a container as quickly as possible, with no mixing, to avoid the loss of volatile fractions.

7.3.7 DEEPER SOIL SAMPLING BY SONIC OR PERCUSSION DRILL RIG CORES

A solid core of soil can be collected using a sonic or percussion drill rig. Both types use a hollow core tube pushed into and then extracted from the soil.

SUGGESTED PROCEDURE

1. The sonic or percussion drill rig and the split tubes used to dig the hole must be uncontaminated and cleaned with water/power washer prior to and between sample collection sites.
2. Once the split tube full of soil is extracted from the hole, the tube can be opened and a solid core of soil can be laid out on the plastic drop sheet. The soil core can be split using a cutting tool made of wire which slices the center of the core in a lengthwise direction.
3. The split soil core can be examined and sampled according to the nature of the contamination. Frequently, there are visible lenses of contamination straight or diagonally across the soil core caused by preferential pathways where the soil conditions/particle size has allowed the contamination to migrate through a particular layer.
4. Due to the split spoon pushing down through the soil, the contamination from one level may be smeared along the outside of the soil core to another level. To avoid cross contamination of soil layers, use a clean

stainless steel spoon to scrape the center of the core to collect the sample and avoid collecting soil from the sides.

5. Collect the required volume of soil and remove pebbles and stones over a predetermined size and any wood or organic debris using clean stainless steel tweezers or instruct the laboratory to do so.
6. Where organic contaminants are known or suspected, transfer the sample to a container as quickly as possible, with no mixing, to avoid the loss of volatile fractions.

7.4 GRANULAR MATERIAL SAMPLING

Granular materials such as detergents and pelletized or powdered chemicals may be stored in bags, bulk containers, and road or rail tankers. Detergents are often tested for phosphorus pentoxide (P_2O_5) or elemental phosphorus (P) and other solid chemicals may be contaminated with regulated or banned substances. Samples may be collected from manufacturers, formulators or retailers in unopened boxes.

ASSEMBLE THE EQUIPMENT

- ☐ Appropriate protective gear to handle metals and organics contaminated samples and eye protection, respiratory protection against dust and vapours, gloves and coveralls
- ☐ Sample bottles depend on the type of contaminant but are usually wide mouth glass jars with foil lined or Teflon lined lids. See SECTION 2.9.2
- ☐ Polyethylene drop sheets – minimum 1 m x 1m
- ☐ Stainless steel trays for sample placement, or
- ☐ Plastic trays lined with aluminum foil or polyethylene depending on the type of contaminant
- ☐ Stainless steel or brass bag/grain sampler (also called "grain bag triers")
- ☐ Assorted stainless steel spoons and/or scoops
- ☐ Tape which can be used to re-seal holes in bagged materials

7.4.1 SAMPLING BAGGED GRANULAR MATERIALS

Bagged granular materials may be sampled by opening the bag and sampling from the top and extracting a sample with a stainless steel spoon, scoop, or by using the stainless steel/brass bag sampler (grain bag triers). See SECTION 4.7

1. Place the bag in a position so that if cut or punctured, the contents will not spill out.
2. The stainless steel bag sampler (grain bag trier) consist of a hollow tube with an open slot just before the penetration point. The tube is inserted into the bag with the open slot facing upwards.
3. The sample container is held at the open end of the tube so that as sample pours into the open slot, the particles slide down the tube into the sample container.
4. After sampling is complete, the steel bag sampler is withdrawn and the hole is sealed with tape to prevent further spillage.

7.4.2 SAMPLING BOXED OR CONTAINERIZED GRANULAR MATERIALS

Boxed or containerized granular materials can be sampled by either sending the entire box to the laboratory if it is small enough or by collecting a subsample from a large container. The size of the subsample from a large container must be representative; therefore, care must be taken to ensure the contents of the container are well mixed.

- If the contents of the container are well mixed, a subsample may be taken by opening the container and scooping out a sample with a stainless steel spoon or scoop and placing the required volume in a sample container.
- If the contents of the container are not well mixed, and if safe to do so, the contents may have to be transferred to another container or stainless steel tray and mixed using stainless steel spoons. The mixing process must consider dust and fume generation safety issues.

8 GASES AND AIR DEPOSITION (DUST) SAMPLING

Gases and air deposition (dust) sampling

Sampling protocols for air sampling tend to be complex and technical. For these reasons, air sampling is usually carried out by experienced contractors or trained specialists.

Air sampling may be carried out for several reasons:
Safety: Air may be toxic or explosive and cause injury, death and/or serious harm and damage to property
Environmental Impact: Air contaminants may cause environmental damage. High ozone levels may cause damage to crops and corrosion to property, and can impact respiratory systems. Toxic particulate fallout may poison soils or crops and contaminate agricultural animals, spoiling meat and dairy products and creating health hazards for animals and people.

8.1 GENERAL PRINCIPLES OF AIR SAMPLING

Air sampling is significantly affected by weather, making it much more random than most other forms of sampling. Wind directions constantly change therefore outdoor sample sites must be chosen strategically to minimize influence from obstructions, buildings, trees or other landscape features. Precipitation can act as a stripping agent which affectively washes gases and particulates from the air. Therefore sampling sites and periods must take these factors into account.

8.1.1 AIR SAMPLING TECHNIQUES

Air sampling generally falls into two categories, sampling for particles or sampling for gases. Particulate sampling is either a dust settling method or a filtration method. The dust settling method usually involves the use of a canister or pad. The filtration method normally involves a pump or a fan which forces air through particulate filters, which may be paper or glass fibre, and collects airborne particles. The volume of air filtered must be measured to determine concentration.

Grab or composite sampling of gases may involve collecting a volume of gas for further testing or absorbing gases onto reactive surfaces for instantaneous colorimetric testing. Collecting a sample of air from the area of interest over a short period of time may be done by means of hand-held samplers with small pumps and sorbent sampling tubes. The sorbent sampling tubes collect contaminants by drawing air through specific sorbent materials which trap the contaminant of interest. Portable sorbent tubes are usually powdered solids that change color by reacting with specific gases.

FIGURE 8.1:
Chronic air pollution requires sampling techniques that quantify environmental and health risks. (Courtesy of the Netherlands - ILT)

Larger gas emission stacks can be sampled by samplers using sorbents that may be liquids or solids and that vary depending on the contaminant. The volume of air drawn through the sorbent material must be measured and recorded to determine concentration. Large gas emission samples may also be collected using an evacuated chamber (e.g. air sampling canister) which when opened fills with the air to be analysed. Closing the container makes an airtight seal. Another technique is to use a pump system to take a pressurized sample. Sampling for gases is usually done from points of emission, such as smoke stacks or at points of reception such as air intake vents or ambient areas inside or outside of buildings or other structures.

8.2 INSTRUMENTS USED IN AIR SAMPLING

Instruments vary according to the desired analytical target and range in measuring capability, portability and cost.

8.2.1 DUST FALLOUT SAMPLERS

Dust fallout may occur from a one-time catastrophic event (such as an explosion and/or fire) or from chronic industrial operations, traffic or fuel combustion, energy generation and refining complexes. Dust fallout samplers are used to collect dust over varying periods of time depending on the event and contaminant they are designed to collect.

8.2.2 VERTICAL TOP OPEN CANISTER DUST SAMPLER

A vertical top open canister sampler is usually mounted on a two metre high stand in an area away from the impact of buildings, trees or other structures that can disrupt air flow.

FIGURE 8.2:
Dustfall sampler lid is removed and positioned in the sampler. (Courtesy of Canada - DOE)

- ☐ Appropriate protective gear to handle metals and organics contaminated samples and eye protection, respiratory protection against dust and vapours, gloves and coveralls
- ☐ Samplers may be designed to form their own containers which only need to be removed from the sampler stand, closed with the appropriate lid, and shipped to the laboratory
- ☐ Sample bottles depend on the type of contaminant but are usually wide mouth glass jars with foil lined or Teflon lined lids. For common dustfall/heavy metals, plastic containers with plastic lids are normally used. See FIGURE 8.2.
  For organic compounds, use wide mouth glass containers, see TABLE 2.9.2.2
- ☐ Sampler stand
- ☐ Sampler collection containers

SUGGESTED PROCEDURE

1. The canisters may be cleaned, sealed and pre-weighed before transporting and mounting on the stand.
2. Locate an area with the minimum of air disturbances such as buildings, bridges or other structures. A rooftop or an open field is preferred.
3. Erect the sampling stand in a secure manner and place the sample canister in the holder.
4. The sample canister should face vertically upward so that sampling is "non-directional" in that there is no bias to where the pollution comes from.
5. The canisters are mounted on a pole, usually 2 metres above the ground and left in position for 10 to 30 days.
6. The date and time of mounting are recorded upon set up and take down.
7. The canister can be sampled on site or sealed upon take down and transported to the laboratory for removal of content and analysis.

8.2.3 DIRECTIONAL (VERTICAL SIDE OPEN) CANISTER DUST SAMPLER

Directional dust samplers are intended to determine if there is a specific directional component to the pollution source. Therefore, they may be specifically oriented towards a known or suspected source.

ASSEMBLE EQUIPMENT

- ☐ A vertical mounted canister stand that has four or more canisters with a slot cut in one side and top and bottom caps.

SUGGESTED PROCEDURE

1. The canisters may be cleaned and pre-weighed before mounting on the stand.
2. Locate an area with the minimum of air disturbances such as buildings, bridges, or other structures. A rooftop or an open field is preferred. If a specific sources is suspected, select an area which may be specifically impacted.
3. Erect the sampling stand in a secure manner and place the sample canister in the holder.
4. The slots may be set to the four directions of the compass or with one slot directed towards the suspected pollution source. Make a notation as to which settings are used.
5. The canisters are mounted on a pole, usually 2 metres above the ground and left in position for 10 to 30 days.
6. The date and time of mounting are recorded upon set up and take down.
7. The canister can be sampled on site or sealed upon take down and transported to the laboratory for removal of content and analysis.

8.2.4 STICKY PAD TOP (FRISBEE) DUST SAMPLER

Sticky pads generally consist of an adhesive pad which may be "semi directional" by having the pad mounted face up to the sky. Dust fall angling from a primary direction will tend to collect on the side of the pad nearest the source.

ASSEMBLE EQUIPMENT

- ☐ Assemble stands
- ☐ Sticky pads

SUGGESTED PROCEDURE

1. Pads may be mounted in a horizontal position face up to the sky, or
2. Pads may also be mounted in a vertical position in the four directions of the compass or with one facing the suspected pollution source.
3. Record how the pads are deployed.
4. The pads are mounted on a pole, usually 2 metres above the ground and left in position for 10 to 30 days.
5. The date and time of mounting are recorded upon set up and take down.
6. These types of pads may be photographed or scanned by computer and software used to distinguish and quantify dust. The software can distinguish between dust and insects.

8.2.5 HIGH VOLUME AIR SAMPLER

These samplers require expertise and should only be operated by people who are technically qualified. High volume air samplers generally use an intake fan mounted below a filter. The fans generally have a volume measuring mechanism to provide an estimate of the total volume of air passed through the filter. This is important because as particulate deposits on the filter it clogs the filter and slows air flow.

Typically, the sampler has a filter 17.8 cm x 23.9 cm or 406 cm^2, through which air is drawn at the rate of 1.1 m^3/min to 1.5 m^3/min. The filter picks up particles 25 µm - 50 µm in aerodynamic diameter, depending on wind speed and direction. The size of the opening to the filter and the volume of air filtered over a given time affect the size range of the particles collected. Therefore, samplers should have uniform sample air inlets that allow an air flow rate of between 20 cm^3/s to 35 cm^3/s, ideally 25 cm^3/s +/- 2 cm^3/s. Filters may be made of glass fibre or cellulose. Glass fibre filters collect at least 99% of particles 0.30 µm or larger; these filters have low resistance to air flow and little affinity for water. Samples collected on glass fibre filters are suitable for a wide variety of analyses: organic pollutants, inorganic contaminants, trace metals and several non-metallic substances. They are excellent for monitoring gross radioactivity. Spectrophotometer-quality grade filters have low metal content and are suitable for metal analysis.

8.2.5.1 Glass fibre filters - Use and problems

It is not possible to sample for materials that are already present in the filters in substantial amounts. To control this problem, a statistically significant random sample of new filters should be analysed to determine whether the filter blank concentration is high enough to interfere with a specific analysis.

- Glass fibre filters are resistant to humidity but can take up enough water to distort final weight values.
- To control humidity, they must be desiccated and weighed prior to use.
- Care must be taken to avoid fibre loss during handling.
- The glass fibres themselves are alkaline and will react with acidic gases in the sample air, giving artificially high results. This effect usually happens early in the sampling period and depends on the composition of the filter and the levels of acid gas. The error introduced is probably small, but may be a problem when relatively small amounts of particulate are encountered.

8.2.5.2 Cellulose filters - Use and problems

Cellulose filters are used less frequently than glass fibre filters and they have low metal content, making them suitable for metal analyses. Some problems with them are:

- They may clog rapidly. Care must be taken to ensure that the filter/fan system has a mechanism to record the drop in air flow as the filter becomes less permeable and that it is replaced before lack of airflow becomes critical.

- They may absorb water and should be dried by desiccation before and after use.
- They may produce nitrate and sulphate artefacts during the digestion/analytical process which could interfere with analytical quantification of these materials. These problems can be compensated for by using a control blank filter which is analysed without exposure and the artefacts can be subtracted from the exposed filters.
- Volatile particles may be lost during sampling, shipment, and storage before the filter is weighed. These losses should be minimized by pre-weighing and then storing in a sealed desiccated container. After exposure, they should be removed from the holder and placed in a sealed desiccated container and weighed as quickly as possible before the fibres re-absorb moisture from the air at the laboratory.

8.2.5.3 Other high volume air sampling problems

- Filters (especially glass filters) may lose fibres due to handling. The filters must be handled with tweezers between the pre- and post-sampling weighing to avoid accidentally losing filter fibres, otherwise weights would provide artificially low results.
- Wind can deposit particulate on the filter outside the sampling period. Therefore, the filter must be placed inside the desiccation container as soon as possible after it is removed from the filter holder.
- Improper recording, power failure, or malfunctions of the filter fan can lead to inaccurate timing of the sampling period. Therefore, the sampler must have an operational recorder or be inspected on a regular basis.
- The exhaust air outlet from the sampler must be directed away from the intake (at least 40 cm away), to ensure that the exhaust does not recirculate through the sampler and cause filtered air to re-cycle giving artificially low results.

SUGGESTED PROCEDURE

1. Assemble the high volume sampler as recommended by the manufacturer.
   When handling filters, ensure that they are:
   - Tagged for identification
   - Inspected visually for holes, tears, or other imperfections
   - Kept from being folded or creased
   - Conditioned in a controlled environment for at least 24 h before use. (This is normally 15º - 30ºC varying no more than + 3ºC; relative humidity < 50%, with no acidic/basic gases)
   - Pre-weighed as a desiccated dry filter to the nearest milligram before installation
2. Position the sampler away from buildings, trees or structures that can highly disturb air flow. Commonly, they are positioned on the roofs of buildings.

3. Install the filter and turn on the fan.
4. Record date and time of installation and start up and shut down and filter removal.
5. Remove and store the filter in an appropriate sealed container for transport to the laboratory.
6. Desiccate the filter and record the dry weight.
7. The filter may be further processed by extraction for organic analysis or digestion for metals analysis.

8.2.6 PORTABLE CHEMICAL REACTIVE GAS SAMPLERS

Portable gas samplers are available from suppliers which can analyse up to 500 different compounds. The samplers generally consist of a hand-held pump with a detector attachment. The detector is a glass tube with a powdered chemical absorbent that reacts with the gas to produce a color change. The ends of the glass tube are broken and the tube is attached to the pump. Air is pumped at a particular rate and time period. The gas, if present reacts with the absorbent to produce a color change in proportion to the concentration. These types of samplers are useful for emergency situations or to determine if site entry may lead to exposure to hazardous gas situations. They are less suitable for continuous monitoring situations since the detector tubes may only be used once. Variation exists between tubes made by different manufacturers. Chemicals similar to the analyte of interest may interfere with the reaction in the tube. The tubes are also affected by high humidity and have a limited shelf life.

ASSEMBLE EQUIPMENT

- ☐ Appropriate portable gas sampler
- ☐ Appropriate detector tubes for the gas sampler

SUGGESTED PROCEDURE

1. Read the manufacturer's instructions on use.
2. Use the appropriate absorbent for the suspected gas.
3. Break the tubes and insert the detector into the holder.
4. Turn on the pump and obtain a reading.

8.2.7 PORTABLE PHOTO IONIZATION GAS SAMPLERS

Portable photo ionization detectors (PIDs) can be used for numerous organic compounds. They generally consist of a hand-held pump connected to a detector which has a gas intake port.

FIGURE 8.3:
Portable photo ionization detectors.
(Courtesy of United States –EPA, Canada - DOE)

8.2.7.1 Specific gas is known

The photo ionization detectors may be calibrated to a specific gas by using calibration standards, which is useful if a single gas is known or suspected. The detectors are non-specific in that they may detect a mixture of compounds and therefore the reading may also include other gases and measurement accuracy may be plus or minus 25%. Therefore manufacturer's instructions specific to each instrument should be followed for calibration and use. Compounds which may be detected include common gasoline components, industrial cleaning agents, dry-cleaning agents, and solvents.

8.2.7.2 Gas mixture is unknown

When the amount and type of organic vapours are unknown, instruments such as portable photoionization detectors or portable flame ionization detectors, when operated in a total readout mode or as a chromatography, should be used to detect organic vapours. Until specific constituents can be identified, the readout indicates total airborne substances to which the instrument is responding. When specific constituents have been identified and the instruments are calibrated correctly to measure these constituents, readings in ppm can be obtained with some degree of confidence.

8.2.7.3 Gas mixture may be combustible

Very high readings on a portable photoionization detector or a portable flame ionization detector may also indicate the possible displacement of oxygen or the presence of combustible vapours.

8.2.7.4 Gas mixture may contain inorganic vapours

The portable flame ionization detector has no measuring capacity for inorganic vapours or gases, while the portable photoionization meter's detection capacity for these vapours is limited. The meters have other limitations as well. Users should consult the operating manuals for information on what the meters can and cannot detect.

8.2.7.5 Analyzing soil gas

These detectors may also be used to analyse gas vapour from contaminated soil samples, especially from areas of hydrocarbon spills.

There are several methods by which to acquire a soil gas sample:

ASSEMBLE EQUIPMENT

- ☐ Appropriate portable photoionization meter
- ☐ Appropriate sample jars. See SECTION 2.9.2
- ☐ Appropriate soil sampler. See SECTION 7.3
- ☐ Aluminum foil

SUGGESTED PROCEDURE

The protocol depends on the physical situation. However, for all common scenarios:

- Read the manufacturer's instructions on use.
- Use the appropriate calibration gas.

Spill of fuel or solvent to soil surface

1. Collect a sample of soil and place in a 125 to 250 ml wide mouth jar leaving a 2 cm head space.
2. Cover the jar with aluminum foil to seal the head space.
3. Allow the vapour to fill the head space for a period of time (e.g. 15 minutes).
4. Insert the detector hose through the aluminum foil into the head space.
5. Start the pump and analyse the head space gas.
6. Record the date, time, and reading results.

Spill of fuel or solvent to soil subsurface

1. Connect a stainless steel soil vapour probe to the PID.
2. Insert the soil vapour probe into the soil to the suspected depth of the spill.
3. Start the pump and analyse the soil vapour space gas.
4. Record the date, time and reading results. For certain situations where liquids have leaked under structures such as buildings or paved areas, it may be necessary to drill through the concrete or pavement to access the underlying contaminated soils.

8.2.8 OXYGEN METERS

Oxygen meters are used to monitor oxygen levels in the air, usually about 20% by volume. In general, if this level falls below 19.5%, respiratory equipment will be needed. Concentrations of about 25% carry a risk of combustion. If the meter reports a drop in oxygen levels, this could reflect either the consumption of oxygen (by combustion or reaction) or an increase in the levels of some other gas. Oxygen meters are also affected by temperature variations and high levels of carbon dioxide, which can shorten the lifespan of the oxygen sensor. VHF and UHF radio transmission signals can interfere with the instrument and produce false readings. Strong oxidizing chemicals such as ozone or chlorine can also interfere with oxygen meters.

8.2.9 COMBUSTIBLE GAS INDICATORS (CGIS)

Combustible gas indicators (CGIs) measure the concentration of a flammable gas or vapour in air. At or below the lower explosive limit (LEL)

of a combustible gas or vapour, the concentration is too low to support combustion. Above the upper explosive limit (UEL), the mixture is too rich to support combustion. At concentrations between the two, the vapour will ignite if brought into contact with a spark or flame. CGIs are affected by temperature, VHF and UHF radio transmissions and oxygen deficient atmospheres. Organic lead vapours, sulphur compounds and silicone compounds will foul the instrument and acidic gases can corrode it.

8.2.10 EMISSIONS STACK SAMPLING

Stack sampling is a specialized process requiring equipment and expertise that is often supplied by consultants. Government inspectors in most countries will not usually do the sampling but will witness the sampling by other qualified persons. The following description is provided to illustrate the general process of stack sampling to help the inspecting officer understand the sampling process.

8.2.11 GENERAL PROCESS FOR STACK GAS SAMPLING

The general process for stack gas sampling involves extracting the gas directly from the exhaust stack and either passing it through chambers that selectively remove specific gases or pumping it into sealed bags or canisters for laboratory analysis. Some samplers may be equipped with analytical capability, providing results to a portable or fixed recording device. Air flow in pipes is subject to turbulence, therefore the sampling site must be as free of turbulence as possible. Since air flow is slow at the pipe edges due to friction and faster as it moves towards the center, the sampling technique must accommodate this. The sampler will generally have a variable rate pump which can match the gas extraction rate to the internal exhaust stack flow rate. Gases inside exhaust stacks are generally hot and may condense if extracted into a colder sampler. Therefore, samplers are usually equipped with heat tracing tape to keep the gases hot while they are being extracted.

ASSEMBLE THE EQUIPMENT

- ☐ Appropriate protective gear to handle metals and organics contaminated samples and eye protection, respiratory protection against dust and vapours, gloves and coveralls
- ☐ Stack sampler with:
  - appropriate stainless steel sample intake probe
  - temperature control/heat tracing on the stainless steel sample intake probe to
  - prevent pre-mature condensation of gases in the probe
  - variable rate vacuum pump so that the gas extraction rate can be matched to the velocity of gas in the exhaust stack
  - gas/vapour extraction solvent canisters (these canisters may contain liquids that selectively dissolve the gases of interest), or
  - gas/vapour absorbent canisters (these canisters may contain solids that selectively bind the gases of interest), or
  - gas containment canisters (these are solid containers that are filled under pressure with the gas sample), or

- gas containment bags (these are expandable bags that are filled under pressure with the gas sample)

SUGGESTED PROCEDURE

1. Elbow- and T-joints or other changes in pipe diameter will cause air flow disturbances, therefore select a sample site that is as far away from disturbances in the pipe as possible.
2. Round pipes will have to be sampled in at least two perpendicular cross sections.
3. Rectangular pipes will have to be sampled in at least two parallel cross sections.
4. Insert the gas sampling probe into the exhaust stack.
5. Set the temperature tracing on the probe so as to extract the gas at iso-temperature so that it does not condense in the sampling tube.
6. Set the extraction flow rate at iso-kinetic rate so that the extraction of the gas occurs at exactly the flow rate at the current position of the probe.
7. Collect the sample in the appropriate container for the type of gas being tested.

Note: Sampling for inorganic pollutants (e.g. sulphur, ozone, carbon mono- or dioxide and nitrous oxides NO_x) in ambient air generally relies on fully automated, non-portable, continuous analysers with electronic data logging. These analysers use designated U.S. EPA reference methods and must be routinely calibrated under field conditions using span materials certified by the National Bureau of Standards (unless local regulations specify another source of calibration gases/materials). Sampling for polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), dioxins and other toxic substances can be done with absorbents or polyurethane foam cartridges; analyses are carried out in specialized labs.


BACKGROUND
SITE
UPSTREAM
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J.D.
SITE
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TOTAL
SITE
#1
DISSOLVE
FIELD
BLANK
2013-04-17
SITE
SITE #1 JD
SITE
2013-

9 SAMPLING BIOTA

Sampling Biota

The most common type of biota sampling for environmental inspectors is:

- **fecal coliforms in water which indicate pollution from human or animal waste**
- **wildlife (fish and birds) impacted by chemical or oil spills**
- **benthic invertebrates as indicators or aquatic health or as impacted by chemical and oil spills**
- **shell fish (salt water), freshwater clams, macrophytes, phytoplankton and zooplankton and bacteria to indicate sewage spills**

Biological samples are more difficult to collect than other samples since many of the organisms collected are mobile and contamination of samples can easily occur.
The collection of biota requires specialized expertise that may be available elsewhere within the country, such as a department of biology, university, consultants, INTERPOL or in other agencies.
Special permits may be required in some jurisdictions to collect biota due to restrictions on harvesting endangered species, to transport species across boundaries or by air, or to use techniques that might otherwise be illegal for the harvesting of biota.

DISCLAIMER
This section does not address the collection of highly pathogenic viruses and bacteria which requires special precautions and highly trained personnel.

9.1 BIOSAFETY LEVELS

Prior to undertaking any sampling for microorganisms, ascertain the biosafety level of the facility to determine the level of personal protective equipment (PPE) required. There are four biosafety risk levels, with a Level 4 rating for facilities handling the most dangerous pathogens.

Warning: For general descriptions of protective gear, see SECTION 2.6.5. However, for serious bio-hazards consult with your local jurisdiction for legally required procedure to deal with biohazards.

9.2 ASEPTIC TECHNIQUE

Bacterial sampling is usually carried out by provincial or federal health officials with proper training in aseptic (sterile) technique. It is extremely important that prior to bacterial sampling you have training in aseptic technique. Aseptic technique is necessary not only to ensure your safety

when dealing with microorganisms, but also to prevent the contamination of the sample with environmental organisms. Contamination can come from the air and surfaces of the area that you are sampling as well as your hands or mucous. Never touch the sample or the inside of containers with your bare hands, or sneeze or cough into the sample. Aseptic technique means to handle all materials in such a way that contamination by biological material on the surfaces of sample equipment and containers does not occur as a result of touching with contaminated gloves or clothing, spreading by airborne or waterborne methods (such as spraying aerosols, or splashing or spraying of contaminated liquids). All surfaces (especially sampling utensils and sample containers/coolers) are clean and free of contaminants.

ASSEMBLE THE EQUIPMENT

Check your equipment before sampling to determine that it is clean/sterile in order to prevent contamination by the equipment.

- ☐ Appropriate personal protective equipment based on the requirements for the containment level. See SECTION 2.6
- ☐ Appropriate sample containers. See SECTION 2.9.3.4. Sample containers should be autoclaved beforehand and therefore sterile.
- ☐ Reusable items such as stainless steel tweezers, forceps, scalpel, sampling spoons, scoop or spatula, biopsy punches and sterile containers. Reusable items should be autoclaved beforehand and put in their proper aseptic containers.
- ☐ Disposable items such as petri dishes, bacterial swab kits, glass or plastic pipettes, rubber vacuum bulbs, and ensure that the packaging for disposable, sterile items is intact.
- ☐ Acquire or prepare a container for the secure storage of contaminated disposable items after use.
- ☐ Acquire or prepare a container for the secure storage of contaminated reusable items after use.
- ☐ Broad spectrum disinfectant, such as Virkon, Wescodyne or isopropyl alcohol
- ☐ Disposable wipes such as cellulose wipes (e.g. KIM wipes)
- ☐ Appropriate tape for re-sealing product containers which have been opened for sampling
- ☐ Sterile cotton swabs or swab kits

9.3 BACTERIAL SAMPLING

Bacterial sampling can be done in liquids, solids (surfaces or cores), standing or flowing water, and water supply sources.

9.3.1 BACTERIAL SAMPLING IN LIQUIDS

SUGGESTED PROCEDURE

1. Minimize the generation of dust or debris into the air so as not to contaminate the sample or yourself.

2. If a sealed and labelled package of the sample is available and is easily transportable, it should be stored at 4°C, properly sealed in a properly labelled shipping container and taken to the lab intact.
3. The liquid should be well mixed so that the sample will be an accurate representation of the contents of the liquid.
4. If sampling from a large container (barrel or tank), do not allow the sampling equipment to touch the bottom, sides or opening of the container in order to prevent contamination.
5. Using a disposable sterile pipette, take the sample from below the liquid surface, as the surface is likely to be contaminated by the air.
6. Transfer the sample to the sample container. Do not touch the sides or bottom of the sample container.
7. For reuseable equipment, wipe excess liquid from reusable sampling equipment to avoid sample contamination. Make sure that reusable equipment is returned to the appropriate storage container.
8. Close, seal and wipe the exterior of the sample container with a broad spectrum disinfectant, such as Virkon or Wescodyne or isopropyl alcohol.
9. Dispose of the contaminated sampling equipment and wipes into the appropriate storage container.
10. The sealed, labelled package of the sample should be stored at 4°C, properly sealed in a properly labelled shipping container and taken to the lab intact.
11. If applicable, re-seal the product container (barrel or tank).

9.3.2 BACTERIAL SAMPLING ON SURFACES

SUGGESTED PROCEDURE

1. Minimize the generation of dust or debris into the air so as not to contaminate the sample or yourself.
2. Wear a face mask and avoid breathing onto the surface. Wear gloves. See SECTION 2.6
3. Extract the sterile cotton swab from the container or swab kit.
4. Swab the surface and place the swab immediately into the swab kit container.
5. Dispose of the contaminated sampling equipment and wipes into the appropriate storage container.
6. The sealed and labelled package of the sample should be stored at 4°C, properly sealed in a properly labelled shipping container and taken to the lab intact.

9.3.3 BACTERIAL SAMPLING IN SOLIDS

SUGGESTED PROCEDURE

1. Minimize the generation of dust or debris into the air so as not to contaminate the sample or yourself.
2. If a sealed and labelled package of the sample is available and is easily transportable, it should be stored at 4°C, properly sealed in a properly labelled shipping container and taken to the lab intact.
3. If sampling from a larger container or bag, take the sample from an unopened container, if possible. Use the appropriate sampling equipment to open the container in a sterile manner.

4. If sampling from a larger container, do not allow the sampling equipment to touch the bottom, sides, or opening of the container in order to prevent contamination.
5. Using a sterile spoon, scoop or spatula, take the sample from below the liquid surface, scrape away the surface is likely to be contaminated by the air.
6. Transfer the sample to the sample container. Do not touch the sides or bottom of the sample container.
7. Close, seal and wipe the exterior of the sample container with a broad spectrum disinfectant, such as Virkon or Wescodyne or isopropyl alcohol.
8. Dispose of the contaminated sampling equipment and wipes into the appropriate storage container.
9. The sealed and labelled package of the sample should be stored at 4°C, properly sealed in a properly labelled shipping container and taken to the lab intact.
10. Re-seal the product container.

9.3.4 BACTERIAL SAMPLING IN FLOWING AND STANDING WATER

Samples can be collected either by sampling directly by holding the sterile sample container in the hand, or by using a sampling device such as an extension pole or other devices listed in SECTION 6.0. The most common need to sample flowing or standing water for bacteria is to determine the release of animal waste or human sewage. Sampling for "coliform bacteria" is commonly done using 250 mL sterile glass bottles. See TABLE 2.9.3.4. The bottles may be held by sterile gloves and/or inserted into sampling poles with clasps or specifically shaped holders.

FIGURE 9.1:
Bacterial sampling of liquid, such as coliform from a beach. (Courtesy of Canada – DOE)

ASSEMBLE THE EQUIPMENT

Check your equipment before sampling to determine that it is clean/sterile in order to prevent contamination by the equipment.

- ☐ Appropriate personal protective equipment based on the requirements for the containment level.
- ☐ Appropriate sample containers. See TABLE 2.9.3.4. Sample containers should be autoclaved beforehand and therefore sterile.
- ☐ Appropriate sample equipment such as sampling poles/depth samplers etc.

SUGGESTED PROCEDURE

1. Remove the lid without touching the inner surface of the lid or the mouth of the bottle.
2. When sampling by hand, dip and hold the sterile container into the current away from the sampler at a depth of 15 cm to 30 cm. If there is no current, an artificial current may be created by moving the bottle horizontally away from the sampler.
3. When removing the bottle from the water, tip the container upwards to allow for approximately 3 cm to 5 cm air above the water level so that adequate mixing can be done at the laboratory.
4. The sealed sample should be stored at 4°C, properly sealed in a properly labelled shipping container and taken to the laboratory.

9.3.5 BACTERIAL SAMPLING FROM TAPS AND VALVES

Tap water may contain free chlorine which needs to be neutralized after the sample is collected.

ASSEMBLE THE EQUIPMENT

Check your equipment before sampling to determine that it is clean/sterile in order to prevent contamination by the equipment.

- ☐ Appropriate personal protective equipment based on the requirements for the Containment Level.
- ☐ Appropriate sample containers. See TABLE 2.9.3.4. Sample containers should be autoclaved beforehand and therefore sterile.
- ☐ Appropriate mix of sodium thiosulphate.

SUGGESTED PROCEDURE

Bacterial analysis should start as soon as possible after sampling, preferably within 1 to 6 hours after sample collection. Consult with the laboratory in regards to sample holding times and arrange for transportation of the samples to comply with holding times.

1. Prior to sampling, flush the water line for approximately 2 to 3 minutes.
2. Use a free chlorine test kit to determine if there is free chlorine present. If free chlorine is present, the sample is unlikely to have live bacteria.
3. Remove the lid without touching the inner surface of the lid or the mouth of the bottle.
4. Do not rinse the sample bottle with the tap water.
5. Hold the sample bottle under the running tap and fill the bottle.

6. If free chlorine is present and a sample is still required:
   - Pour out a small amount of the sample to leave room for the addition of sodium thiosulphate.
   - Add sodium thiosulphate (usually a few drops). Retest the sample with a free chlorine test kit to confirm that there is no free chlorine.
7. Do not cough or breath into the bottle and close the bottle as soon as possible.

9.4 SAMPLING WILDLIFE

Wildlife (fish, birds, land and marine mammals) are usually sampled as a result of shock or poisoning resulting from human related activities such as poisoning, oxygen depletion or temperature increases from municipal or industrial waste discharges, agricultural nutrient or pesticide run-off, water-level management (such as hydroelectric dams), and chemical or other spills. A wildlife kill may result from natural causes such as temperature change, storms, ice and snow cover, decomposition of natural materials depleting oxygen, salinity change, spawning mortalities, parasites, and bacterial or viral epidemics.

1. Document the zones where the kill occurred using GPS and maps.
2. To support the calculation of financial and civil/criminal penalties, carefully inventory the fish/wildlife killed in each zone to estimate the impact in terms of number of dead.

FIGURE 9.2:
Capturing and cataloguing wildlife killed due to pollution. (Courtesy of United States – Ohio EPA)

A field investigation of a wildlife kill may be required to determine the cause (natural or manmade) and whether legal actions are necessary. The general activities of such an investigation are:

- Visual observation
- Collecting samples of fish (including shellfish), water and other biota
- Physical measurements of the environment

In preparing for a field investigation, study area maps and determine the zone of wildlife mortality and the access to it. If surveillance of a particular body of water or area is involved, have present plans and equipment available on a standby basis. Identify waste dischargers. Contact participating laboratories regarding the number and types of samples that will be submitted, types of analyses required, method of sample shipment, and date by which results are to be reported.

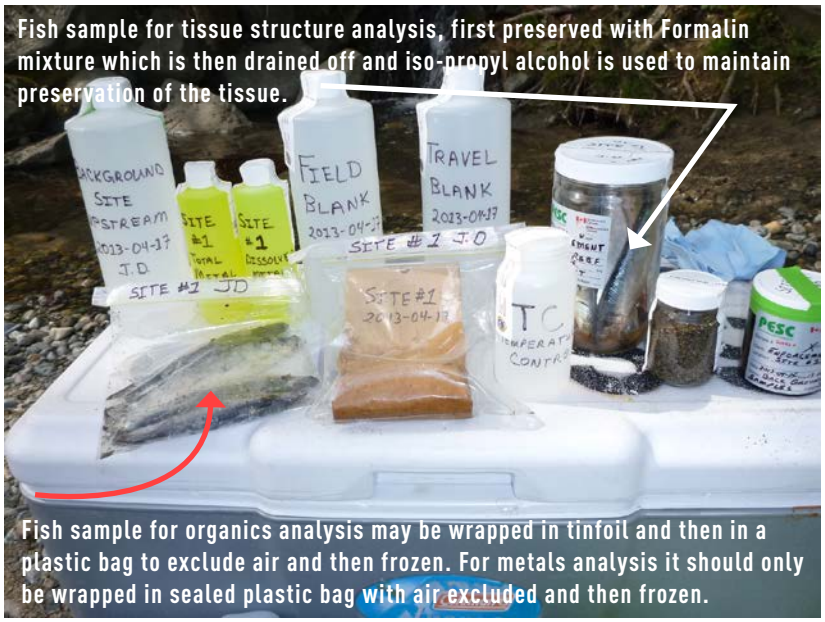

FIGURE 9.3:
Fish sample preservation for metals or organics or tissue structure analysis.
(Courtesy of Canada - DOE)

9.4.1 INVESTIGATING FISH/SHELLFISH KILLS DUE TO POLLUTION

Fish kills will require the collection of fish and water quality samples from the un-impacted and impacted zones. It is imperative to arrive at the scene of the fish kill as soon as possible to maximize the collection and preservation of evidence. For oil or petroleum based pollution, see SECTION 6.3

ASSEMBLE THE EQUIPMENT

- ☐ Appropriate personal protective equipment based on the requirements for the suspected toxicant. See SECTION 2.6.5
- ☐ Appropriate water quality sample containers. See SECTION 2.9.2
- ☐ Appropriate containers to collect samples of the fish which can accommodate the entire fish size.
  Containers may be:
  - 1.0 L or larger wide mouth glass jars
  - Rolls of aluminum foil to wrap the fish
  - Plastic bags to contain the fish
- ☐ Thermometer (hand-held or meter)
- ☐ Dissolved oxygen test (kit or meter)
- ☐ Conductivity meter
- ☐ pH test paper or meter
- ☐ Chlorine test kit or meter
- ☐ Ammonia test kit
- ☐ Long handled nets with a mesh size capable of capturing the fish
- ☐ Ice (if fixatives are not available)
- ☐ Formalin fixative. Formalin is a mixture of 70% water and 30% formaldehyde. It is a fixative to preserve the cell structure in biological samples and is toxic and must be handled with care according to local safe work guidelines.
- ☐ 90% n-propyl alcohol. n-propyl alcohol is an alcohol which is used to preserve the tissue sample for the long term.

SUGGESTED PROCEDURE

1. Include at least one person in the investigation team with experience in investigating fish kills. Local observers may be useful guides to the area.
2. Try to estimate and record the total number of dead and dying animals/fish as accurately as you can.
3. Collect water samples from both polluted and unpolluted areas. If possible start from uncontaminated areas and work towards the source of contamination. Priority should be given to collect from the sites where evidence is believed to be lost the quickest.
4. Collect fish samples as described below from both polluted and unpolluted areas. Samples from small fish species (forage fish) should be pooled to provide adequate sample sizes. If possible start from uncontaminated areas and work towards the source of contamination.
5. Measure and record temperature, pH, dissolved oxygen and conductivity. Make additional tests (chloride, ammonia) depending on suspected causes of the fish kill.
6. Record observations on water appearance, stream flow and weather conditions.
7. Colour photographs are taken to record site conditions and samples.

SAMPLES FOR PATHOLOGICAL ANALYSIS

- Try not to bruise the specimens.
- Fish samples for pathological tissue analysis should not be frozen as ice crystals will destroy the cell structure. If fixatives are not available, wrap the fish in plastic, place on ice packs (or bottles of frozen water) and transport to the pathologist as soon as possible.
- Fish should be placed in a glass jar and formalin fixative is added to the sample to preserve the cell structure of the fish sample for pathological analysis. The sample should soak in the fixative for at least 24 hours and then drained off into a secure waste container.
- After the formalin fixative is drained from the pathological fish sample, 90% n-propyl alcohol is added to preserve the pathological fish sample. The sample should soak in the alcohol and be submitted for pathological tissue analysis.

SAMPLES FOR ORGANIC/PESTICIDE ANALYSIS

- Fixatives or preservatives should not be added to the sample container.
- For organics analysis, fish samples should be wrapped in aluminum foil and sealed in sealable plastic bags with as much of the air excluded as possible.

SAMPLES FOR METALS ANALYSIS

- Fixatives or preservatives should not be added to the sample container.
- For metals analysis, fish samples should be wrapped and sealed in sealable plastic bags with as much of the air excluded as possible.

9.4.2 INVESTIGATING BIRD AND WILDLIFE KILLS DUE TO POLLUTION

Kills involving birds and other wildlife will require the collection of samples of the wildlife and potentially water quality/soil/vegetation samples from the un-impacted and impacted zones. It is imperative to arrive at the scene of the wildlife kill as soon as possible to maximize the collection and preservation of evidence. For oil or petroleum based pollution, see SECTION 6.3.

ASSEMBLE THE EQUIPMENT

If water quality sources of toxicity are suspected, see SECTION 2.9.2.

- ☐ Appropriate personal protective equipment based on the requirements for the suspected toxicant. See TABLE 2.6
- ☐ Appropriate soil quality sample containers. See SECTION 2.9.2
- ☐ Appropriate containers to collect samples of the wildlife which can accommodate the essential parts or the entire wildlife size. Containers may be:
  - 1.0 L or larger wide mouth glass jars to contain wildlife (or parts)
  - Rolls of aluminum foil to wrap the wildlife
  - Plastic bags to contain the wildlife
- ☐ Long handled nets with a mesh size capable of capturing the wildlife
- ☐ Ice (if fixatives are not available)
- ☐ Formalin fixative. Formalin is a mixture of 70% water and 30% formaldehyde. It is a fixative to preserve the cell structure in biological samples and is toxic and must be handled with care according to local safe work guidelines.
- ☐ 90% n-propyl alcohol. n-propyl alcohol is an alcohol which is used to preserve the tissue sample for the long term.
- ☐ For disinfection equipment, see SECTION 9.6, as similar precautions are recommended as for doing a farm inspection.

Note: Soil and product samples may also have to be collected. See also SECTION 7

SUGGESTED PROCEDURE

1. Include at least one person in the investigation team with experience in investigating wildlife kills. Local observers or wildlife conservation officers may be useful guides to the area.
2. Try to estimate and record the total number of dead and dying animals as accurately as you can.
3. Some animals may be too large for transport to the laboratory. Consult with the local analytical and pathology laboratory as to what animal parts are required for analysis. Common parts are mouth, tongue, stomach contents, liver and fat tissue. If parts must be cut out, obtain the assistance of someone who is trained in identification and tissue removal techniques.
4. Collect and store the entire wildlife in a container or collect the parts of the wildlife recommended by the laboratory or pathologist, as outlined below.

5. Record observations of the site and weather conditions.
6. Colour photographs are taken to record site conditions and samples.

SAMPLES FOR PATHOLOGICAL ANALYSIS

Try not to bruise the specimens.

- Animals or animal parts samples for pathological tissue analysis should not be frozen as ice crystals will destroy the cell structure. If fixatives are not available, wrap the animals or animal parts in plastic, place on ice packs or bottles with frozen water, and transport to the pathologist as soon as possible.
- If fixative is available, animals or animal parts should be placed in a glass jar and formalin fixative is added to the sample to preserve the cell structure of the animal sample for pathological analysis. The sample should soak in the fixative for at least 24 hours and then drained off into a secure waste container.
- After formalin has been drained from the pathological animal sample, 90% n-propyl alcohol is added to preserve the pathological animal/tissue sample. The sample should soak in the alcohol and be submitted for pathological tissue analysis.

SAMPLES FOR ORGANIC/PESTICIDE ANALYSIS

- Fixatives or preservatives should not be added to the sample container.
- For organics/pesticide analysis, animals or animal parts samples should be placed in glass jars or wrapped in aluminum foil and sealed in sealable plastic bags with as much of the air excluded as possible.
- The samples should be kept at 4ºC or frozen and transported to the laboratory as soon as possible.

SAMPLES FOR METALS ANALYSIS

- Fixatives or preservatives should not be added to the sample container.
- For metals analysis, animals or animal parts samples should be wrapped and sealed in sealable plastic bags with as much of the air excluded as possible.
- The samples should be kept at 4ºC or frozen and transported to the laboratory as soon as possible.

9.5 SAMPLING VEGETATION

SUGGESTED PROCEDURE

1. If you need to take vegetation samples, collect them separately using shears or other tools to cut the sample and place in a jar.
2. Collect vegetation samples from both polluted and unpolluted areas. If possible start from uncontaminated areas and work towards the source of contamination. Priority should be given to collect from the sites where evidence is believed to be lost the quickest.
3. Vegetation samples should be stored at 4°C if examination of cell structure is important.
4. Vegetation samples should be frozen if organic or heavy metals analysis is required.
5. Decontamination of sampling equipment may be required. See also SECTION 9.2.

FIGURE 9.4:
Sterilizing boots and vehicle using a chloride bleach spray before and after a farm inspection to prevent transfer of harmful organisms from farm to farm.
(Courtesy of Canada – DOE)

9.6 SAMPLING IN FARMS

When conducting farm inspections you should follow bio-security procedures taken by practicing veterinarians. This is to prevent the transfer of harmful bacteria or viruses from hands, clothing and vehicles from one farm to another, reducing the risk of causing infection of livestock and preventing the needless destruction of farm animals. Failure to do so could result in widespread farm infections and financial liability costs.

ASSEMBLE THE EQUIPMENT FOR THE REQUIRED SAMPLING

- ☐ See the appropriate manual section for the type of equipment

ASSEMBLE THE EQUIPMENT FOR STAFF AND FIELD VEHICLES DISINFECTION

- ☐ Rubber boots that can be cleaned and then reused
- ☐ Disposable heavy gauge garbage bags
- ☐ Washable/reusable coveralls or disposable coveralls

- ☐ Hair nets
- ☐ Disposable or washable rubber gloves
- ☐ Antibacterial waterless soap
- ☐ Disinfectant in solution (e.g. Virkon)
- ☐ Water for additional solution if needed
- ☐ Tub with lid to contain disinfectant solution which is large enough to step in
- ☐ Long handled scrub brush
- ☐ Paper towels
- ☐ Antibacterial handy wipes
- ☐ Hand pressurized sprayer

The following are basic steps to reduce the risk of spreading contamination from a farm visit:

- Park your vehicle away from the barn area in an area as free from manure as possible.
- If going near the barn/barnyard to inspect or into fields containing animal waste, change into clean coveralls. Then put on disinfected boots (disinfect in and out).
- Although it is unlikely that samplers would be required to go into the barn, be prepared to have a shower and wear a helmet or hair net if required.
- Avoid unnecessary contact with livestock, their manure and feed.
- Avoid recently emptied barns.
- Do not touch farm pets; they are in routine contact with livestock, the barn and barnyard environment.
- Conduct the required inspection/sampling.

When the required inspection/sampling is complete, initiate disinfection protocol.

1. Fill the wash tub with water and add disinfectant.
2. Brush boots in disinfectant first and rinse with clean water.
3. Remove coveralls and store in a plastic bag for disposal (if disposable) or for washing if reusable.
4. If the vehicle/tires have become contaminated with animal waste, wash first with soap and water.
5. Fill the hand pressurized sprayer with disinfectant and spray the circumference of the tires to sterilize them and prevent tracking of contaminants/bacteria/viruses to other farms.

9.7 USING PLANTS TO DELINEATE POLLUTION (PHYTO-SCREENING)

Plants and trees can absorb contaminants dissolved in groundwater and transport them up their stems. This enables the collection of information on the underlying groundwater and soil chemistry through the sampling of tree cores for contaminant analysis. The chemical content of tree cores can be useful indicators of subsoil pollution without disrupting the surrounding environment or risking exposure to contaminants in the underlying soil or groundwater. Modern analytical methods have allowed detection of groundwater contaminants such as chlorinated volatile organic compounds (CVOCs), explosives, and some heavy metals at low levels. The chemical analysis of tree/plant stem tissue provides preliminary information (for mapping, etc.) of subsoil contaminants and has been termed phyto-screening.

FIGURE 9.5:
Phyto-screening by collecting plant growth rings may be cost effective for initial screening of contaminated soil and groundwater.
(Courtesy of HPC-Envirotec)

ASSEMBLE THE EQUIPMENT FOR THE REQUIRED SAMPLING

- ☐ Appropriate sample container for the type of analysis, usually wide mouth glass jar. See SECTION 2.9.2
- ☐ Wood corer
- ☐ Hammer

1. Contamination spread by groundwater may be absorbed by plants and located in their growth rings.
2. Drill into the trunk to obtain a cross-section of rings.
3. Measure the rings to estimate the time when the contamination impacted the plant and collect a sample at critical rings to verify presence of the contaminant.

The following are basic steps in collecting a phyto-screening sample:

1. Determine a sampling strategy, either by collecting samples from plants along a known contaminant path or by establishing sample sites in concentric circles around a suspected source.
2. Use the wood corer to create a small 0.5 cm diameter hole in the tree, extracting a 10 cm long core of wood.
3. Insert the core sample into the appropriate container.
4. Collect enough samples to establish an inferred path of contamination.
5. Submit the sample for digestion/extraction (depending on the chemical component being investigated) to the appropriate laboratory using the appropriate analytical method.
6. Follow up samples of soil and/or groundwater may need to be collected to confirm an inferred path of contamination.

9.7.1 ANALYSING PLANT TISSUE FOR CHEMICAL COMPONENTS (DENDRO-CHEMISTRY)

The analytical method used to analyse the wood sample (dendro-chemistry) will depend on the suspected contaminant. Dendro-chemistry has successfully utilized several analytical techniques including energy-dispersive X-ray fluorescence (EDXRF), proton-induced X-ray emission (PIXE), inductively coupled plasma-mass spectroscopy (ICP-MS) and atomic emission spectroscopy (AES). The EDXRF methods are favored because of their capacity for simultaneous analysis of about 30 marker elements.

The marker elements which can be detected by these methods are heavy metals, chlorine, fluorine and bromine.

9.7.2 USING PLANTS FOR DATING OF POLLUTION IMPACTS (DENDRO-CHRONOLOGY)

Annual tree growth rings can preserve past environmental chemical changes in the soil and groundwater. The year the chemical is absorbed by the plant roots can be correlated to the chemical concentration in the tree ring. The correlation of the tree ring to the date must consider changes in the environment and an understanding of tree biology, tree physiology and tree infections.

Dating of pollution impact and criminal pollution is important for courts in case of prosecution. Phyto-screening and dendro-chemical investigation can increase the understanding of current and past environmental chemical release events, termed phyto-forensics.

The following are the basic steps in dating a pollution event:

1. Collect a subsample of the length of the wood core that correlates to the date of interest by cutting the sample into sections according to the number of tree rings that correspond to years of growth before, during and after an incident.
2. Analyse each subsample for the chemical component to obtain the chemistry profile of the plant tissue in that ring.
3. Plot the change in chemical constituent concentration against the age of the tree ring (or section of tree rings) to estimate the date that the pollution arrived at that point.

The investigation can indicate a chemical change in the annual rings. This information can be combined with groundwater, soil and soil vapor data, knowledge of pollutant sources (types and locations, etc.) and knowledge of tree species to correlate to the time of a pollution event.


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10 SAMPLING HAZARDOUS WASTE

Sampling Hazardous Waste

No universally accepted standardized methods exist for collecting hazardous materials. Contaminated sites and/or hazardous waste, by their nature and definition, are likely to contain randomly distributed contaminants at concentrations that are unknown and in potentially reactive states that are likely to be harmful to health or cause serious injury or death. The purpose of the following section is to provide a general overview of the investigation of a hazardous waste site and should be read in conjunction with HAZARDOUS WASTE SCENARIOS.

DISCLAIMER

Each sampling episode will need a Task Hazard Analysis and a well-designed plan for site entry, exit and safety that complies with local regulations. See SECTION 2.6. This manual is not designed to provide detailed information on how to design a hazardous waste site entry plan and should not be relied upon for the development of such a plan. INTERPOL recognizes that sampling of hazardous wastes requires specialized training and equipment. Personnel not trained in the collection of hazardous wastes should not undertake such activities.
The following information is presented so as to make the environmental investigator aware of the general criteria and hazards which may be encountered when dealing with a hazardous waste investigation.

FIGURE 10.1:
Essential steps in dealing with a hazardous waste site.
(Courtesy of United States – EPA, Canada - DOE)

1. Secure the site to prevent exposure and preserve evidence.
2. Implement health and safety protocols. Inventory evidence and sample sites.
3. Use sterile procedures. Collect sample evidence and take photographs.
4. Package the sample evidence and preserve continuity to avoid tampering.
5. Ensure health and safety by proper decontamination and site clean-up.
6. Submit samples for analysis. Write up witness statements and obtain expert reports.

10.1 SOURCES OF HAZARDOUS WASTE

In contrast to routine environmental samples, waste samples generally contain high to extremely high levels of contaminants. They are often collected from drums, tanks, rail tankers, spills, and areas in the immediate vicinity of an incident. Waste samples are usually considered hazardous samples. It is essential to distinguish between environmental and hazardous waste samples for the purposes of choosing sampling equipment, for personal safety precautions, complying with transportation requirements, and for notification of the laboratory.

10.2 COMMUNICATING LEGAL INVESTIGATION ISSUES AND STRATEGIES WITH HAZARDOUS WASTE SITE FIRST RESPONDERS

The primary objective of hazardous waste site first responders will be to secure the site, prevent further discharges and clean up the site. This could destroy evidence essential to the legal investigation. It is essential that legal environmental investigator communicate with hazardous waste site first responders to ensure that evidence critical to an investigation is preserved as much as possible. Therefore, in cooperation with the waste site first responders, a decision needs to be made as to the purpose of the inventory and sampling prior to disturbing the accident/crime scene. A complete inventory will help establish the order of magnitude of the potential or actual environmental risk/damage which may affect legal remedies and penalties according to local legislation. If it is possible, and in the interest of public and environmental safety, the following essential steps should be implemented prior to the hazardous waste first responders entering the site:

1. Secure the site to prevent unauthorized entry and exit.
2. Establish the health and safety protocol for entry and exit. See SECTION 2.6
3. Establish a sample/evidence handling area.
4. Record all available information concerning each container in a permanent manner, including:
   - Type of container
   - Capacity (estimated or actual)
   - Markings, label and origin
   - Condition
5. Take photographs to provide a permanent record.
6. Secure the required samples and documentary evidence.
7. Notify the laboratory of the type and quantity of samples expected.
8. Initiate the containment and cleanup of the site.

10.3 NOTIFICATION OF THE LABORATORY REGARDING HAZARDOUS WASTE SAMPLES

Hazardous waste samples can create serious hazards that affect laboratory personnel. For this reason, all hazardous samples should be clearly identified and documented prior to submission to the laboratory so that the analysts can take appropriate precautions to prevent personal injury and contamination of the laboratory.

The laboratory will take special precautions for the receipt, handling, storage and analysis of the hazardous waste samples. Very high concentrations of contaminants can result in damage to or contamination of the analytical equipment at the laboratory. The analysts need to know in advance that the samples are hazardous waste and if possible the approximate concentrations so that they can properly handle the samples, usually by making dilutions so that they can be safely analysed. The dilutions will be taken into account when calculating the final concentrations.

10.4 SAMPLING HAZARDOUS WASTE – CREATING AN INVENTORY

For legal purposes, it may not be necessary to sample every container of hazardous waste at a site. The sampling plan should identify the minimum number and types of samples that need to be collected to support legal charges.

For the purpose of environmental assessment and cleanup of the hazardous waste site, it is necessary to inventory and possibly collect a sample from each container. This work is usually assigned to a contractor that specializes in the assessment and cleanup of hazardous waste which often occurs simultaneously with the legal investigation of the site or after the legal investigation has been completed.

10.5 SAMPLING HAZARDOUS WASTE – SELECTING A SAMPLING TECHNIQUE

The technique used to collect a sample of hazardous waste must consider:

- Type of container
- Physical condition of the container
- Type of product it contains
- Safety hazard risk

Each hazardous waste container that is required for evidence should be sampled individually. Common sampling procedures are provided in the following sections. Further information can be obtained from the US EPA Document, "Samplers and Sampling Procedures for Hazardous Waste Streams", EPA-600/2-80-018, January 1980 which can be found at http://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=30000APW.txt

Depending on the location and position of containers holding hazardous wastes, it may be necessary to set the containers upright or move them before sampling or place them into containment structures. Take extreme care to ensure that no rupture or leakage occurs, both to ensure your safety and to prevent spillage. Depending on the sampling objective, individual or composite samples may be done at the site or in the laboratory on a weight/weight or volume/volume basis before analysis may be permissible.

10.5.1 ASSEMBLE THE EQUIPMENT REQUIRED FOR SAMPLING HAZARDOUS WASTE

The general types of equipment necessary for hazardous waste sampling are:

- ☐ Protective gear to handle the chemicals suspected or identified in the health and safety plan. See SECTION 2.6.
  See also: US Government Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health (NIOSH) Database http://www.cdc.gov/niosh/data/
- ☐ Safety equipment including life vests for working on a boat for deep water and shoreline sampling
- ☐ Equipment to establish a decontamination site. See HAZARDOUS WASTE 1
- ☐ Equipment to establish a command and control site.
- ☐ Equipment to collect specific samples. See also US EPA Document, "Samplers and Sampling Procedures for Hazardous Waste Streams", EPA-600/2-80-018)
- ☐ Non-sparking barrel bung wrench
- ☐ Non-sparking flash light
- ☐ Peristaltic pump with appropriate sample tubing
- ☐ Polyethylene drop sheets – minimum 1 m x 1 m
- ☐ Stainless steel (aluminum or plastic) trays for sample placement, or
- ☐ Plastic trays lined with aluminum foil or polyethylene depending on the type of contaminant
- ☐ Distilled/de-ionized water in wash bottles, if sampling for non-organics
- ☐ Reagent grade acetone/hexane in wash bottles, if sampling for organics
- ☐ Disinfectants and cleaning soaps for decontamination
- ☐ Specialty equipment for opening hazardous waste containers
- ☐ Enamel (orange) spray paint for marking containers

10.6 SAMPLING HAZARDOUS WASTE CONTAINERS

Opening containers which contain hazardous waste presents numerous safety hazards which can result in serious injury or death. The following are examples of techniques commonly used for opening containers of various types and sizes.

10.6.1 SAMPLING BARRELS OF LIQUID HAZARDOUS WASTE

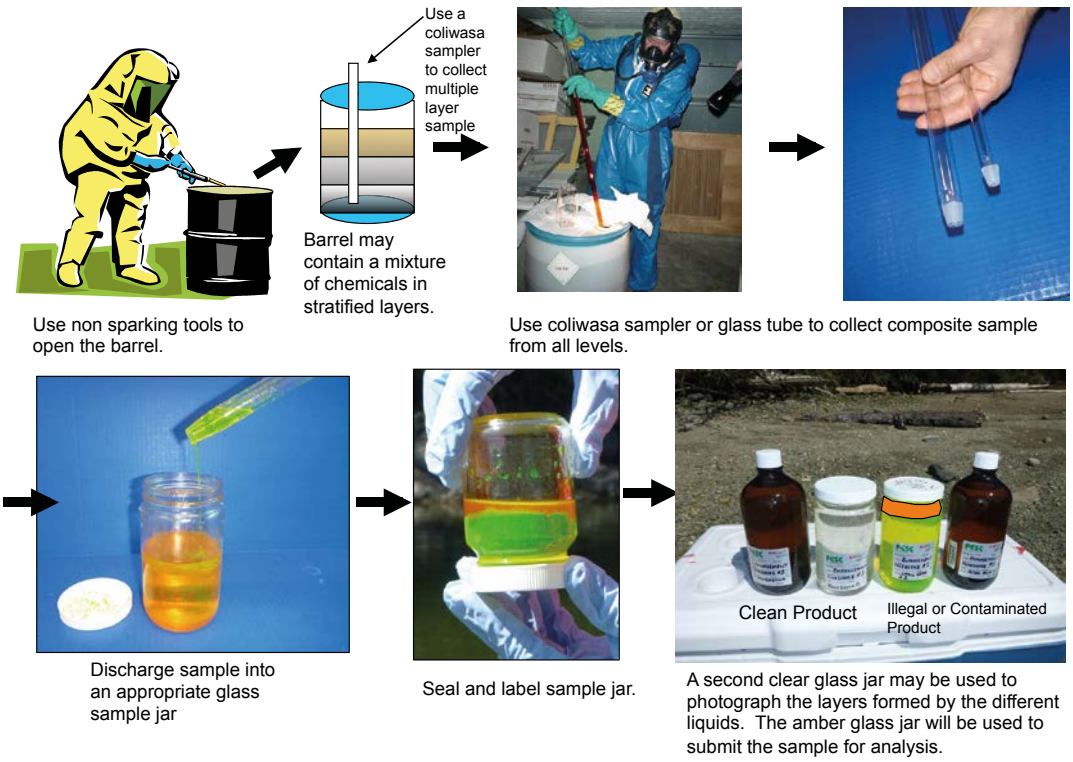
Containerized hazardous liquids may be in any form of container and are often corroded, pressurized and at risk of sudden pressure release, ignitable or explosive. These risks must be assessed and mitigating measures must be implemented to eliminate or reduce the risks to acceptable levels by experienced hazardous waste sampling staff.

ASSEMBLE EQUIPMENT

Containerized hazardous liquid may require one or more of the following non-sparking tools and associated equipment:

- ☐ Remote barrel opener
- ☐ Non-sparking barrel opener
- ☐ Container penetrating apparatus
- ☐ Wide-mouth sample jar
- ☐ Aluminum, stainless steel or plastic tray to contain drips from the sampler
- ☐ COLIWASA (glass or plastic depending on the type of material sampled)
- ☐ Absorbent paper towels to clean utensils and spills.

FIGURE 10.2:
Sampling barrels of liquid hazardous waste which may have layers of contamination. (Courtesy of United States – EPA, Canada - DOE)



SUGGESTED PROCEDURE

1. Place the wide-mouth sample jar into the containment tray.
2. Select the correct device to safely open the container.
3. Insert the sampling device to collect a sample from top to bottom of the barrel.

10.6.2 SAMPLING BULK TANKS OF LIQUID WASTE USING A SINGLE COMPOSITE BOTTLE OR COLIWASA

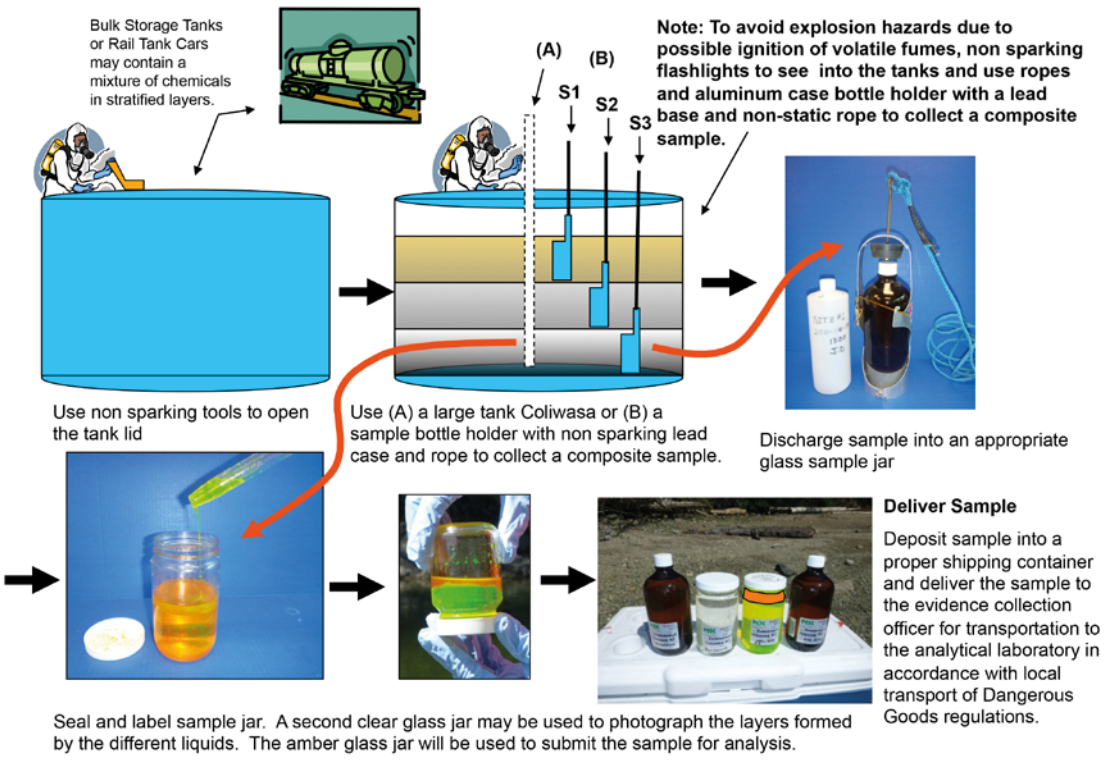
Bulk storage tanks or rail cars are often corroded, pressurized and at risk of sudden pressure release, ignitable or explosive. These risks must be assessed and mitigating measures must be implemented to eliminate or reduce the risks to acceptable levels by experienced hazardous waste sampling staff.

ASSEMBLE EQUIPMENT

Containerized hazardous liquid may require one or more of the following non-sparking tools and associated equipment:

- ☐ Non-sparking tools/wrenches to open bulk tank or rail car lids
- ☐ Non-sparking sample container holder and ropes, and/or
- ☐ Non-sparking COLIWASA of sufficient length to reach the bottom of the tank and/or
- ☐ Non-sparking peristaltic pump and hoses
- ☐ Wide-mouth sample jar
- ☐ Aluminum, stainless steel or plastic tray to contain drips from the sampler
- ☐ Absorbent paper towels to clean utensils and spills

FIGURE 10.3:
Sampling bulk tanks of liquid waste which may have layers of contamination.
(Courtesy of Canada - DOE)



SUGGESTED PROCEDURE

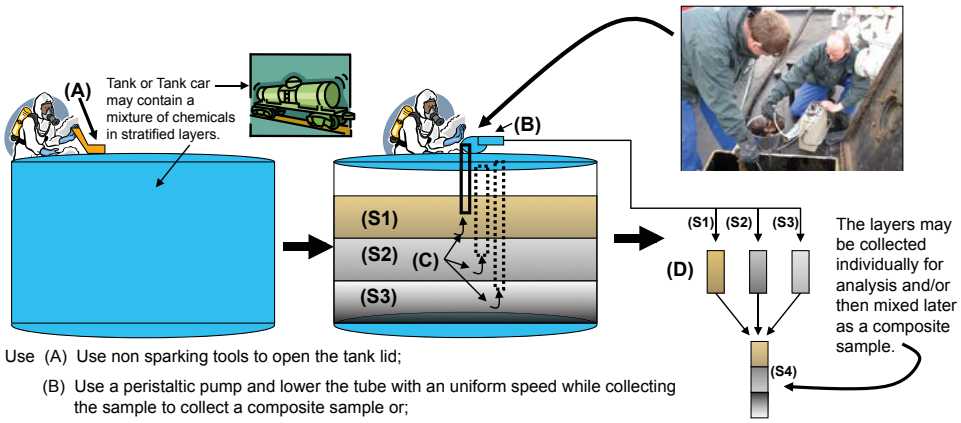
1. Place the wide-mouth sample jar into the containment tray.
2. Select the correct device to safely open the tank.
3. Insert the sampling device to collect a sample from top to bottom of the tank.

FIGURE 10.4:
(Courtesy of United States – EPA, Canada - DOE)

10.6.3 SAMPLING BULK TANKS OF LIQUID WASTE USING PUMPS

Peristaltic pumps use a vacuum to transport the samples. This vacuum may cause some degassing and loss of volatile organic compounds (VOCs) from the sample. When precise quantitative data for VOCs and dissolved gases are not required, peristaltic pumps may be used.

NOTE: Care must be taken to ensure there are no electrical sparks hazards from the power supplies (batteries) electrical chords or pumps when volatile organics are present due to explosion hazards. I.e. locate the pump/ battery as far away from the sample/vent openings as possible. Ensure containers have a proper electrical grounding to avoid static charge buildup and electrical arcing which could cause an explosion and/or fire.



Use (A) Use non sparking tools to open the tank lid;

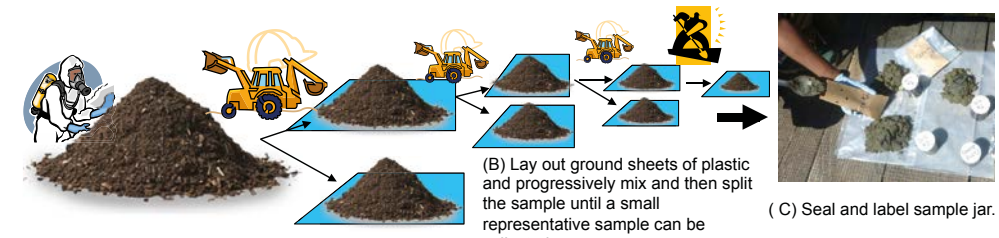
(B) Use a peristaltic pump and lower the tube with an uniform speed while collecting the sample to collect a composite sample or;

(C) Lower the tube to specific depths, fill a sample bottle and then lower to new depth(s) and collect subsequent samples for individual analysis (S1, S2, S3) or;

(D) Combine equal portions of the individual samples as a composite sample (S4) later after the individual samples have been collected. Retain the residual individual samples (S1, S2, S3) for subsequent analysis if required.

FIGURE 10.5:
(Courtesy of United States – EPA, Canada - DOE)

10.6.4 SAMPLING BULK PILES OF SOLID WASTE USING SPLIT SAMPLES



(A) Depending on the size of the pile, hand methods (shovels) or mechanical methods (excavator) of mixing and sampling may be required. (See 11.5.4 for Fractional Sampling technique.)

(B) Lay out ground sheets of plastic and progressively mix and then split the sample until a small representative sample can be collected.

(C) Seal and label sample jar.

(C) Collect Samples in proper containers.
Depending on the nature of the product, choose plastic or glass container and wrap it in a sealed bag in order to guaranty the safety of the expert investigators and laboratory's employees. (See Section 13)

(D) Deliver Sample

Deposit sample into a proper shipping container and deliver the sample to the evidence collection officer for transportation to the analytical laboratory in accordance with local transport of Dangerous Goods regulations.

10.6.5 SAMPLING BULK PILES OF SOLID WASTE USING FRACTIONAL SAMPLING[1]

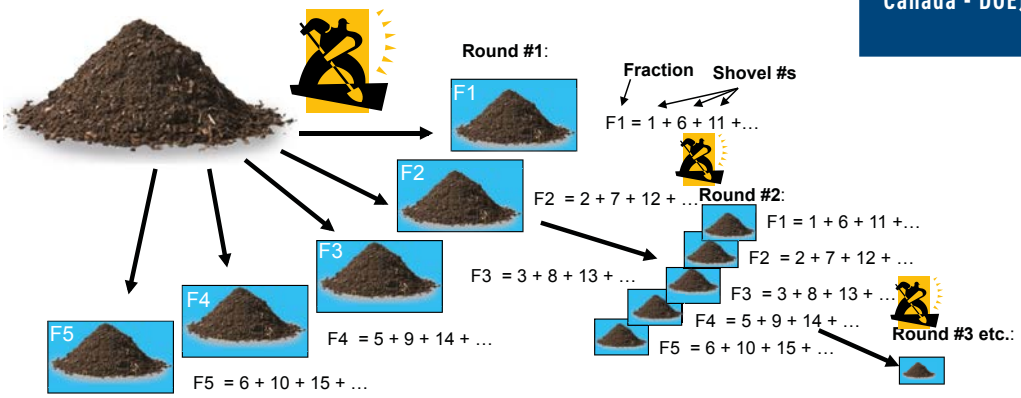


FIGURE 10.6:
(Courtesy of United States – EPA, Canada - DOE)

Round #1: Fractional sampling using a hand shovel can be used to reduce a sample to a size suitable for sending for analytical testing. A number of plastic sheets are laid out. (In this example 5 sheets) and each shovel full is placed on the sheet progressively moving to the next sheet and then returning back to the original pile. This creates a number sequence for each pile.

Round #2: If the first round of fractioning piles are too large, a random selection can be made of one of the piles and the process of Fractioning is repeated using a smaller Round #1 pile as the source.

Round #3: The process can be repeated until an appropriate sample size is obtained.

1) Ref: USEPA, "Guidance for Obtaining Representative Laboratory Analytical Subsamples from Particulate Laboratory Samples" , EPA/600/R-03/027 November 2003.

10.6.6 SAMPLING BULK PACKAGES OF SOLID WASTE

Containerized hazardous solid materials such as sludges, granular materials or powder may be in any form of container and are often corroded, pressurized and at risk of sudden pressure release, ignitable or explosive. These risks must be assessed and mitigating measures must be implemented to eliminate or reduce the risks to acceptable levels by experienced hazardous waste sampling staff.

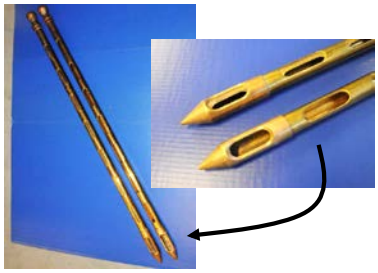
ASSEMBLE EQUIPMENT

Containerized hazardous solid materials such as sludges, granular materials or powder are usually sampled using one of the following non-sparking tools:

- ☐ Wide-mouth sample jar
- ☐ Scoop or trowel
- ☐ Sampling trier (small trier)
- ☐ Grain sampler

SUGGESTED PROCEDURE

1. Select the correct device to safely open the container.
2. Insert the sampling device into the centre of the materials.
3. Collect a core of material from a point diagonally opposite the point of entry.
4. Retrieve the sample and immediately transfer it into the sample bottle.
5. If the sampling device is disposable, it may be left in the container sampled. Otherwise decontaminate the device thoroughly before collecting the next sample.



(A) Select target bags: Where there are a large number of bags, use mathematic formula or a random number table in order to select the sample bag.
(B) Mark or identify the bags being sampled: and record the information in your notes.

(C) Sample Granular material: If the material is granular in texture use stainless steel "Seed Bag Samplers" with slot size appropriate for the type of material.

(E) Deliver Sample

Deposit sample into a proper shipping container and deliver the sample to the evidence collection officer for transportation to the analytical laboratory in accordance with local transport of Dangerous Goods regulations.

(D) Collect Samples in proper containers.
Depending on the nature of the product, choose plastic or glass container and wrap it in a sealed bag in order to guaranty the safety of the expert investigators and laboratory's employees. (See Section 13)

WARNING

Disposal of all hazardous waste should be done according to the existing municipal by-laws or provincial/state/federal regulations.

FIGURE 10.7:
(Courtesy of United States – EPA, Canada - DOE)

10.7 ISOTOPE-FRACTIONING

Isotopes are an atomic variation within the atoms of chemical elements where the nucleus of the atom has the same number of protons but different atoms have different numbers of neutrons. For example, a carbon atom has 6 protons but may have 6, 7 or 8 neutrons giving three different masses of carbon (^{12}C, ^{13}C, ^{14}C). Metals may also have such variations; for example, selenium, which can be toxic to fish and vertebrates, has ^{80}Se, ^{79}Se, ^{78}Se, ^{77}Se, ^{76}Se and ^{75}Se, and strontium has ^{87}Sr and ^{86}Sr, which can be used for source tracking.

The ratios of these isotopes in an environmental sample can help identify its source and its age. For example, a pollutant source may have a specific carbon ($^{12}C/^{13}C$) ratio or a river water source may have a specific strontium ($^{87}Sr/^{86}Sr$) ratio due to the geology of the rocks in the watershed. A hazardous waste may have a specific contaminant with a unique isotope ratio; for example, chlorine ($^{35}Cl/^{37}Cl$) isotopes in chlorinated chemicals such as PCBs, pesticides and solvents can be tracked to the source.

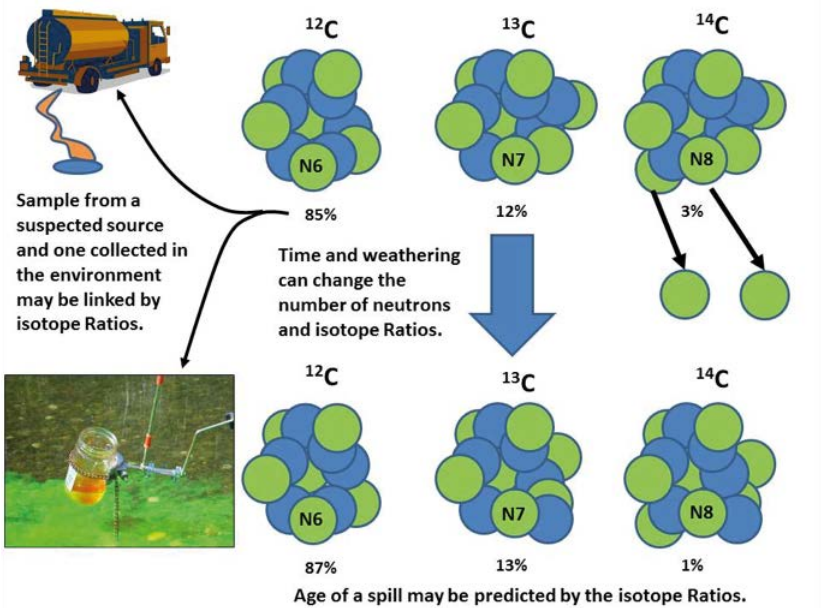


FIGURE 10.8:
Isotope ratios can be used for linking a pollution source to receptors and for estimating age/time of release. (Courtesy of Canada – DOE and Genesis Environmental Sciences Ltd.)

10.7.1 IDENTIFICATION OF A POLLUTANT'S ORIGIN IN ENVIRONMENTAL SAMPLES USING ISOTOPES

In cases where hazardous waste or a polluting effluent has been discharged or dumped and there has been little or no opportunity for chemical radioactive decay changing the original isotope ratios of the elements such as carbon, nitrogen or heavy metals, the environmental sample can be compared to a source sample for chemical fingerprinting.

SUGGESTED PROCEDURE:

- ☐ Collect contaminated environmental samples (soil, sediments, water, biota - fish, plants, animals).
- ☐ Sample the source suspected to be at the origin of the pollution (e.g. residues in drums, trucks, tanks, pipes, facilities, ships, etc.).
- ☐ Analyse the samples for the suspected isotope ratio of the contaminant, for example carbon (12C/13C) in primarily hydrocarbon pollutants; strontium ($^{87}Sr/^{86}Sr$), lead ($^{206}Pb/^{207}Pb/^{208}Pb$) and selenium ($^{74}Se/^{76}Se/^{77}Se/^{78}Se/^{78}Se/^{80}Se$) from metallic or coal mining sources; or chlorine ($^{35}Cl/^{37}Cl$) isotopes in case of chlorinated organics such as PCBs, chlorinated pesticides and chlorinated solvents.

If the isotope relationships of samples of residues in trucks, tanks, pipes, facilities, ships, etc., are identical to the ratios from environmental or biota samples a criminal relationship/responsibility may be possible to prove.

ASSEMBLE THE EQUIPMENT FOR THE REQUIRED SAMPLING OF FISH/ ANIMAL TISSUE

- ☐ Appropriate sample container for the type of analysis, usually a wide mouth glass jar. See SECTION 2.9.2
- ☐ Small tissue saw
- ☐ Scalpel or razor knife
- ☐ Stainless steel tweezers
- ☐ Stainless steel pliers
- ☐ Isopropyl alcohol for disinfectant

- ☐ Protective latex gloves
- ☐ Anesthetic and syringe if sampling live fish/animals

BASIC STEPS IN COLLECTING A FISH/ANIMAL TISSUE SAMPLE

1. When possible, consult with a biologist or biochemist as to which tissue is best to sample.
2. Use the anesthetic to numb the area of a live fish/animal to be sampled (dead animals do not need the anesthetic).
3. For fin ray sampling in fish, measure approximately 2 cm from the joint and use the small tissue saw to make two cuts about 1.0 cm apart into the fin ray.
4. Use the scalpel or razor knife to slice between and connect the bottom of the two cuts on both sides of the fin ray.
5. Use the stainless steel plier to remove the tissue and place in the appropriate sample container and store at 4°C or freeze if long transport to the laboratory is required.
6. Submit the sample to the laboratory for thin slicing, mounting and laser ablation. Note: Depending on the chemical component being investigated, this technique is highly specialised and must be sent to the appropriate laboratory using the appropriate analytical method.

10.7.2 DATING OF POLLUTION AND POLLUTION IMPACT USING ISOTOPE RATIOS

Refining or processing of petroleum, coal or lignite to produce gasoline, solvents or other organic compounds does not normally alter the isotope ratios from their natural states. Therefore, the degradation caused by microbiological modification of the isotope ratios can be used for pollution dating. Bacteria prefer to digest organic molecules composed of the lighter carbon isotopes such as ^{12}C instead of those containing heavy ^{13}C isotopes. The reason is that molecules containing heavy isotopes (e.g.^{13}C) are more stable than the molecules containing lighter isotopes (e.g.^{12}C). The same applies to molecules with ^{35}Cl isotopes instead of ^{37}Cl and for oxygen, sulfur, etc.

If a waste is released and soil or groundwater is contaminated with organic compounds such as petroleum/waste oil, chlorinated solvents or pesticides, it is possible to estimate the age of the pollution based on isotope ratios. Mechanisms such as bio-degradation and natural attenuation will tend to favor the removal of the lighter isotopes.

For example, the $^{12}C/^{13}C$ ratio may be much higher close to the source or date of a spill. As the contaminants move away from the spill site or have longer periods for bacterial action, the heavier isotopes will start to form the majority of the atoms; for example, ^{13}C atoms form the major component of the $^{12}C/^{13}C$ mixture. The time for a chemical to decrease to half its concentration is called its "half-life". Knowing the half-lives of isotopes and environmental factors, such as groundwater velocity, allows the estimation of age and time from when a spill or pollution event

occurred, possibly allowing correlation to criminal activity that caused the event.

SUGGESTED PROCEDURE

1. Collect a sample from points along the suspected pollutant pathway, e.g. two groundwater wells several hundred metres apart.
2. Submit the samples for isotope ratio analysis.
3. Evaluate the isotope ratios for chemical species and concentration, and evaluate if there is both a chemical fingerprint and a significant difference in the ratios which correlate to the expected factors responsible for degradation.

11 PREPARING TO SHIP LEGAL SAMPLES

Preparing to Ship Legal Samples

Inspectors go to considerable effort and expense to obtain representative samples, but all this work can be negated if the samples fail to arrive at the lab in a secure manner, in good condition, and within the required time frame. Samples should be shipped so they reach the laboratory as soon as possible, within the analytical holding time period. Delays in transporting samples must be avoided and care must be taken to ensure that samples are kept at the proper temperature.

11.1 APPLY LEGAL SEALS TO SAMPLE CONTAINERS

Prior to shipping, all legal samples should have legal seals applied to them. Samples can be sealed by:

- Wrapping the container lid tightly, glue side to glue side with seal tape, Teflon tape or strapping tape, and marking the tape with the samplers initials, or
- Placing the sample into individual self-sealing plastic bags. If possible, do not place more than one sample into a bag, as there may be confusion if a sample leaks or the glued on labels detach from the sample container.

FIGURE 11.1:
Legal seals can be made of prepared tamper-proof tape or of common tape. It is important to initial the seams of the tape and keep markings to a minimum to uniquely identify the sample. (Courtesy of Canada - DOE)

11.2 FILL IN THE CHAIN-OF-CUSTODY FORM AND RECORD CONTACT INFORMATION

Legal samples require that the physical control or continuity of a sample be documented from the time it is taken until the time it is destroyed. This is documented on a chain-of-custody form. See SECTIONS 2.4.6.5 AND 12.2

Each person that takes possession of the sample(s), that has direct access to the samples and those who open them must sign the chain-of-custody form. (**Note:** If the samples are sealed in a locked cooler and transported by a courier, the courier would not have direct access to them and thus would not sign the chain-of-custody form.) The form is signed by the sampler, the officer (if an officer took them into custody), the analyst or anyone else to whom it is given possession and direct access to attest that the samples have always been secure while in their possession and could not have been tampered with at any stage. It is always best to limit the number of people to whom the custody is transferred as every person could potentially be called as a witness to testify about their involvement with the sample.

If the samples cannot be personally delivered by the sampler/officer to the laboratory, a copy of the chain-of-custody form should be sealed in an envelope and attached to the outside of the shipping container. When it is received at the laboratory, the analyst who is to handle the samples should receive the samples and sign the chain-of-custody form. If shipping samples by courier, air freight or similar means, make a note of the waybill number and laboratory address in the legal notebook.

11.3 CONTACT THE RECEIVING LABORATORY

Advise the laboratory that the sample(s) will be shipped and give the waybill information. Keep the original waybill in the investigation file. This allows the laboratory analyst time to prepare to receive the samples and take custody of them.

11.4 SHIPPING CONTAINER PREPARATION

Shipping containers must be packed so as to protect the sample containers from vibration, shock and temperature variations.

- To reduce the risk of contamination from a broken sample container, it is advisable to line a sturdy container or cooler with a large plastic bag.
- Samples may be bagged individually and put into the container.
- Add freezer gel packs if the sample needs to be kept cool and pack with non-flammable absorbent material. Adding ice may result in

FIGURE 11.2:
Legal samples packed in a cooler with ice gel packs and spacers and various sample containers. (Courtesy of Canada-DOE)

the melt water contaminating the samples or causing the sample labels to detach from the samples.

- A Temperature Control Sample or TC Sample may be added to the shipping container if it contains water samples which must be kept at 4°C. This is a small tightly capped bottle (100 mL to 250 mL) of clean water. When the shipment reaches the laboratory, the analyst can measure the temperature of the TC Sample with a thermometer without disturbing the actual legal sample(s), to determine if they have been kept at the proper temperature.
- Do not overload shipping containers. Remember that 10 kg may be the cut-off weight under transport of dangerous goods requirements. Ten 1 L bottles of sample, plus packing materials and the container weight, would exceed this.
- To help ensure that liquid samples stay upright, you may block them in with empty sample bottles, freezer gel packs or pieces of cardboard.
- Take photographs of the samples in the shipping container (cooler) before the container (cooler) is sealed.
- Seal the liner bag.
- Put the sample laboratory submission sheet into a moisture-proof bag and enclose it within the sample shipping container.
- Close and seal the shipping container with a lock, legal seal or by wrapping in tape and signing and dating the tape so that it cannot be opened without damaging the sealing tape.
- Ensure that each shipping container is labelled with the destination, return address and any required safety markings and labels, as well as any special instructions, such as "FRAGILE," "KEEP COOL," "DO NOT FREEZE," "KEEP FROZEN," "THIS END UP."
- The shipping containers must also be marked with the appropriate labels and other information as required under the relevant legislation related to the transport of dangerous goods and the International Air Transport Association/International Civil Aviation Organization (IATA/ICAO).
- Samples from any one location should be kept together. If samples must be separated and placed in more than one shipping container, a copy of the sample submission form pertaining to those samples should be enclosed with the containers.
- Insert a copy of the chain-of-custody form and a second copy of the sample submission sheet into an envelope, seal the envelope and attach it to the outside of the shipping container.

- Take photographs of the samples in the shipping container (cooler) after the container (cooler) is sealed.

Note: If samples are being delivered to the laboratory in person, you should maintain custody of the samples at all times (e.g. lock vehicle doors).

11.5 SHIPPING DANGEROUS GOODS

Some samples contain dangerous goods (e.g. fuel samples) and may be covered by local legislation which allows for a conditional exemption if the samples are carried by the inspector and are in a suitable means of containment. Check local legislation to determine if samples are exempt. Shipment of oil/petroleum/volatile samples must be in accordance with applicable legislation related to transportation of dangerous goods. If shipping by air, a shipping agent may be used to insure proper packaging and documentation.

11.6 SAMPLE PRESERVATIVES AS DANGEROUS GOODS

Check with local legislation in regards to the transport of preservatives as dangerous goods. Of particular interest is the shipment of nitric acid (for use in sampling metals). Similar checks need to be done for other preservatives such as hydrochloric acid, sodium hydroxide, formaldehyde, hexane and chromic acid.

The more stringent requirements of the International Air Transport Association / International Civil Aviation Organization (IATA/ICAO) must be met if the shipment is by air. Airlines may refuse a shipment if it is not properly documented, even if there is an exemption for limited quantities. You may have to phone ahead to make an appointment with an employee trained in transportation of dangerous goods at the airline company, since one may not always be readily available at smaller airports.

11.7 SPECIAL SHIPPING CIRCUMSTANCES (TOXICITY/BIOASSAY SAMPLES)

Toxicity samples may be soil, solids, semi solids and liquid. Do not allow water samples to freeze. Freezing may cause the containers to crack as well as alter the sample integrity. Samplers should also be aware of any applicable legislation related to the transportation of dangerous goods and IATA requirements when shipping preservatives – most are classified as dangerous goods.

11.7.1 TOXICITY SAMPLES SOIL OR SOLIDS

Toxicity samples are to be placed in 25 L (5 gallon) plastic pails with thick gauge polyethylene plastic bags/liners. Once the sample has been taken, the pail liner is to be sealed with tape or a numbered seal which can close the liner to prevent leakage. The pails lids are then closed and sealed with tape. Laboratory analytical instructions and a chain-of-custody sheet should be enclosed in a sealed envelope and securely attached to the pail(s).

11.7.2 TOXICITY SAMPLES LIQUIDS

Liquid bioassay samples, because of their size, can be shipped without special packaging if they are in solid 20 L to 40 L polyethylene containers. The lids to the containers should be sealed with tape and initialled. Laboratory analytical instructions and a chain-of-custody sheet should be enclosed in a sealed envelope and securely attached to the containers.

11.8 STANDARD METHODS OF WATER AND WASTE WATER ANALYSIS

Due to the diverse and complex methods and changes in technology, this manual cannot specify all the methods for analysis of samples.

When shipping samples, the instructions for the type of analysis should be included with the shipping papers so that the receiving laboratory and analyst understands what must be done with the samples. The type of analytical method will be dictated by the scenario and the information required.

Reference methods which have been used extensively in forensic environmental investigations can be found at the following reference sites:

Standard Methods for Water and Waste Water Analysis
http://standardmethods.org/

International Standards Organization (online registry of methods that can be purchased)
http://www.iso.org/iso/home/store/catalogue_tc/catalogue_tc_browse.htm?commid=54346


FROM/DE
REF
Ste;
Environment Canada
TO/A
2645 Dollarton HWY
North Vancouver, BC V7H 1B
(604) 664-4099
NOTE
DATE
09 May 2013
PIECES
2 of/de 2
PIN: 329 883 621 578
Dangerous Goods
Marchandises dang.
Limited Quantity/ Quantité limitée
LIMITED
QUANTITY
S-11796, ULINE, 1-800-295-5510
Ethanol
UN 1986

12 APPENDICES

12.1 GLOSSARY OF TERMS

Analyte: the chemical substance of interest during analysis

Aqueous: dissolved in water

Background (Control) sample: a sample of soil, water, air or other medium that is not believed to be impacted by the deleterious environmental discharge and is believed to represent a "clean sample" Bioassay: (or biological assay) a technique used to determine the toxicity of a sample by exposing test organisms (often fish or invertebrates) to it and measuring its effects on their survival and development.

Blanks: a quality control method for determining background contamination. Travel blanks determine shipping and laboratory sources of contamination. Field blanks determine ambient contamination from sampling and the laboratory. Equipment blanks determine how well the sampling equipment has been decontaminated between sampling. Material blanks test whether the construction materials used in the experiment (i.e. pumps and pipes) can potentially contaminate water samples.

Chain-of-custody: documentation of the collection, transfer, and analysis of a sample required to ensure the integrity of the sample as evidence.

Composite sampling: a technique whereby multiple samples are collected from the same location at different times, and then combined and treated as a single sample.

Conductivity: a measure of the ability of water to transmit an electrical current. It reflects the concentration of inorganic dissolved chemicals.

Control site: a location with similar physical characteristics and climate to the zone of impact that is used to determine what levels of analyte exist naturally prior to contamination.

Data Quality Objectives: the type, quantity, and quality of data needed to reach defensible decisions or make credible estimates.

Detection level/limit: Smallest analyte concentration for which there is a stated probability (usually 95% or 99%) of detection.

Dissolved oxygen: a measure of the amount of gaseous oxygen in water.

Field spike: a field sample to which a known amount of the analyte of interest is added during sampling, used to identify the background effects of conditions in the field, transportation and the sample matrix.

Grab sample: a sample taken at a single time and location.

Holding time: the length of time between when the sample is collected and when the sample is fixed or analysed.

Iso-concentrations: boundaries where the concentration of a contaminant is the same, particularly used when mapping the migration of a contaminant in groundwater or soils.

Isotopes: variants of the same chemical element. While the atoms have the same number of protons in their nuclei, they have a different number of neutrons.

Leachate: water that is mixed with a contaminant where the water has partially or totally dissolved the contaminant from its source. For example, water percolating through a domestic waste landfill will "leach" heavy metals from the landfill and discharge a mixture of water and heavy metals in a mixture called "leachate".

Legal sampling: sampling that has been conducted in such a way that the results of its analysis can be used in a court of law. Procedures must be followed to prove the chain-of-custody of the samples and to prove that they have not been tampered with.

Matrix: the components of a sample other than the analyte, i.e. the substance in which the analyte is contained.

Organic solvents: carbon-based chemical substances that are commonly used as industrial cleaners. Many organic solvents are considered carcinogenic.

Oxidizing agents: a chemical that will remove electrons from surrounding molecules.

pH: a measurement of the concentration of hydrogen ions in a sample, which reflects whether the sample is acidic or basic. A pH of 7 is a neutral, a pH greater than 7 is basic, and a pH less than 7 is acidic.

Phytoforensics: the analysis of the chemical components of plants to determine the past or current presence of a contaminant.

Polychlorinated biphenyls: man-made carbon-based chemicals that have a number of industrial applications (as coolants, lubricants, plasticizers,etc.). Many are considered toxic. They are odorless and clear to yellow in color, and range from oily liquids to waxy solids.

Quality control: the system of guidelines, procedures and practices designed to regulate and control the quality of products and services, ensuring that they meet pre-established performance criteria and standards. Receiving environment sample: a sample of soil, water, air or other medium that is believed to be contaminated by a deleterious environmental discharge.

Sensitivity: the capability of a method or instrument to discriminate between measurement responses of a variable of interest.

Source Sample: a sample of the material that was discharged into the environment. Preferably collected directly from the source before it mixes with the local soil, water or air.

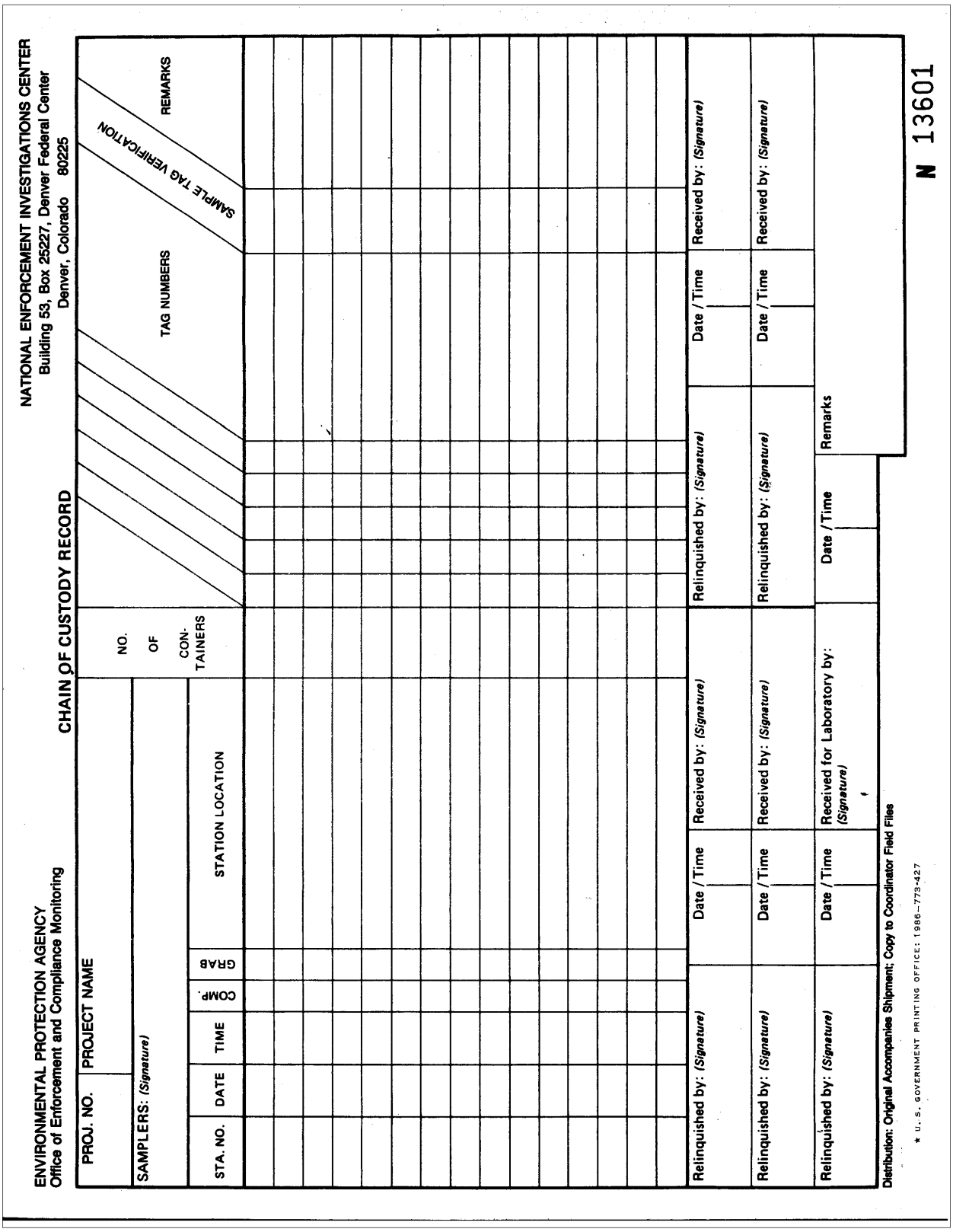
Turbidity: a measure of the clarity of water, which reflects the amount of solid material suspended in the water column.

Volatile organic compounds: carbon-based compounds which evaporate at ambient temperatures and which can affect air quality. Common sources of VOCs include paints, varnishes, cleaning supplies, building materials, and fuels.

Zone of Impact: the physical area affected by a pollution event.

12.2 SAMPLE CHAIN-OF-CUSTODY FORM

12.2.1 COURTESY OF US ENVIRONMENTAL PROTECTION AGENCY



ENVIRONMENTAL PROTECTION AGENCY
Office of Enforcement and Compliance Monitoring

NATIONAL ENFORCEMENT INVESTIGATIONS CENTER
Building 53, Box 25227, Denver Federal Center
Denver, Colorado 80225

CHAIN OF CUSTODY RECORD

PROJ. NO. | PROJECT NAME

SAMPLERS: (Signature)

STA. NO.	DATE	TIME	COMP.	GRAB	STATION LOCATION	NO. OF CON-TAINERS	TAG NUMBERS	SAMPLE TAG VERIFICATION	REMARKS

Relinquished by: (Signature) | Date / Time | Received by: (Signature)
Relinquished by: (Signature) | Date / Time | Received by: (Signature)
Relinquished by: (Signature) | Date / Time | Received for Laboratory by: (Signature)

Relinquished by: (Signature) | Date / Time | Remarks
Relinquished by: (Signature) | Date / Time | Received by: (Signature)
Relinquished by: (Signature) | Date / Time | Received by: (Signature)

Distribution: Original Accompanies Shipment; Copy to Coordinator Field Files

★ U.S. GOVERNMENT PRINTING OFFICE: 1986—773-427

N 13601

12.2.2 COURTESY OF ENVIRONMENT CANADA

ENVIRONMENT CANADA/ENVIRONNEMENT CANADA

Sample Submission and Chain of Custody Sheet / Données sur la provenance et de la continuite-de garde de l'échantillion
Emergencies Operational Analytical Laboratories and Research Support Division
Division d'urgences, laboratoires d'analyses opérationnelles et soutien à la recherche

PAGE ___ OF _____

Initials/Initiale: _____

SAMPLED BY		**DATE SUBMITTED**	Time/Heure __:__
SUBMITTED BY		**Priority**	Urgent ( ) Rush ( ) Regular / Régulier ( )
RESULTS TO			Légal ( )
ADDRESS		REF # / Dossier / NEMISIS #	
		GROUP # (Internal Use)	
TEL:	**FAX:**	**e-mail**	

*PLEASE DO NOT WRITE IN GRAY FIELDS

	NLIMS Sample # (internal use)	Sample ID / No de l'échantillon No information about target of investigation or specific location should be recorded/ Aucune information sur la cible d'une enquête ou d'un emplacement spécifique doit être enregistrée	Security Seal Broken / Sceau de sécurity endommagé: Cooler Glaciere (Y/N)	Bottle Bouteille (Y/N)	Matrix & Size / Matrice et volume W-Water S-Solid	Date Sampled / Date échantillonné	Time Sampled / Temps d'échantillonage	Grab/ Composite ponctuel / composite	Temp Celcius	Description No information about target of investigation or specific location should be recorded/ Aucune information sur la cible d'une enquête ou d'un emplacement spécifique doit être enregistrée	Preserved conservé Y / N	Hazard *
1												
2												
3												
4												
5												
6												
7												
8												
9												
10												
11												
12												

Analysis requested / Type d'analyse requise				

HAZARDS: 0- Nonhazardous 1- Combustible 2- Corrosive 3- Radioactive 4- Cyanide 5 - Toxic 6- Unknown 7- Biohazard

Chain of Custody Record / Registre de continuite-de garde

Relinquished by / Dessaisi par: (name & signature / nom et signature)	Date/Time/Heure:	Received by / reçu par: (name & signature / nom et signature)	Date/Time/Heure:	Remarks/Remarques:
Relinquished by / Dessaisi par: (name & signature / nom et signature)	Date/Time/Heure:	Received by / reçu par: (name & signature / nom et signature)	Date/Time/Heure:	Remarks/Remarques:
Relinquished by / Dessaisi par: (name & signature / nom et signature)	Date/Time/Heure:	Received by / reçu par: (name & signature / nom et signature)	Date/Time/Heure:	Remarks/Remarques:
Relinquished by / Dessaisi par: (name & signature / nom et signature)	Date/Time/Heure:	Received by / reçu par: (name & signature / nom et signature)	Date/Time/Heure:	Remarks/Remarques:
Relinquished by / Dessaisi par: (name & signature / nom et signature)	Date/Time/Heure:	Received by / reçu par: (name & signature / nom et signature)	Date/Time/Heure:	Remarks/Remarques:
Relinquished by / Dessaisi par: (name & signature / nom et signature)	Date/Time/Heure:	Received by / reçu par: (name & signature / nom et signature)	Date/Time/Heure:	Remarks/Remarques:

Revision 2014.01

CONTINUITY REPORT CONTINUED

MOVEMENT OF ITEMS OR SAMPLES

Item # or Sample #				
________	From : ________ sig. : ________ Recip: ________ sig. : ________ @Locn: ________ Date : ________ Time : ________hrs	Transfer →	From : ________ sig. : ________ Recip: ________ sig. : ________ @Locn: ________ Date : ________ Time : ________hrs	Transfer →	From : ________ sig. : ________ Recip: ________ sig. : ________ @Locn: ________ Date : ________ Time : ________hrs
________	From : ________ sig. : ________ Recip: ________ sig. : ________ @Locn: ________ Date : ________ Time : ________hrs	Transfer →	From : ________ sig. : ________ Recip: ________ sig. : ________ @Locn: ________ Date : ________ Time : ________hrs	Transfer →	From : ________ sig. : ________ Recip: ________ sig. : ________ @Locn: ________ Date : ________ Time : ________hrs
________	From : ________ sig. : ________ Recip: ________ sig. : ________ @Locn: ________ Date : ________ Time : ________hrs	Transfer →	From : ________ sig. : ________ Recip: ________ sig. : ________ @Locn: ________ Date : ________ Time : ________hrs	Transfer →	From : ________ sig. : ________ Recip: ________ sig. : ________ @Locn: ________ Date : ________ Time : ________hrs
________	From : ________ sig. : ________ Recip: ________ sig. : ________ @Locn: ________ Date : ________ Time : ________hrs	Transfer →	From : ________ sig. : ________ Recip: ________ sig. : ________ @Locn: ________ Date : ________ Time : ________hrs	Transfer →	From : ________ sig. : ________ Recip: ________ sig. : ________ @Locn: ________ Date : ________ Time : ________hrs
________	From : ________ sig. : ________ Recip: ________ sig. : ________ @Locn: ________ Date : ________ Time : ________hrs	Transfer →	From : ________ sig. : ________ Recip: ________ sig. : ________ @Locn: ________ Date : ________ Time : ________hrs	Transfer →	From : ________ sig. : ________ Recip: ________ sig. : ________ @Locn: ________ Date : ________ Time : ________hrs
________	From : ________ sig. : ________ Recip: ________ sig. : ________ @Locn: ________ Date : ________ Time : ________hrs	Transfer →	From : ________ sig. : ________ Recip: ________ sig. : ________ @Locn: ________ Date : ________ Time : ________hrs	Transfer →	From : ________ sig. : ________ Recip: ________ sig. : ________ @Locn: ________ Date : ________ Time : ________hrs

The Item(s) was / were returned sealed.	❑ All	❑ Some (#________)	❑ None
The Item(s) was / were returned permanently scribed.	❑ All	❑ Some (#________)	❑ None
The Item(s) was / were returned permanently initialled.	❑ All	❑ Some (#________)	❑ None
The Item(s) was / were returned permanently dated.	❑ All	❑ Some (#________)	❑ None

The Item(s) #(s): ____________ was / were destroyed upon instruction from: ____________________

____________________ Date: __________ By: ____________________ Initials: __________

Form: Leg_ContinuityRpt_v00a

Page ___ of ___

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12.4 ACKNOWLEDGEMENTS

COUNTRY	AGENCY
Algeria	Police Scientifique et Technique
Argentina	Policia Federal Argentina
Australia	Australian Maritime Safety Authority
Australia	Department of Environment, Water, Heritage and the Arts
Austria	Federal Ministry of the Interior
Belgium	Federal Judicial Police
Belgium	Parquet General Brussels
Benin	Service de l'Identité Judiciaire
Botswana	Directorate of Public Prosecutions
Botswana	Waste Management & Pollution Control
Brazil	Federal Police
Brazil	Instituto Geral de Perícias, Depto. de Criminalística
Canada	Environment Canada
Canada	Royal Canadian Mounted Police
Canada	Department of Justice
Chile	Policia de Investigaciones de Chile
Comoros	BP 10
Croatia	Ministry of Environmental Protection
Finland	National Bureau of Investigation, Forensic Laboratory
France	Central Environmental & Public Health Crime Department
France	IRCGN - Forensic Laboratory of the Gendarmerie Nationale
France	Laboratoire Central de la Préfecture de Police

Germany	Bundeskriminalamt
Germany	LKA Berlin (Crime Investigation Department)
IGO	World Bank
India	Central Bureau of Investigation
Indonesia	Indonesia National Police - Makassar Branch
Israel	Israel Police Headquarters
Israel	Ministry of Environment
Italy	Carabinieri Environment Protection
Italy	INTERPOL NCB Rome
Italy	Corpo Forestale dello Stato
Italy	Servizio per la Cooperazione Internazionale di Polizia
Japan	National Research Institute of Police Science
Jordan	Ministry of Environment
Jordan	Public Security Directorate
Kenya	National Environment Management Authority
Korea (Rep of)	National Institute of Scientific Investigation
Kuwait	Criminal Evidences General Department
Liberia	Environmental Protection Agency
Mauritania	Consoler du Direction Générale de la Sûreté Nationale
Mexico	Dirección General de Asuntos Policiales Internacionales e INTERPOL
Mexico	Procuraduría Federal de Protección al Ambiente
Nigeria	Forensic Unit, Nigeria Police
Nigeria	National Environmental Standards and Regulations Enforcement Agency (NESREA)
Norway	National Authority for Investigation and Prosecution of Economic and Environmental Crime in Norway

Portugal	Criminal Police
Qatar	Ministry of Interior
Rwanda	Kigali Forensic Laboratory
South Africa	South African Police Service
Sweden	National Laboratory of Forensic Science
Sweden	National Police Board
Thailand	Hazardous Waste Management Division, Pollution Control Department
Thailand	Royal Thai Police
The Netherlands	Ministry of Infrastructure and the Environment
The Netherlands	National institute for Public Health and the Environment
The Netherlands	National Police Agency of The Netherlands (NPN)
The Netherlands	National Public Prosecutor's Office
The Netherlands	Netherlands Forensic Institute
The Netherlands	Seaport Police Rotterdam
The Netherlands	VROM Inspectorate
Togo	General Direction of Customs
Turkey	Ministry of Environment and Forestry, Department of Environmental Inspection
United Arab Emirates	RAS Alkhana Police
United Arab Emirates	Sharjah Police
United Kingdom	North Wales Police
United Kingdom	Rural Payments and Inspections Directorate of the Scottish Government
United States of America	Coast Guard
United States of America	Environmental Protection Agency
United States of America	Fish and Wildlife Service
United States of America	National Oceanic and Atmospheric Administration

Vietnam	INTERPOL Vietnam
Zimbabwe	Environmental Management Agency

ACADEMIC AND NON-GOVERNMENTAL ORGANIZATIONS

Rudjer Boskovic Institute, Croatia

TRACE the Wildlife Forensics Network - Royal Zoological Society of Scotland

Universita degli Studi di Trieste, Italy

University of Oklahoma, USA

CORPORATE

André Godoi Environmental Intelligence, Brazil

DPRA

Environment International

Exponent®, Inc

Genesis Environmental Sciences Ltd., Canada

HPC Envirotec

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