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5 Measurement of Supporting Environmental Variables

5.1 Overview

A number of key environmental variables will be measured to aid in the interpretation of both the benthic and fish survey data. There are also site-specific variables that may be measured where applicable. When a specific concern is identified (e.g. eutrophication), selection of appropriate site-specific variables should consider the concentration of the variable in the effluent and known/predicted dilution factors. Cost savings can be realized by analyzing samples likely to have the highest concentrations first and stopping when a pattern of undetectable samples emerge.

According to the *Regulations Amending the Pulp and Paper Effluent Regulations*, pulp and paper mills are required to conduct water quality monitoring when fish population and benthic invertebrate community surveys are conducted and to collect and analyze sediment samples from sampling areas during the benthic invertebrate community survey.

This chapter provides guidance for the EEM requirements and recommendations for water (Section 5.2) and sediment quality monitoring (Section 5.3) and the use of chemical tracers (Section 5.5). Magnitude and geographic extent and investigation of cause are briefly discussed in this chapter. However, for mills moving to magnitude and geographic extent and investigation of cause additional information can be found in Chapter 12.

The required and site-specific variables for water quality monitoring and sediment monitoring are listed in Tables 5-1 and 5-4, respectively.

5.2 Water Quality Monitoring

5.2.1 Overview

According to the *Regulations Amending the Pulp and Paper Effluent Regulations* water quality monitoring will be conducted when fish population and benthic invertebrate community surveys are conducted. Water quality monitoring is conducted by collecting and analyzing samples of water to compare the water quality in the exposure area and the reference area or exposure areas with gradually decreasing effluent concentrations. The parameters, which will be analyzed for water quality monitoring, are listed below:

- water temperature;
- depth;
- concentration of dissolved oxygen;
- pH levels (freshwater);
- electrical conductivity (freshwater);
- hardness (freshwater);

- total phosphorus (freshwater);
- total nitrogen (freshwater);
- total organic carbon (freshwater); and
- salinity (marine and estuary)

Water samples will be collected at all biological monitoring sampling areas. A representative sample can be collected from various stations to get an estimation of the variability and determine if concentrations of the contaminants are homogenous within the sampling area. However, this may not be sufficiently robust to assess data statistically. More sampling stations within each area may help to better understand contaminant concentrations in the exposure area.

In addition to these required parameters, it is also recommended that the following variables be examined (see Table 5-1 for other site specific variables):

1) Soluble Reactive Phosphorus (SRP); and/or
   Total Dissolved Phosphorus (TDP); and
2) Nitrite-Nitrate NO2-NO3 and Ammonia NH4 and/or
   Total Kjeldahl Nitrogen (TKN); and
3) Total Dissolved Organic Carbon (DOC).

The above recommended parameters will help provide a complete picture of the nutrient relationships at a given site. Soluble reactive phosphorus has also been referred to as dissolved inorganic phosphorus and orthophosphate (Wetzel 2002).

A summary of the analytical methods for the required and recommended water quality parameters can be found in Table 5-3.

Table 5-1: Supporting environmental variables in water for freshwater (F) and marine (M) habitats.

Required Variables*	Site-specific Variables	Habitat (F,M)	Justification
Dissolved Oxygen		F, M	Dissolved oxygen can be decreased by mill effluents due to BOD.
Water Temperature		F, M	Mill effluents may cause increases in water temperature in receiving waters.
Salinity		M	Changes in estuarine conditions may affect benthic communities.
PH levels, electrical conductivity, hardness	Alkalinity	F,	Provides information for water quality.
Total Nitrogen	Nitrate-nitrite, ammonia, and total kjeldahl nitrogen (TKN)	F	Nitrogen is often a secondary limiting nutrient in freshwater.
	Sodium	F	Sodium may be a good tracer in freshwater.
Total organic carbon	Total dissolved organic carbon, particulate carbon	F	Carbon is a nutrient source for microbes. Mills discharge quantities of these carbon sources.
Depth		F,M	Water depth has a major effect on invertebrate communities.
	Colour or Turbidity; optical depth or transparency	F, M	Mills may discharge effluents, which are coloured. This may reduce the light available for primary production.
Total phosphorus	Soluble reactive or total dissolved phosphorus	F	Phosphorus is often the limiting nutrient in freshwater. Mills may discharge P which could lead to nutrient enrichment.
Latitude, longitude		F,M	Provides station location information
	Algal biomass as chlorophyll or ash-free dry mass		Algae in the water column (lakes) or on benthic substrates provides a food source for higher trophic levels.
	Current velocity		Can provide information on equivalence of sampling stations.
	Bankfull channel width		Provides habitat structure information

* Required under the *Regulations Amending the Pulp and Paper Effluent Regulations.*

5.2.2 Collection of Water Samples

This section provides guidance on the preparation, collection, handling, storage, transportation of water samples, field measurements and observations.

5.2.2.1 Preparation for the field

The reagents for cleaning, operating or calibrating equipment, collecting, preserving and/or processing samples should be handled by appropriately qualified personnel and the appropriate data for health and safety (e.g., Material Safety Data Sheets) should be available.

Written protocols and standard operating procedures (including QA/QC requirements) should be readily accessible at all times, to ensure proper and safe operation of equipment. Data forms and log books should be prepared in advance so that field notes and data can be quickly and efficiently recorded. Extra forms should be available in the event of a mishap or loss. These forms and books should be waterproof and tear resistant. Under certain circumstances, audio or audio/video recordings may prove valuable.

All equipment used to collect and handle samples should be cleaned and all parts examined to ensure proper functioning (e.g., on-site assembly or operation) prior to going into the field. A repair kit should accompany each major piece of equipment in case of equipment failure or loss of removable parts. Back-up equipment, batteries, and sampling gear should be available. Sampling equipment used for field measurements of water quality parameters should be properly calibrated or standardized according to the manufacturer's recommendations.

All sample containers and required preservatives should be provided by the laboratory hired to conduct the analyses of samples. Bottles should preferable be, unused and purchased as certified clean. If bottles are reused, they should be cleaned by a documented cleaning procedure with a bottle lot number control system, and cleanliness demonstrated by the use of blanks.

Storage, transport, and sample containers, including extra containers in the event of loss or breakage, should be pre-cleaned and labelled appropriately (i.e., with a water-proof adhesive label to which the appropriate data can be added, with an indelible ink pen capable of writing on wet surfaces). The containers should have lids that are fastened securely and the appropriate container lids and lid liners should be used to prevent contamination (e.g., lid liners should be lined with an inert material like Teflon®, not paper or cardboard). A sample-inventory log and a sample-tracking log should be prepared in advance of sampling. The responsibility for these logs should be assigned to one individual who will be required to monitor the samples from the time they are collected until they are analysed and disposed of, or archived.

5.2.2.2 Field Measurement of Water Quality Parameters

Standard *in situ* water quality parameters are dissolved oxygen, pH, conductivity, water temperature, and salinity. Total water depth at the water sampling area and water depth from which the water sample was collected will be recorded. Optical depth or transparency should also be measured in the field. Measurements of standard water quality parameters can be taken in the water directly, from a sample container in the boat, or on shore immediately after collection of the water, as long as the water is collected at the appropriate depth. If dissolved oxygen measurements are sampled on the shore special care should be taken to ensure that air is not introduced into the sample.

In shallow water bodies ≤ 2m deep, standard water quality parameters need only be measured at mid-depth. If the depth ranges from 2 to 4 m, standard water quality measurements should be taken at two depth intervals, approximately 25 cm above the bottom and 25 cm below the surface. In deeper bodies of water, measurement of standard water quality parameters should be taken throughout the water column.

For deep samples, a peristaltic sampler, with appropriate lengths of Teflon® tubing, should be used in preference to other types of pumps. If other types are used, they should be teflon-coated and non-metallic. Sampling should proceed from the least contaminated to the most contaminated station with two thorough rinses of pesticide-grade acetone or methanol and distilled water between stations (Environment Canada 1995). The solvent rinsate should be collected and returned to the laboratory for proper disposal. Laboratory blanks of the samplers should be run before and after use to demonstrate that no contamination is imparted to samples.

Profiles can be facilitated through the use of a data logger (or equivalent) equipped with a dissolved oxygen probe and associated stirrer, as well as pH, conductivity, depth and temperature probes, which evaluate water column quality simultaneously. Such a unit is particularly useful for deeper evaluations (> 50 m). During profiling, the operator is able to visually review incoming data, noting particular areas of interest during descent and ascent of the unit (e.g., conductivity spikes, thermoclines, unusual data records, etc.). This information is recorded either manually or directly stored in the data logger. To supplement computer records, parameter readings should be stored manually onto field data sheets (every 2 or 5 m) depending on total depth profiled.

At shallow depths, hand held meters are often the most convenient way to measure *in situ* water quality parameters. They are light and several models are now available that can measure standard water quality parameters. The probes, and the cables connecting them to the hand held unit, can range from 2 to 5 m, limiting the use of such a unit. These meters tend to require more regular maintenance and calibration, therefore extra care should be taken to make sure that the meters are in proper functioning order, and calibration and maintenance logs should be kept on file.

Water depth can be measured indirectly using a sonar based fish finder, or directly using a calibrated tape, sounding cable, or rod. Recommended accuracy is as follows:

Water depth less than 2m: recommended accuracy of ± 25 cm
Water depth of 2 to 10 m: recommended accuracy of ± 50 cm
Water depth greater than 10m: recommended accuracy of ± 1 m

Optical depth is a measure of the transparency of water, and can be measured with a turbidity meter, in the field or in the laboratory. Optical depth can also be measured using a Secchi disk. The disk is 20 cm in diameter, and is painted white in two opposite quarters, and black in the other two. The disk is attached to a calibrated tape. To measure optical depth, the disk is lowered into the water in the shade until it has disappeared. It is then raised slowly, and the water depth at which it reappears is recorded. At least two measurements should be made at each station, and optical depth estimated based on the median value of the measurements. Measurements should be made at midday, and sunglasses should not be worn while measurements are made (Nielsen and Johnson 1983).

Water quality data should be screened on site during sample collection to ensure against the measurement and recording of false readings. This will permit the use of alternative instrumentation or instrument checks in the event of equipment or sampling error. All sampling and monitoring equipment should be checked and calibrated daily, if necessary, to ensure good working condition.

Additional field measurements and observations recommended to be recorded include:

- sample number, replicate number, site identification (e.g., name);
- time and date of the collection of the sample;
- ambient weather conditions, including wind speed and direction, wave action, current, tide, vessel traffic, temperature of both the air and water, thickness of ice if present;
- sampling area location (e.g., positioning information) and location of any replicate samples;
- type of platform/vessel used for sampling (e.g., size, power, type of engine);
- name of personnel collecting the samples;
- details pertaining to unusual events which might have occurred during the operation of the sampler (e.g., possible sample contamination, equipment failure, unusual appearance , control of vertical descent of the sampler, etc.); and
- deviations from SOPs.

5.2.2.3 Collection of Water Samples for Laboratory Analyses

Water samples collected in the field and sent to a laboratory for analysis make up the bulk of the water quality monitoring.

In general, samples should be collected at two depth intervals: the subsurface (epilimnion) and near bottom (hypolimnion) in order to obtain samples from both areas of the water column (above and below the thermocline). If the water depth is ≤ 2 m it is sufficient to collect water samples only at mid-depth or at least 15 cm below the surface. Samples collected below the surface of the water can be collected by hand directly into the sample

bottle.

Water collections at discrete depths should be facilitated through the use of appropriate samples (e.g Niskin sampler, non-metallic 2-16 L Van Dorn or 0.5-8L Kemmerer samplers). For streams, depth integrated samplers which are representative of the suspended sediment and related substances can be used. These samplers can be used from a boat, bridge, or ice surface, and usually require two persons for safe operation. For very deep samples, a peristaltic sampler is preferred to other types. If other samplers are used they should be Teflon-coated.

The water sampler should be triple rinsed with the water from the sampling station between each sample. In addition, it is recommended that sampling in the reference area be completed first to avoid any potential contamination of the sampler with water from exposure area. The sampler should be double rinsed with pesticide-grade acetone or methanol between sampling areas, particularly if it is not possible to complete sampling in the reference area first.

When collecting water samples, it is important to use as many of the following ultra trace techniques and proper water sampling protocols as possible:

- Sampling should proceed from the least contaminated to the most contaminated station;
- Sample bottles and caps should be rinsed three times prior to water collection;
- No preservatives should be placed into the sampling bottles prior to sample collection;
- Samples should be collected with the bottle mouth facing up-current away from the sampler's hand;
- At no time should the inside of the sample container, the bottle mouth, or the inside of the container lid be touched by sample collectors, even while wearing disposable gloves;
- Sample collectors should wear unlined latex or nitryl gloves to avoid contamination of the sample;
- Label all samples immediately and clearly and follow proper preservation techniques. Record all sampling data in the field notebook immediately;
- Caps of water containers should be held lid-down during sample collection; and
- The sampling point locations be recorded.

5.2.2.4 Sample Storage and Shipping

Table 7-2 summarizes recommended sample handling procedures and containers for the different analytical variables that may be included in the EEM monitoring program, e.g. bottle types for each variable or group of variables. These materials are considered as the best materials for the specific variable groups. Where appropriate, preservatives should be added to the sample bottle immediately on completion of the collection. The actual sample volumes required may vary depending on the needs of the laboratory.

It is recommended that samples be cooled to 4ºC during collection and stored at the same temperature for shipping to minimize degradation. Samplers should also be refrigerated, and shipping coolers equipped with ice packs or bagged ice to ensure that samples are kept cold. Speed in shipping (within 24 - 48 hours maximum) by pre-arranged transport is

recommended.

Samples should be transported to a laboratory as soon as possible after collection. Analyses should be completed within the accepted storage times, which will vary depending on the variable (Table 5-2). Storage time is defined as the time interval between the end of the sample collection period and the initiation of analyses. All samples should be stored for as short a time interval as possible and under conditions that minimize sample degradation. Samples should be maintained at temperatures above their freezing point and under 10°C, with minimal exposure to light.

Table 5-2: Handling recommendations for receiving water samples.

Analysis	Container	Volume[1]	Preservative	Maximum Storage
TOC[4]	HDLPE[2]	100 mL	H_2SO_4 to pH 2	10 days
DOC	HDLPE	100 mL	Filter, then H_2SO_4 to pH 2	10 days
Chlorinated Phenols, Guaiacols, Catechols	Amber Glass	1 L	4°C Filter, then H_2SO_4 to pH 2 for chlorinated phenols only	7 days to extraction
Resin and Fatty Acids (chlorinated and nonchlorinated)	Amber Glass	1 L	4°C or 0.5 g ascorbic acid plus 2 pellets NaOH	7 days or 14 days
Dioxins	Amber Glass	4 L	4°C	30 days
pH	HDLPE	1 L	4°C	Immediately
TSS, BOD_5[4]	HDLPE	1 L	4°C	4 days
Nutrients (Total P, NO_2+NO_3 NH_3-N, TKN)	Glass	250 mL	H_2SO_4 to pH 2; 4°C for total P only	10 days
Chlorate	HDLPE	100 mL	4°C	28 days
Sublethal toxicity	Non-toxic Material[3]	2 L	Exclude air	3 days
Soluable Reactive Phosphorus EPA 365.1	Glass	50 ml	H_2SO_4 to pH < 2 and cooled to 4°C at the time of collection.	28 days
Total Dissolved Phosphorus EPA 365.1	Glass	50 ml	H_2SO_4 to pH < 2 and cooled to 4°C at the time of collection.	28 days
Colour (APHA 1995)	Glass	50 mL samples	Pre-treatment for turbidity removal	Reasonable period; storage may affect colour.
Turbidity EPA 180.1; APHA 1992, 1995	Clear, colourless glass or plastic	A representative sample	No chemical preservation is required. Cool sample to 4°C.	48 hours

Hardness		1 L	None (better if measure on site)	28 days
Conductivity		1 L	None	6 months
Alkalinity (APHA 1995)	Polyethylene or borosilicate glass bottles	50 mL	Not required	1 day; if biological activity is suspected, within 6 h

Additional Reference: U.S. Environmental Protection Agency. 1993. Methods for Determination of Inorganic Substances in Environmental Samples, EPA –600/R/93/100. Environmental Monitoring Systems Lab., Cincinnati, Ohio.

[1] Suggested sample size

[2] High Density Linear Polyethylene

[3] Polyethylene or polypropylene is recommended.

[4] Sample containers should be filled to exclude air (no headspace) to prevent degradation of the sample during storage and transport.

Refer to NLET 1994a,b;1996

Table 5-3: Summary of analytical method principles for receiving waters.

Parameter	Sample Preparation	Instrumental Method	Matrix Detection Limits Water	Precision[1]	Accuracy[2]	References
Chlorate	Filter or centrifuge sample to remove solids which may plug ion chromatograph.	Ion chromatography using Dionex AS9 column or equivalent.	20 $\mu g \cdot L^{-1}$	± 10%	80-120%	U.S. EPA (1991)
Chlorinated Dioxins and Furans	Spike samples with isotopically labelled PCDD/F surrogates; extract with solvent and concentrate; clean-up as required including back extraction with acid/base, gel permeation, alumina, silica gel, activated carbon; concentrate to known micro-volume and add isotopically labelled performance standards immediately prior to instrumental analysis.	High resolution gas chromatograph coupled to high resolution mass spectrometer with computerized data system (HRGC/HRMS/DS); minimum two characteristic ions per congener group; 5-point calibration over linear range of MS	2-4 $pg \cdot L^{-1}$ 4-8 $pg \cdot L^{-1}$ 4-8 $pg \cdot L^{-1}$ 6-12 $pg \cdot L^{-1}$ 8-16 $pg \cdot L^{-1}$	±20%	Native Compound Spike 80-120% Surrogates 40-130%[3]	Environment Canada (1992b) U.S EPA (1990a)
Chlorophenols, Chloroguaiacols, Chlorocatechols	Spike samples with appropriate surrogates; in-situ acetylation followed by solvent extraction OR acidification to pH 2, solvent extraction/ concentration, extract acetylation or methylation; addition of internal standard immediately prior to instrumental analysis.	HRGC/LRMS/DS in Selected Ion Monitoring (SIM) mode using a minimum of two ions (1 quantitation, 1 confirmation) in correct abundance ratio within established retention time windows.	0.02-0.05 $\mu g \cdot L^{-1}$	± 20 %	70-110%[3] (Phenols and Guaiacols) 40-90%[3] (Catechols)	NCASI (1986) Carron and Afghan (1989) Lee *et al.* (1989) U.S. EPA (1991) Alberta Environment (1991) Morales *et al*. (1992)
Nutrients-Ammonia	For manual determination, effluent samples and some waters will require distillation.	Manual measurement of indophenol blue at 630 nm OR Automated distillation, reagent addition and colour measurement at 630 nm on segmented flow analyzer.	0.005 $mg \cdot L^{-1}$	± 10%	95-105%	NLET (1994a) APHA (1989, 1992 1995)
Nutrients - Nitrate Plus Nitrite	None	Manual or automated reduction cadmium, addition of reagents to form azo dye, measurement of colour at 520 nm.	0.01 $mg \cdot L^{-1}$	± 20% at 0.5 $mg \times L^{-1}$	95-105%	NLET (1994a)) APHA (1989, 1992 1995)
Nutrients - Total Kjeldhal Nitrogen	For manual determination, digestion with sulphuric acid/potassium sulphate/ mercuric oxide solution required prior to distillation and instrumental determination of ammonia.	Manual measurement of indophenol blue at 630 nm OR Automated digestion, distillation, reagent addition, and colour measurement at 630 nm by segmented flow analyzer.	0.02 $mg \cdot L^{-1}$	± 10%	95-105%	APHA (1989, 1992, 1995)

1. Acceptable performance for duplicates based on 1 standard deviation derived from historical data.
2. Acceptable performance for recovery of reference material or spikes, based on 1 standard deviation derived from historical data.
3. Control limit (± 3 SD) based on recovery of surrogate compound spikes.

Table 5-3: Summary of analytical method principles for receiving waters (continued).

Parameter	Sample Preparation	Instrumental Method	Matrix Detection Limits Water	Precision[1]	Accuracy[2]	References
Nutrients - Total P	For manual determination, digestion by sulphuric acid/potassium persulphate OR sulphuric acid/potassium sulphate/ mercuric oxide if TKN being analyzed at same time.	Manual measurement of molybdate blue complex at 880 nm OR Automated digestion, reagent addition, and colour measurement at 380 nm by segmented flow analyzer.	[1] 0.002 mg•L^{-1}	± 10%	95-105%	NLET (1994a) APHA (1989, 1995)
Soluble Reactive Phosphorus	Sample is passed through a 0.45 micron pore size filter; Persulphate digestion in an autoclave.APHA 4500-P B	Automated colourimetery with ascorbic acid reduction at 880 nm.		± 10%		APHA 4500-P E
Total Dissolved Phosphorus	Samples is passed through a 0.45 micron pore size filter.APHA 4500-P B	Automated colourimetery with ascorbic acid reduction at 880 nm. Seimi-Automated Colorimetry, measured by the direct colorimetric analysis procedure		± 10%		APHA 4500-P E
pH	None	Electrometric	NA	± 0.05	± 0.1	NLET (1994a) APHA (1995)
Resin and Fatty Acids	Spike all samples with o-methyl podocarpic acid surrogate; adjust pH to 9 and extract with methyl t-butyl ether and concentrate; derivatize by methylation with diazomethane using tricosanoic acid addition as recovery check.	HRGC/LRMS in SIM Mode using minimum of two characteristic ions per compound in correct abundance ratios within established retention time windows.	0.2-0.5 µg•L^{-1}	± 20%	60-120%[3]	Alberta Environment (1990, 1991) Voss and Rapsomatiotis (1985) NCASI (1986) OMOE (1989)
BOD_5	Treat to remove interferences from residual chlorine, sulphide and adjust pH to 6.5-8.3; dilute samples to provide minimum D.O. depletion of 2.0 mg•L^{-1} and minimum D.O. concentration of 1.0 mg•L^{-1}; for pulp and paper mill samples use acclimatized seed.	Measure dissolved oxygen by stirring BOD probe calibrated against Winkler, or use Winkler.	2 mg•L^{-1}	± 15% (Inter-laboratory)	80-120%	NLET (1994a) APHA (1989)
Total Organic Carbon (TOC)	Acidify to pH 2 and purge with nitrogen to remove inorganic carbon.	High temperature combustion with infrared detection of CO_2 OR Ultraviolet/persulphate digestion with colourimetric or infrared detection of CO_2.	1.0 mg•L^{-1}	± 5	95-105%	NLET (1994a) APHA (1989, 1992, 1995)
Total Suspended Solids (TSS)	**Effluents and Fresh Waters:** Filter sample through washed, dried pre-weighed Whatman GFC glass fibre filter, and dry filter and solids at 105ºC to constant weight	Determine weight change in filter gravimetrically.	2 mg•L^{-1}	± 10%	90-110%	APHA (1989) NLET (1994a)
	Marine Receiving Waters: Filter through pre-weighed Nuclepore 0.4 mm membrane filter, wash thoroughly with distilled water, dry at 80°C and re-weigh		50 µg•L^{-1}	±20%	NA	Sundby (1974)
Algal Biomass		Chlorophyll or ash-free dry mass				APHA (1995)
Alkalinity						APHA (1995)
Colour		platinum-cobalt method				APHA (1992, 1995)

Conductivity		Hydrolab, YSI (600-series) or CTD multi-probes	
Current Velocity		Global Flow Probe current meter	
Hardness			APHA (1995)
Dissolved Oxygen		Hydrolab, YSI (600-series) or CTD multi-probes. May need to use Winkler titration method for QA comparison to meters	
Salinity		In situ YSI meter (600-series) or salinity meter which indirectly utilizes conductivity and temperature	APHA (1992)
Dissolved Sodium		Flame atomic emission spectrophotometry	APHA (1992, 1995)
Temperature		Hydrolab, YSI (600-series) or CTD multi-probes.	
Chlorophyll a	Phytoplankton: Samples are concentrated and extracted with an acetone-water mixture (9:1 v/v), and stored at –4.0 degrees centrigrade for at least 2 hours, then centrifuged. The concentration of chlorophyll a is calculated from the optical densities of the supernatant, measured on a spectrophotometer or, for greater sensitivity of low chlorophyll a samples, on a fluorometer Periphyton: Samples are concentrated and extracted with an acetone-water mixture (9:1 v/v), and stored at –4.0 degrees centrigrade for at least 2 hou then centrifuged. The concentration c chlorophyll a is calculated from the optical densities of the supernatent measured on a fluorometer (APHA 10300-B		APHA 10200-H (Phytoplankton) APHA 10300-C-6 (Periphyton)
Turbidity		turbidimeter	APHA (1992, 1995)

5.2.3 Laboratory Analyses of Samples

Laboratory analyses should be carried out in a qualified laboratory by trained personnel operating under quality controlled conditions and using documented standard operating procedures (SOPs). It is recommended that laboratories being used to generate data for the pulp and paper EEM program are accredited by the Standard Council of Canada through the Canadian Association for Environmental Analytical Laboratories (CAEAL) or the Ministère de l'Environnement (MENV) du Québec. These accreditation organizations follow "International Standards Organization" (ISO) standards, which focus on the quality system and practices of a laboratory.

5.3 Sediment Monitoring

5.3.1 Overview

According to the *Regulations Amending the Pulp and Paper Effluent Regulations*, as part of

each benthic invertebrate community survey completed for biological monitoring studies, mills are required to collect and analyze sediment samples. The overall purpose of sediment monitoring is to answer the question: “Are there habitat differences that may contribute to effects in the benthic invertebrate community”?

The sediment samples will be analyzed for:

- particle size distribution;
- total organic carbon;
- the ratio of carbon to nitrogen (marine and estuarine water);
- redox potential (Eh) (marine and estuarine waters); and
- total sulphides (marine and estuarine waters).

Justification and analytical methods for the required and recommended sediment variables are listed in Tables 5-4 and 5-5, respectively.

Sediment samples will be collected at the same sampling area and at the same time as benthic invertebrate samples. A representative sample can be collected from various stations to get an estimation of the variability and determine if concentrations of the contaminants are homogenous within the sampling area. However, this may not be sufficiently robust to assess data statistically. More sampling stations within each area may help to better understand contaminant concentrations in the exposure area. Each study design for benthic invertebrate community surveys will identify the sediment sample collection and laboratory analysis methods to be used (field and laboratory methodologies selected). The results of these analyses will be included in the interpretative report. The results of analyses of particle size distribution and total organic carbon will be used to determine if there are habitat differences between the exposure and reference areas, to aid in the interpretation of the results of benthic invertebrate community surveys.

For monitoring programs where the sampling of benthic invertebrates is conducted in erosional habitat, sediment sampling may not be possible as a standard supporting environmental variable, therefore in these cases the sediment monitoring data would not be reported. Some methods for retrieving sediments from erosional zones require elaborate equipment or two field visits, one for the placement and one for the collection of sediment traps. However, site specific conditions may warrant the consideration of sediment sampling in some erosional habitats as useful information regarding exposure can be obtained with these methods. These approaches could be considered during the study design exercises for magnitude and geographic extent or investigation of cause as an additional supporting variable or tool for determining effects.

Table 5-4: Supporting environmental variables in sediment for freshwater (F) and marine (M) habitats.

Required Variables*	Site Specific	Habitat (F,M)	Justification
Sediment ratio of carbon to nitrogen		M	Ratio of carbon to nitrogen is affected by terrestrial (wood) versus aquatic plant sources of marine deposition
	Total Nitrogen Total Phosphorus	F	Mill effluents may elevate nutrient concentrations
Sediment Total organic carbon or Loss on ignition		F	Effects may be related to inputs from organic material.
Particle size analysis:	Matrix: framework ratio, degree of embeddedness, texture, colour and thickness of layers in cores	F, M	Differences in physical structure of the habitat can influence invertebrate community structure.
Sediment Eh (redox)*		M	Sediment redox provides an indication of the anoxic/oxic boundary in sediments.
Sediment total sulfides*		M	Sulfides in marine sediments indicate the extent and nature of microbial response to organic enrichment.

*Required under the *Regulations Amending the Pulp and Paper Effluent Regulations*.

Table 5-5: Summary of analytical method principles for sediment.

Parameter	Sample Preparation	Instrumental Method	Matrix Detection Limits	Precision (% rel std dev)	Accuracy (% recovery)	Reference Methods
Chlorinated Dioxins and Furans	Air dry, weigh and spike with isotopically labelled surrogate standards. Extract prepared sample, concentrate and clean-up per effluent method.	HRGC/HRMS/DS per Effluent Method	TCDD/F 1pg•g^{-1} P5CDD/F 5pg•g^{-1} H6CDD/F 5pg•g^{-1} H7CDD/F 5pg•g^{-1} 0.1-0.5 mg•g^{-1} Depending on Isomer OCDD/F 10 pg•g^{-1}	± 20%	40-120%	U.S. EPA (1990a) U.S. EPA (1990b) Environment Canada (1992a) See Table 5-4 Chlorophenol method
Chlorophenol, Chloroguaiacol, Chlorocatechol Isomers	Weigh out wet sediment and spike with surrogate; extract and concentrate; derivatize with large excess of acetic anhydride.	HRGC/LRMS per Effluent Method.	10-50 ng•g^{-1} depending on isomer	± 20%	70-110% 50-90%	Birkholz *et al.* (1988) Hynning *et al*. (1989) Lee *et al.* (1989)
Chlorinated Resin and Fatty Acids	Extraction as per Chlorophenols; no clean-up; derivatize as per Resin and Fatty acids in Effluents.	HRGC/LRMS per Effluent Method	0.1 µg•g^{-1}	± 20%	70-120%	See Table 5-4 Morales *et al.* (1992)
Particle Size	Freshwater: Dry and sieve standard series. Marine: Wash through 63 mm sieve; <63 mm fraction recovered for weighing; >63 mm fraction dried and sieved in standard series.	Determine percent of each sieve fraction gravimetrically. OR laser particle size method using Malvern 2600L laser particle size analyzer.	±0.1%	NA	NA	Walton (1978) Tetra Tech (1986)
Total Sulphide	5 ml of sediment is squeezed into airtight container with 5ml of sulphide antioxidant buffer (SAOB) solution.	MV readings are made within 3 hours, using silver sulphide and double junction reference electrodes				Tetra Tech (1986); Wildish et al. (1999); Hargrave et al. (1995); Bugden et al. (2001).
Volatile Residue (SVR) or Loss on Ignition (LOI)	Sample is oven-dried	Gravimetric analysis after ignition in muffle furnace at 550°C				APHA (1992) Tetra Tech (1986)

Table 5-5: Summary of analytical method principles for sediment (continued).

Parameter	Sample Preparation	Instrumental Method	Matrix Detection Limits	Precision (% rel std dev)	Accuracy (% recovery)	Reference Methods
C:N (organic C to total N)		Measure TOC as per below, measure total N as per total C				Calvert *et al*. (1995) MacDonald *et al.* (1991)
Eh	Measured with sediment still in core tube.	Calibrated probe is pushed into sediment.				Hargrave *et al.* (1995); Wildish *et al* 1999; *Bugden et al* 2001
Total Organic Carbon	Sample is dried, ground to pass #80 sieve; treat with sulphurous acid to remove inorganic carbon and dry;	(e.g. Perkin-Elmer CHN analyzer) OR Determine COD and divide result by 2.6. OR use USEPA (1986) Method 9060A - total carbon analyzed using Leco induction furnace, carbonate carbon analyzed using a Leco gasometer. TOC reported as difference between total C and carbonate C	NA	NA	NA	American Soils Association (1982) Hargrave *et al.* 1997 U.S. EPA (1986)
Total Organic Nitrogen	Weigh sample and tranfer contents to a kjeldahl flask	Macro-Kjeldahl Method				APHA 1995
Total Nitrogen	The sample is oxidized in a pure oxygen environment. The resulting gases are then controlled to exact conditions of pressure, temperature and volume. The product gases are separated under steady-state conditions and are measured as a function of thermal conductivity	CHN analyzer				350.3M
Total Phosphorus	Determine phosphorus concentration on the digest using the ascorbic acid method (for samples that range between 0.01 to 6 mg P/L) or the vanadomolybdophosphoric acid method (for samples that range between 1 to 20 mg P/L)	Perchloric acid digestion				6010A

5.3.2 Collection of Sediment Samples

This section provides guidance on the collection, handling, storage, transportation of sediment samples, field measurements and observations.

5.3.2.1 Field Measurements and Observations

Field measurements and observations are critical to any sediment collection study. It is recommended that the following information (Mudroch and MacKnight 1991) be recorded at the time each sediment sample is collected from a sampling area:

- sample number, replicate number, site identification (e.g., name);
- time and date of the collection of the sample;
- ambient weather conditions, including wind speed and direction, wave action, current, tide, vessel traffic, temperature of both the air and water, thickness of ice if present;
- sampling area location (e.g., positioning information) and location of any replicate samples;
- type of platform/vessel used for sampling (e.g., size, power, type of engine);
- type of sediment collection device and any modifications made during sampling;
- the water depth at each sampling area and the sediment sampling depth;
- name of personnel collecting the samples;
- details pertaining to unusual events which might have occurred during the operation of the sampler (e.g., possible sample contamination, equipment failure, unusual appearance of sediment integrity, control of vertical descent of the sampler, etc.);
- description of the sediment including texture and consistency, colour, odour, presence of biota, estimate of quantity of recovered sediment by a grab sampler, or length and appearance of recovered cores (photographs provide a good permanent record of a retrieved sample);
- deviations from SOPs; and
- unusual or unpredicted events.

5.3.2.2 Criteria for Selection of a Sample Collection Device

There are numerous methods and procedures reported in the literature which describe how to collect sediment samples in different types of environments (for reviews see Baudo *et al.* 1990; Mudroch and MacKnight 1991; ASTM 1992a; Burton 1992). Environment Canada (1994), Baudo *et al.* (1990) and Håkanson and Jansson (1983) suggest several factors that should be considered for the selection of sediment samplers and sampling location. The ideal sediment sampler should for the most part:

- permit free water passage during descent, to avoid a pressure wave;
- have a sharp-edged cutting surface, a small edge angle, smooth inside surface, and small wall thickness to minimize disturbance;
- close tightly for the ascent;
- allow subsampling;
- have the capability of adjusting weight for penetration of different substrates;

- be able to retrieve a volume of sediment large enough to meet the analytical test requirements;
- effectively and consistently retrieve sediments from various water depths;
- effectively and consistently retrieve sediments from the desired sampling depth;
- not contaminate or influence the nature of the sediment;
- require a minimum of supportive equipment;
- be easy and safe to operate and not require extensive training of personnel; and
- be easily transported to and assembled at the sampling site.

Table 5-6 and Figures 5-1, 5-2 and 5-3 present information to help determine the most appropriate sampling device for a freshwater, marine or estuarine environment. Most sediment samplers are designed to consistently isolate and retrieve a volume of sediment to a required depth below the sediment surface with minimum disruption to the integrity of the sample and no contamination of the sample. Maintaining the integrity of the collected sediments is of primary concern in most studies, since disrupting the structure of the sediment may change the physicochemical and biological characteristics, which in turn could influence the partitioning, complexation, speciation and bioavailability of the toxicants. Sometimes it is also important to maintain the profile if sectioning is required at different depths. These issues become even more important during investigation of cause monitoring studies when sediment may be collected for toxicity tests or more complex analytical methods (Chapter 12). In general, it is recognised that it is difficult to collect a sediment sample with most sampling devices without some degree of disruption.

There are three main types of sediment samplers; grab, core and dredge samplers. For the initial cycles grab samplers are recommended. Corers should be reserved for magnitude and geographical extent and investigation of cause studies. Grab samplers are used to collect surficial sediments for the determination and assessment of the horizontal distribution of sediment characteristics. The advantages and disadvantages of the various grab samplers are summarized in Table 5-6 and discussed briefly below. Details on this topic can be found in de Groot and Zschuppe (1981), Baudo *et al.* (1990), ASTM (1992a), Burton (1992) and Sly and Christie (1992).

Grab samplers have the advantage of being easy to handle and operate, readily available, moderately priced, versatile in terms of substrate type, and they can collect either small volumes (0-10 cm deep; e.g., Birge-Ekman, Ponar, mini-Ponar, or mini-Shipek) or large volumes (0-30 cm deep; e.g., Van Veen, Smith-McIntyre, Petersen). Careful use of these sampling devices avoids most of the problems associated with unpredictable penetration of sediment, loss of sediment from tilting or washout upon ascent, mixing of sediment layers upon impact, loss of fine-grained surface sediments from the bow wave during ascent, and susceptibility to the influences of waves and currents (Plumb 1979; Golterman *et al.* 1983; Blomqvist 1990; Baudo *et al.* 1990; ASTM 1992a).

Dredges are used primarily for the collection of benthos, since they are usually equipped with net sides designed to filter out fine-grained sediments and retain coarse sediments and fauna. It is virtually impossible to accurately measure the surface area covered by the dredge sampler, or judge the depth to which the sediment sample has been collected. In

addition, sediment integrity is disrupted, pore water excluded, and fine-grained sediments lost during ascent using dredge samplers. For these reasons, only grab (initial cycles) and core samplers (magnitude and extent and investigation of cause) are being recommended for collection of sediments.

Table 5-6: Advantages and disadvantages of the different grab devices most commonly used to collect sediments (ASTM 1992a; Mudroch and MacKnight 1991).

Grab Sampler /Dimensions	Use	Sediment Depth Sampled (cm)	Volume of Sediment Sample (cm^3)	Advantages	Disadvantages
Orange-Peel Grab, Smith-McIntyre Grab	Deep lakes, rivers and estuaries.	0-30	10,000-20,000	Designed for sampling hard substrates*	Loss of fine-grained sediment; heavy relative to other grabs; may require winch; possible metal contamination
Birge-Ekman – small	Lakes and marine areas. Soft sediments, silt and sand	0-10	≤ 3400	Designed for fine-grained soft sediments and mixtures of silt and sand; light weight therefore easy to operate manually	Restricted to low current conditions
Birge-Ekman – large	Lakes and marine areas. Soft sediments, silt and sand	0-30	≤ 13,300	Designed for fine-grained soft sediments and mixtures of silt and sand; large sample obtained permitting subsampling	Restricted to low current conditions; penetration depth exceeded by weight of sampler in very soft sediment
PONAR Grab - standard	Deep lakes, rivers and estuaries. Useful on sand, silt or clay	0-10	7,250	Most universal grab sampler; adequate on most substrates; large sample obtained intact, permitting subsampling; good for coarse and firm bottom sediments	Shock wave from descent may disturb fine-grained sediment; possible incomplete closure of jaws results in sample loss; possible contamination form metal frame construction
PONAR Grab – mini	Deep lakes, rivers and estuaries. Useful on sand, silt or clay	0-10	1,000	Adequate for most substrates that are not compacted	Smaller volume does not minimise disturbance to sample
Van Veen	Deep lakes, rivers and estuaries; useful on sand, silt or clay; effective in marine environments in deep water and strong currents	0-30	18,000-75,000 18-75 L	Adequate on most substrates; large sample obtained intact, permitting subsampling; available in stainless steel	Shock wave from descent may disturb fine-grained sediment; possible incomplete closure of jaws results in sample loss; premature closing in rough waters; possible contamination from metal frame construction
Petersen Grab Sampler	Deep lakes, rivers and estuaries. Useful on most substrates	0-30	9,450	Large sample; can penetrate most substrates	Heavy, likely requires winch; no cover lid to permit subsampling; all other disadvantages of Ekman and Ponar

* Defined here as rubble or coarse to very coarse unconsolidated bottom.

Grab Sampler /Dimensions	Use	Sediment Depth Sampled (cm)	Volume of Sediment Sample (cm^3)	Advantages	Disadvantages
Shipek Grab Sampler - standard	Used primarily in marine waters and large inland lakes and reservoirs; not useful for compacted sandy clay or till substrates	0-10	3,000	Sample bucket may be opened to permit subsampling; retains fine-grained sediments effectively	Possible contamination from metal construction; heavy, may required winch
Shipek Grab Sampler -mini	Lakes, useful for most substrates that are soft	0-3	500	Easily operated by hand from most platforms	Requires vertical penetration; small volume; washout of fine-grained sediment; premature closing

Figure 5-1: Recommend sediment samplers for different types of freshwater environments (after Environment Canada 1994).

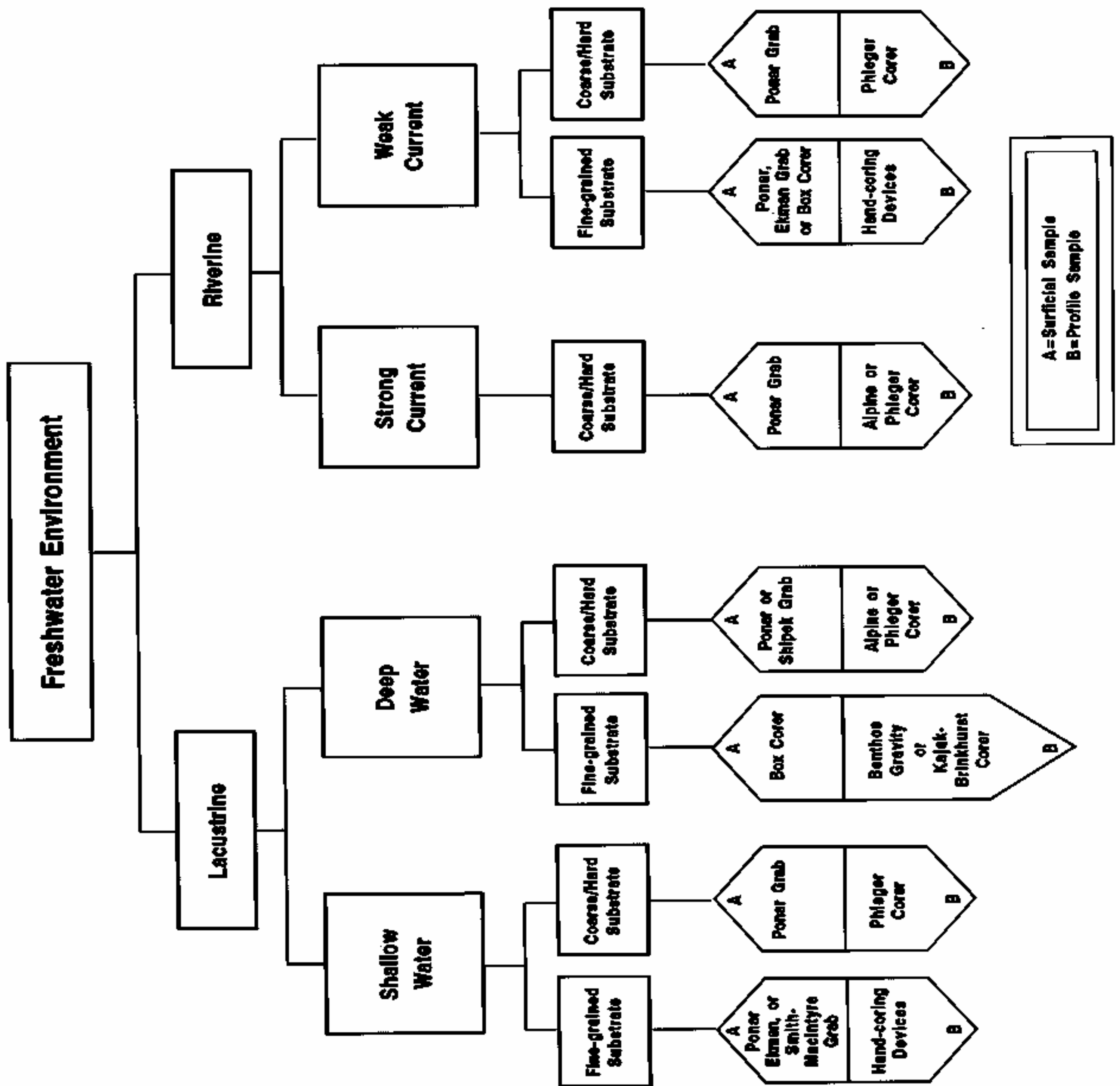


Figure 5-2: Recommended sediment samplers for different types of estuarine environments (after Environment Canada 1994).

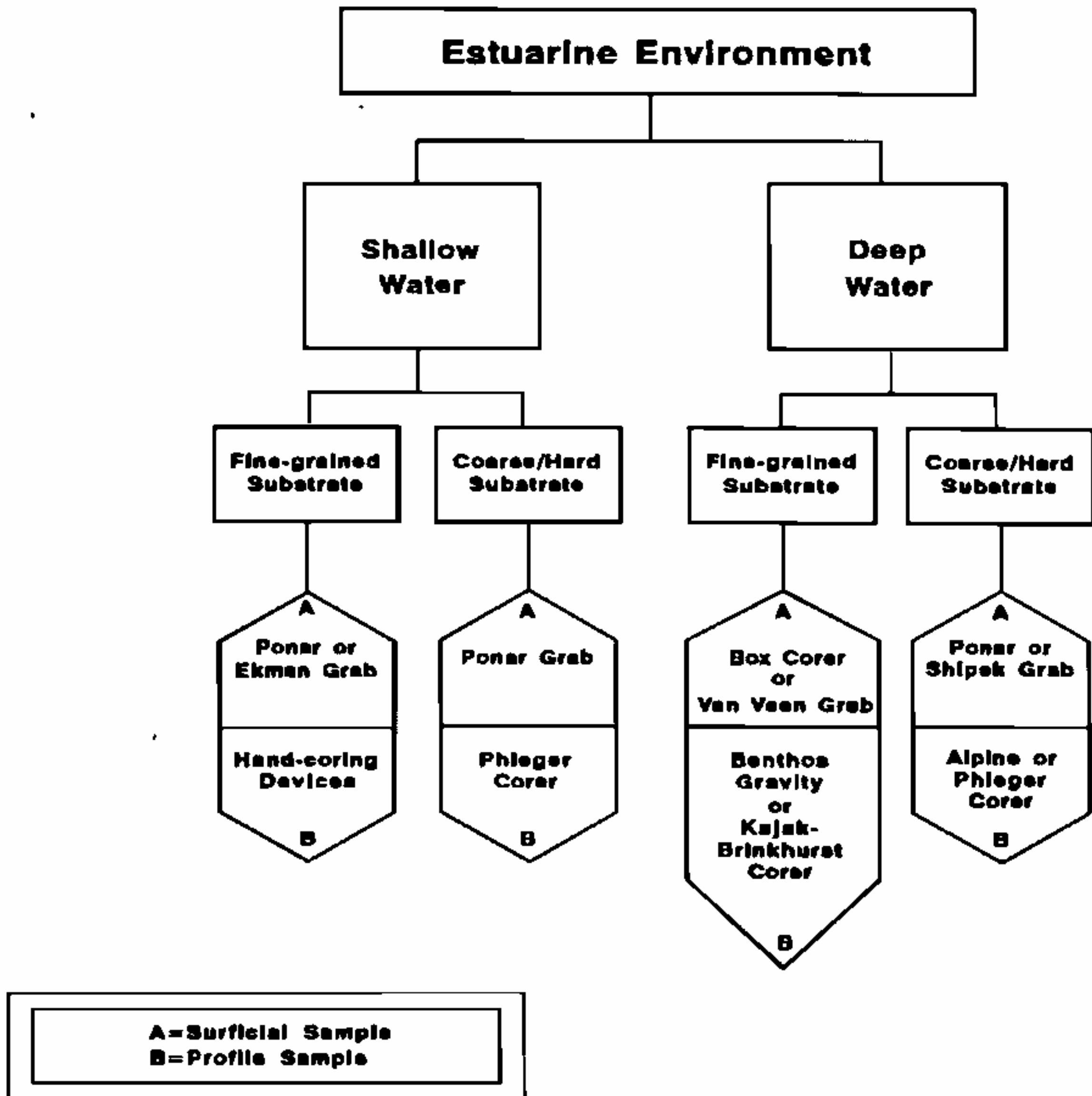
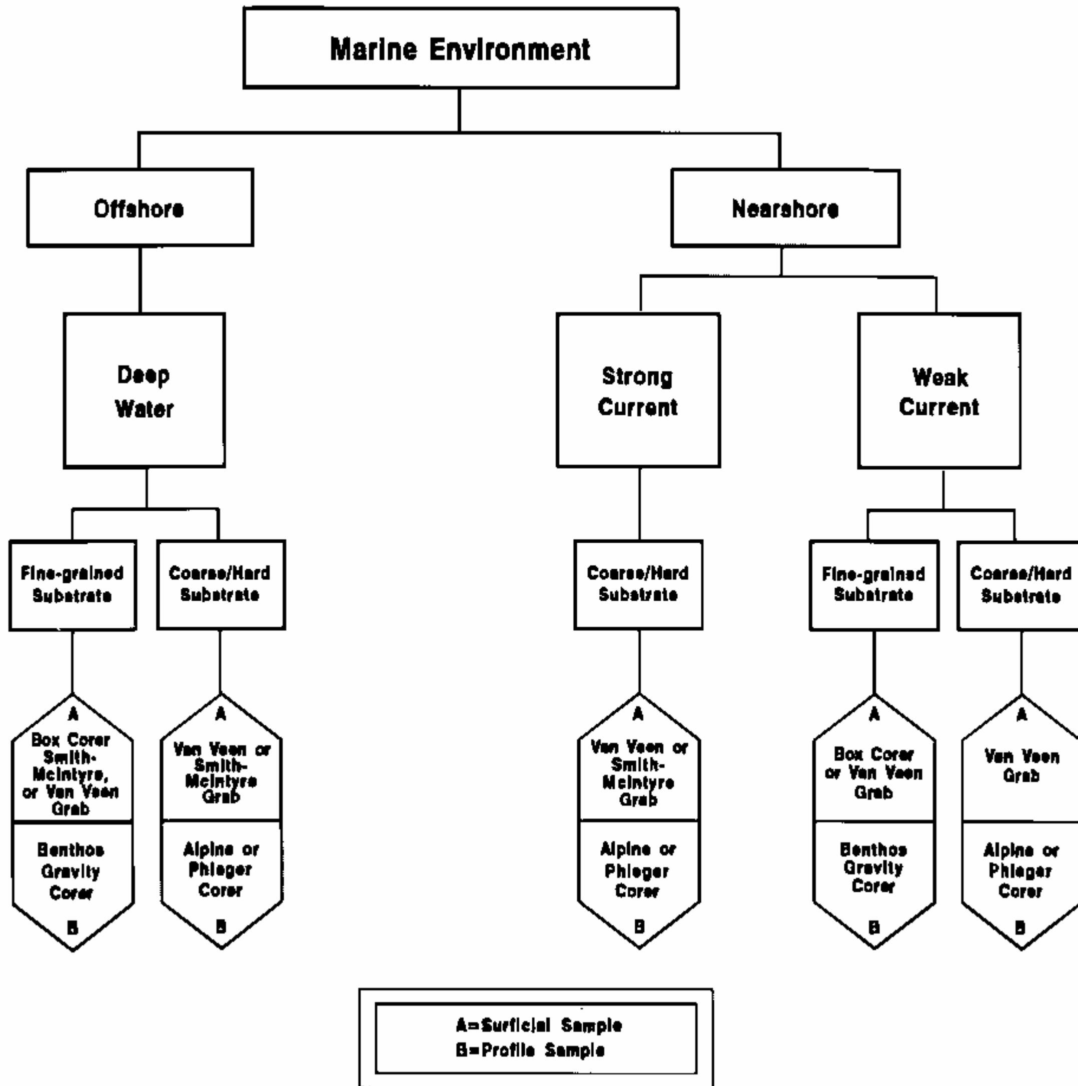


Figure 5-3: Recommended sediment samplers for different types of marine environments (after Environment Canada 1994).



5.3.2.3 Collection Device Penetration Depth

The desired depth of sediment penetration is a decision that depends upon the type of sampling device, the nature of the sediment, and the volume of sediment required. The actual depth of penetration depends primarily on the type of sampling device and the nature of the sediment. Generally, the most recently introduced contaminants of concern and most infaunal organisms are found in the upper 2 cm, and epifaunal organisms have access to this horizon (Burton 1992). Therefore, a preferred penetration depth of 10-15 cm and a minimum penetration depth of 6-8 cm are recommended to ensure minimum disturbance of the upper layer during sampling. This depth is also appropriate for

monitoring studies where historical contamination is not a priority (upper 0-5 cm of sediment).

5.3.2.4 Sample Size (volume of sediment)

The recommended minimum volume or weight of sediment required for each end use is summarized in Table 5-7. Accordingly, the sample size should be determined on a case-by-case basis. Before commencing a sampling program, the type and number of analyses and tests should be determined, and the required volume or weight of sediment per sample calculated. Each physico-chemical test requires a specific amount of sediment. After the sample size is determined, it is important to compare the sample size required with the capacity of the sampler to deliver the desired amount of sediment (Table 5-6), and reassess the number of replicate samples per station. The volume or weight requirements might dictate further sample handling such as subsampling, compositing, or sample splitting.

Table 5-7: Minimum volume or weight of sediment required for a specific end use.

End Use	Volume (mL)	Weight [1]	
		(g dry weight)	(g wet weight)
Physical/Chemical Analyses:			
Inorganic Contaminants	90	10	100
Other Chemical Constituents (e.g., TOC, moisture content)	300	60	330
Particle Size	230	50	250
Pore water Extraction[4]	2000	NA	3200
Preparation of Elutriate	1000	200	1100

[1] Based on a specific gravity of 2.0, a moderate organic matter content, and a water content of 90%
[2] Based on the average requirement for three tests
[3] Based on an average of 3 L of sediment per sample; an additional 3 L is required for each replicate
[4] Based on a specific gravity of 2.0, a moderate organic matter content, and an extractable water content of 40%
NA Not applicable

5.3.2.5 Grab Sampler Operation

When collecting bottom sediments with grab samplers, the speed of descent of the sampling device should be controlled and the sampler should not be permitted to "free fall". To minimize twisting during the descent, a ball bearing swivel should be used to attach the sampler to the cable. The sampler should contact the substrate or be positioned just above it and only its weight or piston mechanism should be used to force it into the sediment. The winching system should be in place to control both the ascent and descent of the sampling device, especially in deep water. After the sample is contained, the sampling device should be lifted slowly off the bottom, then steadily raised to the surface at about 30 cm/s. When the sampler is brought to the surface, the outside of the sampler should be carefully rinsed with water from the sampling area to remove material that could potentially contaminate the sample during transfer, and inspected to ensure that the sampler has closed properly.

The standard operating procedures specific for each grab sampler should be followed in order to ensure proper operation of the sampler.

Regardless of the type of samplers used, standard operating procedures for each device should be immediately accessible, and all personnel involved with the collection of samples should be familiar with these procedures. The sampling vessel or platform should be stationary, and sufficiently stable to permit inspection and handling of the retrieved sample. Field notes should accompany each sample that is collected. The sampling device should be cleaned thoroughly between sampling areas by dipping the sampler into and out of the water at a rapid speed to wash the sediment off. Alternatively, a hose can be used to wash the sediment off of the sampler with water from the sampling area. The sampler should be rinsed with water from the next sampling area before collecting a sample.

Summary of recommended operations and procedures for grab devices:

- the grab samplers recommended for the collection of depositional sediments in freshwater, estuarine, and marine environments are presented in Figures 5-1, 5-2 and 5.3, respectively;
- a minimum penetration depth of 6-8 cm is recommended for surficial sediment sampling; however, a depth of 10-15 cm is preferred;
- appropriate winching systems are needed to control the rate of ascent and descent of the samplers in deeper water;
- the sampling vessel or platform should be stationary, and as stable as possible;
- field notes and/or measurements should accompany each sample;
- if sediments adhere to the outside of the sampler, the external surface of the sampler should be carefully washed/rinsed with clean water upon retrieval before the sample is transferred to a storage container;
- the sampler should be rinsed thoroughly with water at the sampling area, and rinsed with water from the next sampling area before collecting a sample. Equipment used in the handling of sediment should also be washed thoroughly between samples; and
- a sample should meet the criteria of acceptability (Section 5.3.2.6) before it is considered adequate.

5.3.2.6 Criteria of Acceptability of Samples

All samples should be visually inspected to ensure that:

- the desired depth of penetration has been achieved; and
- there is no evidence of incomplete closure of the grab sampler, or that the grab sampler was inserted on an angle or tilted upon retrieval (i.e., loss of sediment).

If the collected sample fails any of the criteria listed above, then the sample should be rejected and another sample collected at the site. The location of consecutive attempts should be as close to the original attempt as possible and, where the direction of the current is known, consecutive attempts should be located in the opposite direction of the current or "upstream". Rejected sediment samples should be discarded in a manner that

will not affect subsequent samples at that sampling area or other possible sampling locations.

5.3.2.7 Replicate Samples

When conducting benthic invertebrate community survey, at least one sediment sample will be collected at each benthic sampling area in reference and exposure areas. Most monitoring studies have traditionally collected only one sample from each sampling area. However, a single sediment sample from a sampling area will impart little information on the variability in the sediment.

Environment Canada (1994) recommends the following for the minimum number of replicate samples:

- If replicate samples from a sampling station are required, the collection of a minimum number of five replicate samples within a sampling station is recommended unless determined otherwise from preliminary sampling and analysis;
- The collection of replicate samples should be mandatory as part of the QA/QC requirements of any good sampling programs and should comply with the data quality objectives; and
- The number of replicate samples should be higher at stations located close to a source of contamination.

Collecting separate replicate samples at each sampling area would allow for quantitative statistical comparison within and among different stations (Holland *et al.* 1993). The collection of separate samples within a sampling area can impart valuable information on the heterogeneity of the sediments. Separate subsamples from the same grab might be used to measure the variation within a sample but not necessarily within the sampling area.

The number of replicates required per sampling area is a function of the need for sensitivity or statistical power. Typically, the smallest deviation from the null hypotheses that is considered scientifically or environmentally important to detect should be decided *a priori*, together with the power of the test that is desired for the specific alternative (Green 1989).

5.3.2.8 Sample Containers

The recommended sample containers for analysis of particle size and total organic carbon are identified in Table 5-8. Whole-sediment samples may be transferred directly from a sampler into a clean, large volume (e.g. >1 L) container. If smaller volumes of sediment are collected or subsampled, then containers with wide mouths and Teflon®-lined lids are recommended for volumes ranging from 250 to 1000 mL.

If samples are to be stored at 4°C, then sample containers should be filled to the rim and air excluded during capping. If samples are to be frozen for storage then glass containers

should not be filled completely. A space of approximately 2.5 cm should be left to accommodate expansion of the sample when frozen, however this will depend on the size of the container and the percent moisture of the sample. The headspace in the container should be purged with nitrogen before capping tightly. Clear glass containers may be wrapped with an opaque material (e.g. clean aluminum foil) to eliminate light and reduce accidental breakage.

Table 5-8: Type of container and conditions recommended for storing sediment samples for analysis.

End Use	Container Type	Wet Weight or Volume of Sample	Storage Conditions	
			Temperature	**Holding Time**
Particle Size Distribution	Teflon®Glass High-density polyethylene containers or bags	250 g	4 - 40°C Do not freeze	≤6 mo
Total Organic Carbon	Teflon®Glass with Teflon®or Polyethylene-lined cap	100 g	4 ± 2 °C	≤ 48 h
Major Ions and elements: eg., (Al, Fe, Mg, Ca)	Teflon®\ High-density polyethylene containers or bags	250 g	4 ± 2 °C	≤ 2 wk
Nutrients: e.g., NH_4-N, NO_2-N, NO_3-N, DOC (pore water*) TKN, TC (particulate)	Teflon®\ Glass with Teflon ® or Polyethylene-lined cap	100 g	4 ± 2 °C	≤ 48 h

* Additional information on sediment pore water including various methods can be found in section 8.4.7 of the Metal Mining EEM Guidance Document 2002.

5.3.3 Sample Handling and Analysis

5.3.3.1 Procedures for Handling of Sediment Samples

Any time that sediment samples are handled, it is recommended that the following procedures be observed:

- sediment might contain a mixture of hazardous substances, so it is prudent to avoid skin contact with sediments by wearing protective clothing and equipment (e.g., gloves,

boots, lab coats or aprons, safety glasses, and respirator) during sampling, sample handling, and the preparing of test substances.

- handling of samples should be performed in a well-ventilated area (e.g., outside, in a fume hood, or in an enclosed glove box) to minimize the inhalation of sediment gases.

- work surfaces should be covered with Teflon® sheets, high-density polyethylene trays, or other impervious or disposable, similarly inert material.

- a spill control protocol should be in place in the laboratory or sampling vessel, and participants in the project should be familiar with all SOPs and recommendations.

5.3.3.2 Subsampling of Sediment Grab Samples

If sediment grab samples are to be subsampled, then access to the surface of the sample without a loss of water or fine-grained sediment is a prerequisite for selection of the sampler.

The non-turbid overlying water, if present, should be gently siphoned off before the sediment is subsampled, using a flat, clean scoop (e.g. Teflon® or a similarly inert, non-contaminating, non-reactive material) or a suitable hand-coring device. The sediment should be collected to a depth of 5 cm. Subsampling the top 2 cm is a common practice when the most recent sediment deposits are of concern, but the actual depth chosen depends on the objectives of the study. Ideally, each subsample should be placed into a clean, separate, pre-labelled container. The labelled sample container should be sealed and the air excluded.

In the event that the collection device does not allow access to the surface, the following procedures should be followed. Upon retrieval of the sample, the contents should be carefully deposited into a clean, inert container that is the same shape as the sampler. The sampler is placed into the container and the jaws opened slowly to allow the sample to be deposited into the container with as little disturbance as possible. Once the sample is in the container, subsamples can be collected from the sample with a hand corer or scoop. The edges of the sample where the sediments may be disturbed during removal from the sampler should be excluded during subsampling.

5.3.3.3 Compositing Sediment Grab Samples

If the objective of the study dictates compositing subsamples from separate grabs within a sampling area, then the subsamples may be placed into one clean sample container and, when full, sealed without trapped air. Compositing of sediment samples or subsamples may also be performed in the laboratory.

5.3.3.4 Transportation and Storage of Sediment Samples

The recommended procedures and conditions for the transportation and storage of sediment samples are as follows:

- the transport container should be refrigerated to 4 ± 2°C or contain ice or frozen gel packs that will keep the field samples below 7°C during transport to the laboratory;
- if field-collected samples are warm (e.g. > 6°C), they should be cooled to between 1 and 6°C with ice prior to placement in the transport container;

- samples should not freeze during transport;

- ideally, a max/min thermometer or a continuous temperature recorder should be placed inside the transport container and the container sealed. Deviations in temperature should be reported;

- light should be excluded from the transport container; and

- all field-collected samples that require further processing before storage should be transported to the laboratory within 72 h, preferably within 24 h, of collection.

Where these conditions cannot be met due to operational constraints, then the storage method and conditions adopted should strive to compromise the integrity of the sample as little as possible (Mudroch and MacKnight 1991).

Each sample container should be properly labelled and stabilized in an upright position in the transport container. Labelling of each sample container should include, at a minimum, the site, station location or identification, the sample type, the method of collection, the name of the collector, and the date and time of collection.

5.3.3.5 Laboratory Test Sample Preparation

Sediment samples should be prepared in a well-ventilated area (e.g., fumehood) and the appropriate health and safety precautions should be followed. Below are some details on sediment preparation techniques used to allocate sediment to test containers:

Homogenising: Mixing by hand or mechanical means may be used to achieve homogeneity of colour, texture and moisture; however, the efficacy of the method should be demonstrated, *a priori*, and the mixing time standardized to ensure consistency and minimize alterations in the size distribution of sediment particles, respectively.

Mixing of sediments should take place in the sample/storage container.

Partitioning: Coning or caking and quartering are the recommended techniques for partitioning the sediment for distribution among test containers. If a sediment splitter is

used, its efficacy should be demonstrated and documented and it should be made of an appropriately inert material.

Drying: Oven drying sediment subsamples (1-5 g of wet sediment) at low temperatures (40-60°C) until a constant weight is reached or freeze drying sediment subsamples are the recommended methods for drying sediment.

Crushing/Grinding: Commercially-available ball and pebble mills are recommended for fine-grinding small volumes of sediment (Mudroch and MacKnight 1991); however, it should be noted that grinding could change the chemistry of the material. Crushing can usually be achieved with a mortar and pestle.

Dewatering: Centrifugation with subsequent decanting of the supernatant is the recommended method for dewatering sediment samples. The centrifugation speed depends on the sample size and particle size (e.g., sediment weight or volume).

5.3.3.6 Prevention of Sediment Sample Contamination

When sediment samples are to be collected for chemical analysis the procedures for the collection, handling, transportation and storage of samples are much the same as those outlined above. However, in such cases it is important that appropriate measures are taken to ensure that sediment samples are not contaminated.

Types of sample containers and conditions recommended for storing sediment samples collected for chemical analysis are described in Table 5-8. All sample containers should be pre-treated prior to receiving a field sample (Environment Canada 1983, 1989). New glass and most plastics should be pre-treated to remove residues, and/or leachable compounds, and to minimize potential sites of adsorption. Pre-treatment includes the following sequence of activities (adapted from Environment Canada 1989):

- scrub with phosphate-free detergent and hot water;
- rinse with high-pressure hot water;
- subject to a 72-h acid bath with 8 M HNO_3 (50 mL of HNO_3 per litre of water);
- rinse four (4) times with hot water;
- rinse three (3) times with DDW (Double Distilled Water); and
- wash bottle caps (Teflon® or Teflon®-lined) with detergent and hot water, and rinse with DDW.

5.3.4 Sediment Parameters

The *Regulations Amending the Pulp and Paper Effluent Regulations* require that sediment samples be analyzed for the parameters, which are listed in section 5.3.1. A brief description of these parameters and other variables are included in this section. Additional sediment parameters may be measured in the field for magnitude and geographic extent or investigation of cause studies.

5.3.4.1 Determination of Particle Size Distribution

The determination of sediment particle size distribution is required each time that a benthic invertebrate community survey is conducted. Particle size is to be determined for a minimum of one sample from each benthic sampling area.

Particle size determination is important for several reasons. Knowledge of the particle size distribution of sediment is very important in the interpretation of the results of chemical or biological analyses. For example, particle size has a significant impact on the structure of the benthic invertebrate communities. It may also provide insight into the origin of sedimentary materials and about the dynamic conditions of sediment transport and deposition. From particle size analysis, specific surface, expressed as m^2/g, can be determined, and with this, the adsorptive capacity of metals and organic substances can be assessed.

Many different classifications of particle sizes exist; however, the following breakdown based on the Wentworth Classification (1922) is recommended for the interpretation of EEM data.

Classification	Particle Size
Gravel	2.0 mm – 16.0 mm
Coarse Sand	2.0 mm – 0.2 mm
Fine Sand	0.2 mm – 0.062 mm
Silt	0.062 mm – 0.0039 mm
Clay	< 0.0039 mm

Samples for particle size analysis can be collected in plastic, glass or metal containers, however, plastic is preferable. Samples should be stored in the dark at 4ºC and analyzed within 14 days of collection.

Procedures for methods of sediment particle size analysis can be found in “Standard Method for Particle-Size Analysis of Soil”, ASTM, D422-63. Particle size analysis or grain size analysis is generally performed in two parts, sieve analysis and hydrometer analysis. The sieve analysis classifies particles greater than 0.06 to 0.075 mm in size (actual minimum size depends on the sieve set used). This is done by wet sieving the sample through a set of at least four sieves, ranging in size from 0.06 mm to 16 mm. The material retained on the sieves is dried and weighed. Particles passing through the 0.06 mm sieve are collected and transferred to a 2-L container, together with the wash water. A hydrometer is used to determine the quantity of particles in this fraction from 0.06 mm down to 0.0014 mm. The data from these two tests is then tabulated and calculated to produce a particle size distribution curve. This curve graphically defines the percentage of material in the different fractions based on the total sample weight.

It is also possible to determine particle size distribution using laser diffraction, and this method is increasingly available. This method is more efficient, and provides higher resolution results than the above methods. A laser diffraction instrument uses light from a

low power helium-neon laser (the analyzer beam). Particles from sediment samples enter the beam via a dispersion tank that pumps the material, carried in water, through a sample cell. The light scattered by the particles is incident onto the receiver lens, which focuses the scattered light onto a diode composed of numerous concentric rings. Through a process of constrained least squares fitting of theoretical scattering predictions to the observed data, the computer calculates a volume size distribution that would give rise to the observed scattering characteristics. No *a priori* information about the form of the size distribution is assumed, allowing for the characterization of multi-modal distributions.

The efficiency of laser diffraction is also a major benefit. A typical measurement takes only a few seconds, and the data are saved digitally, and are instantly available for plotting and other calculations. Often, the entire distribution can be accounted for in a single measurement. Depending on the instrument used, a laser particle size analyser can measure all sizes ranging from 0.05µm - 2000µm. For samples with a size range greater than 2000µm, sieve data can be merged with the laser results. Finally, the results using laser diffraction are very high resolution, and are easily reproducible – a major shortcoming of the hydrometer and sieve methods.

5.3.4.2 Determination of Total Organic Carbon Content

Like particle size distribution, the determination of sediment total organic carbon is required each time that a benthic invertebrate community survey is conducted. Total organic carbon is to be determined for a minimum of one sample from each benthic sampling area.

Carbon is present in sediment in several organic forms such as humic matter, chemical, plant and animal matter as well as inorganic carbonate forms. Organic carbon in sediment and the water column causes a decrease in dissolved oxygen by using up available oxygen, hence creating a more anoxic environment. Also, at certain pH levels, humic substances form complexes with metals, increasing metal solubility in the water column. Two methods are commonly used to analyse total organic carbon (TOC) in sediment. The elemental analyser method, valid for 0.5 mg to 25 mg samples, is based on the use of thermal conductivity. The oxidizing furnace method requires 0.25 g to 0.5 g samples and is based on the use of infrared spectrophotometry.

Elemental analyser: Inorganic carbon is first eliminated by treatment with hydrochloric acid. TOC is then oxidized to carbon dioxide in the presence of a catalyst. The gas produced is separated by chromatography and quantified with a thermal conductivity detector.

Oxidizing furnace: Inorganic carbon is first eliminated by treatment with hydrochloric acid. TOC is then oxidized in the oxidizing furnace in the presence of manganese dioxide. The carbon dioxide formed from the organic carbon is measured directly by infrared absorption at the characteristic wavelength for carbon dioxide.

Procedures for these methods of analyzing TOC in sediment are described in:

Test Methods for Evaluating Solid Waste-Physical and Chemical Methods, USA Environmental Protection Agency, 1986, Method 9060.

APHA. 1995. Standard Methods for Examination of Water and Wastewater. 19th edition, published by the American Public Health Association (APHA).

5.3.4.3 Ratio of carbon to nitrogen for Marine Sediment

Effects on the benthic invertebrate community may occur as a result of organic enrichment in sediments. To determine if organic enrichment is contributing to effects, a combination of measurement techniques should be used in the marine environment. The measurement of total organic carbon (TOC) provides an indication of organic enrichment. Measuring the ratio of carbon to nitrogen (C:N ratio) in marine sediments should provide an indication of the source of the organic enrichment. If the organic enrichment is a result of land based sources (e.g. municipal sewage, pulp and paper effluent), the ratio of carbon to nitrogen will be higher (Hargrave *et al.* 1995). If the organic enrichment is a result of the natural source such as the breakdown of marine aquatic plants, the ratio of carbon to nitrogen will be much lower. Therefore, if the results of a benthic invertebrate community study indicates an effect, and there is evidence that the effect could be due to organic enrichment (elevated TOC, elevated Eh), determining the marine sediment carbon to nitrogen ratio can help identify the source of the organic loading to that ecosystem.

5.3.4.4 Redox Potential (Eh)

In the case of effluent deposited into marine and estuarine water, the redox potential (Eh) will be recorded. Measuring sediment Eh (redox) provides an indication of the oxygen conditions in marine sediments. In the 1998 version of the Pulp and Paper EEM Technical Guidance Document, Hargrave *et al.*1995 was reported as the reference method. This method calls for the direct measurement of Eh in the field with a specific ion meter and a suitable electrode. The probe is inserted directly into the sediment sample to make the measurement. Additional procedural guidance has since been published (Wildish *et al.* 1999, Bugden *et al.* 2001) which provides more specific details on conducting the measurements. All the redox values should be reported in millivolts (mV) and as relative to the normal hydrogen electrode.

5.3.4.5 Sulphides

Total sulphides are also required to be measured in marine and estuarine waters. Sulphides in marine sediments provide information on the extent and nature of microbial response to organic enrichment. In addition to Tetra Tech (1996), Wildish *et al*. 1999, Hargrave *et al*. 1995, and Bugden *et al*. 2001 also provide guidance with sampling for sulphides.

For additional guidance on redox potential and sulphides please refer to the *Additional Technical Guidance for Conducting Redox and Sulphide Measurements in Marine Sediments*, April, 2003, which can be requested from the EEM website

(http://www.ec.gc.ca/eem/).

5.3.4.6 Total Nitrogen and Total Phosphorus

Nutrient enrichment is occurring at some pulp and paper mills, therefore it is recommended that total nitrogen and total phosphorus be measured at all freshwater benthic sampling areas with soft sediment. Nitrogen and phosphorus compounds can greatly contribute to eutrophication and toxicity (USGS 2001). These variables have also been correlated with invertebrate community structure (Rosenbery *et al.* 1997).

5.3.4.7 Impact

A grading of impacts may be designed in the following way (Table 2 in the Additional Technical Guidance for Conducting Redox and Sulphide Measurements in Marine Sediments; Poole *et al.* 1978; Hargrave *et al.* 1995):

1) Gross impact

Impact is present in areas where anoxia occurs, when high TOC levels are combined with anoxic surface sediments (Eh <-100mV, S= >6000µM of $S^{=}$), high C/N, no macrofauna or bioturbation. A sediment profile may show that chemical factors are not just the result of historical impacts from the mill prior to recent improvements in effluent. For instance, if there is no accumulation of natural sediments over historical fibre mats, chances are the impact is an on-going one. However, if the surface layer is obviously an improvement over conditions at depth in sediments, then a historical impact can be inferred.

2) Moderate-high impact

Moderately high TOC and C/N in sediments which are anoxic, Eh about -100 to 0 mV, 1300<S<6000µM, total abundance of macrofauna < 50% stations further away from diffuser, taxa number 10 or less; biomass reduced by >50% from stations further away. This combination can be important because there are areas of natural anoxia (such as Alberni Inlet in B.C.) where the organic content and sulfides are not high. Any biotic reductions in this area would be the result of natural factors rather than the mill.

3) Low impact or enrichment

TOC and C/N relatively normal for the sediment type and natural oxygen conditions, Eh=-100 to 0 mV, 300<S<1300 µM, total abundance as high or higher than stations further away from diffuser, taxa number >50% that of stations further away, biomass >50% as high or even higher than stations further away.

4) Normal

TOC and C/N relatively normal for the sediment type and natural oxygen conditions, Eh>+100 mV, S<300 µM, total abundance, biomass and taxa number greater than stations further away from diffuser. Note that for naturally anoxic conditions these standards do not apply.

5.4 Quality Assurance and Quality Control

Quality assurance and quality control (QA/QC) is a documented system incorporating adequate review, audit and internal quality control. The objective of a QA/QC program is to ensure that all field sampling and laboratory analyses produce technically sound and scientifically defensible results.

Quality assurance is a planned system of operations and procedures whose purpose it is to provide assurance to the client that defined standards of quality are being met. Analytical quality assurance defines the way in which tasks are to be performed to ensure that data meet pre-defined data quality goals. These tasks include not only the analysis itself but all aspects of sample handling and data management.

Quality control is an internal aspect of quality assurance and it refers to activities that are being carried out to implement the quality assurance plan. It includes the techniques used to measure and assess data quality and the remedial actions to be taken when data quality objectives are not realized. Quality control activities ensure that the quality of results meet the needs of the client. Specific quality control measures include mechanisms such as setting data quality objectives and standard operating procedures that apply to field and laboratory aspects of the study.

The following QA requirements as outlined by CAEAL (1991) are recommended by analytical laboratories undertaking chemical analyses as part of the EEM program.

5.4.1 Standard Operating Procedures

Standard operating procedures (SOPs) are fundamental to any QA/QC program. All field and lab procedures should be conducted according to SOPs to ensure quality control. SOPs should describe in detail:

- The sampling methods and procedures, sample handling, labelling, equipment, preserving, record-keeping and shipping requirements of the field programs; and
- The analytical methods and procedures, sample handling, labelling, equipment, test system implementation, record-keeping, etc., of all laboratory analyses.

Each SOP should be a written method accessible to each analyst. SOPs should be based on procedures developed by a standard-setting organization such as Environment Canada, the U.S. EPA, the American Society for Testing and Material (ASTM), or the American Public Health Association (APHA). Where methods are not well validated, it is

recommended that the SOP be thoroughly referenced to the relevant literature and contain all the elements outlined in Canadian Association for Environmental Analytical Laboratories (CAEAL) Inc. (1991), where applicable. In-house validation data should be appended to the SOP and should contain the quality assurance and quality control procedures. These include the types and frequencies of quality control samples to be analyzed, expected levels of precision, accuracy, recovery, and method detection limits.

While chemical analysis procedures tend to be reasonably well-documented, sampling procedures in general, and sampling design in particular, are often overlooked. Sampling error is usually a large component and often the dominant component of uncertainty in environmental measurements. Standard operating procedures will help to reduce this uncertainty or at least ensure that it is quantified.

Emphasis should be placed on measures to prevent inadvertent contamination of samples and to ensure sample integrity. In addition, SOPs will specify the proper preparation of all sampling gear and supplies, and the proper calibration of all instrumentation (such as meters).

5.4.2 General Aspects of Quality Control in the Field

General quality control aspects of a field sampling program are:

- all personnel involved in field procedures should have appropriate education and training;
- sampling methods should be consistently applied among sites throughout the study;
- samples should be collected according to SOPs that should be available to personnel at all times during the field study;
- sampling equipment should be appropriate for the habitat being studied, properly cleaned, and accompanied by the appropriate documentation (i.e., manual, calibration and maintenance schedule);
- all samples should be properly labelled as to date, location, type, number and collector;
- samples should be in the proper container with the appropriate preservative or fixative if necessary;
- field technicians should maintain detailed field notes using indelible ink and water-proof notebooks;
- personnel should use chain-of-custody/sample submission forms and custody seals for contaminant samples;
- personnel should follow appropriate shipping and storage methods; and
- standardized field collection forms should be used during the field program.

5.4.3 Field Aspects of Quality Assurance

Field quality assurance for water quality monitoring should be achieved through several methodologies which include duplicate readings, comparison of readings with known standards, collection of profile samples for analytical evaluation and parameter

evaluation using alternate equipment (e.g., Hanna CTD meter, thermometer, etc.).

Some of the most common quality problems are the result of mislabelling or switching bottles, failure to add proper preservatives, improper storage conditions, sample contamination from sampling equipment and exceeding the holding time. Each sample should be clearly labelled in a manner that identifies the sample and distinguishes it from all other samples. Labels should be filled out in indelible ink and fixed to the sample container such that it will not fall off when wet or during transport.
The field log book is an integral part of the sampling program and forms the basis of the sampling report. Items documented in the log book are often highly relevant to the interpretation of the laboratory data. Any deviations from the sampling plan or any other observation about the sample or the sampling locations should also be noted in the log book. Some common deficiencies in field log books are failure to make planning notes, failure to make notes at the time events occur, failure to sign and date entries and failure to write legibly.

5.4.4 Quality Assurance During Sample Handling, Shipping and Storage

CAEAL (1991) recommends the following with respect to quality assurance during sample handling, shipping and storage.

a) **Chain of Custody** Chain-of-custody forms should be used in the transportation of samples, especially in cases where several contracted parties are involved in the sampling, shipping, and analysis of the samples. An example of a chain-of-custody form is presented in Figure 5-4.

b) **Sample Inspection** The condition of each sample should be noted upon receipt. Discrepancies between required sample conditions and the observed conditions should be recorded in a logbook or on a computer file. It is preferable to preserve samples in the field immediately, however the samples should be preserved immediately if submitted unpreserved, and a record made of the preservation methodology.

c) **Sample Tracking** Samples should be assigned a unique number or code to identify the sample in a tracking system. The sample tracking system should identify the sample, the source, the date of receipt, analyses, due date, and any other pertinent information. A computerized laboratory information management system (LIMS) is recommended for tracking samples in laboratories processing large numbers of samples for a variety of clients.

d) **Sample Storage** Samples should be stored in an assigned location in a refrigerator or sample storage area accessible only to authorized personnel. Samples should be refrigerated at 4ºC, where applicable, and removed only for inspection, logging, and analysis. The temperature of the refrigerator should be measured and recorded daily.

Figure 5-4: Example of a chain-of-custody record (modified from U.S. EPA 1988).

Survey				**Samplers (signature)**					
Station Number	**Station Location**	**Date**	**Time**	**Sample Type Water**		**Preservative added (initial)**	**Seq. No.**	**No. of Containers**	**Analysis Required**
				Comp	**Grab**				

Relinquished by (signature)		**Received by (signature)**	**Date/time**
Relinquished by (signature)		**Received by (signature)**	**Date/time**
Relinquished by (signature)		**Received by (signature)**	**Date/time**
Relinquished by (signature)		**Received by (signature)**	**Date/time**
Dispatched by (signature)	**Date/time**	**Received for laboratory by:**	**Date/time**
Method of shipment:			
Distribution Orig. - accompany shipment 1 copy - survey coordinator field files			

5.4.5 Use of Blanks and Duplicate Samples

The use of blanks and duplicate samples in the field and laboratory is an important component in a quality control program.

Field blanks and field duplicates are essential throughout the execution of a field program involving the collection of water. Field QC samples are used to establish whether any errors are being introduced during the sampling process so that corrective action can be taken if necessary. Field QC samples are distinct from laboratory QC samples as they measure sampling effects rather than laboratory effects.

Field blanks are used to check contamination from all potential sources of contamination of the sample. These include possible contamination of sample bottles, caps, preservatives, equipment, filter paper (if samples are to be filtered), atmospheric

contamination, sampling techniques, and analysis. Field blanks are collected by obtaining blank water (i.e. deionized water) from the laboratory conducting the analyses, transporting the water to the field, and taking it through all sample collection, handling and processing steps that the test samples undergo (e.g., transfer to a sample container, preservation and exposure to the environment). Field blanks are transported, stored and analysed in the same manner as test samples (McQuaker 1999).

Duplicate samples should be taken to verify analytical results and equipment reliance. Field duplicates are used to evaluate homogeneity of the sample site and the ability of the sampling system to take the sample the same way every time. A field duplicate is a completely separate sample, not a split of a single sample into two bottles. Duplicate samples should be treated as blind samples, and are not identified to the laboratory.

The last type of QC sample is the trip blank, also referred to as travel or transport blanks. Trip blanks are used to check contamination from sample bottles, caps and preservatives during transport, storage and analysis. A sample bottle is filled in the laboratory with blank water (i.e. deionized water) and preserved in the same manner as the test samples will be. Trip blanks are transported to the field with regular sample bottles and submitted to the laboratory unopened, together with the test samples. They are opened at the time of analysis, and analysed in the same manner as the samples (McQuaker 1999).

Field and trip blanks, and duplicate field samples should be collected at a frequency of 5 to 10% of the total number of samples. Therefore, if a total of 10 water quality areas were being sampled, only 1 of each of the QC samples should be required. This proportion can be increased if necessary, to monitor errors due to sampling and matrix homogeneity. If field and trip QC samples are not used, any inaccuracy introduced due to sampling will go undetected or be inappropriately attributed to the analytical laboratory. The use of blanks and duplicate samples in the laboratory are further discussed in Section 5.4.5. Table 5-9 summarizes recommended use of blanks and duplicate samples in the field and the laboratory, for larger sampling programs. For routine sampling, with one station from the exposure area and one from the reference area, it is recommended that a single field blank be submitted together with the test samples. In such cases, these samples will be analyzed by the laboratory as a batch, together with samples from other clients. The laboratory will achieve necessary internal QC using the complete batch.

Table 5-9: Summary of recommended use of blanks and duplicate samples in the field and laboratory. Numbers are based on a batch of 20 samples.

Parameter	Number of Samples	Internal or Field QC	Control limits	Description
Field blank	1	Field		Checks contamination as a result of sample handling. One per day per matrix
Trip blank	1	Field		Tests validity of sample preservation and storage conditions. One per day per matrix
Field Duplicate	1	Field		Used to evaluate homogeneity of the sample site and the ability of the sampling system to take the sample the same way every time.
Method Blank	1	Internal	< D.L. or < 0.1 of sample conc.	Checks contamination from reagents and procedures[a]
Laboratory Duplicate Sample	1	Internal		Checks precision of sampling process. One per day per matrix type[a]
Glassware Proof	1	Internal	< D.L. or < 0.1 of sample conc.	Checks contamination of lab glassware used during processing[a]
Standard reference material (SRM)	1	Internal		Checks accuracy of method[a]
Matrix spike	1	Internal	75 to 125%	Used interchangeably with SRM[b]
Calibration control:				
within run (blank and mid-range standard	1	Internal	10% drift max.	Statistical control over calibration can be confirmed between runs by means of two control standards, A and B, and within-run by means of blanks and midrange standards. (King 1976)
between runs (20% and 80% full scale)	2 per run	Internal	± 5% of target value	

[a]Intrinsic to every batch of 20 samples
[b]Used interchangeably with SRM if SRM is not available.

5.4.6 General Aspects of Quality Control in the Laboratory

The following lists the general quality control aspects of laboratory analyses performed:

- data should be verified and validated through transcription checks; chemical data will be verified by reference to the analytical laboratory QA reports accompanying the data.
- data analyses will be repeatable and robust and will be cross-checked with data quality objectives.
- data analyses will be rigorous and defensible and will include the rationale for all statistical analyses and data transformations.

5.4.7 Details on Quality Control Aspects of Laboratory Analyses

Analytical quality control procedures are designed to demonstrate statistical control over calibration, precision, accuracy/bias, and recovery (CAEAL) 1991.

Statistical control over these parameters can be demonstrated by running specific quality control samples during each analytical run (see Table 5-10). The results of these QC samples are compared statistically with confidence intervals calculated from historical data. These confidence intervals or control limits are normally calculated at three standard deviations of the mean of the controlled variable. Warning limits are frequently set at two standard deviations. Indicators of a run considered out of control include the following:

- two successive results for method blanks, laboratory duplicates, standard reference materials, spiked blanks, calibration control samples, or organic surrogate recoveries;
- one of these results outside the control limits.

Quality control data can be plotted on appropriate control charts. Control charts are graphic presentations of the QC data as a function of time or consecutive run number. Control charts demonstrate trends in time and provide graphic evidence of long-term statistical control of the analysis. Control limits and control charts are described in detail in ASTM (1986).

5.4.7.1 Good Laboratory Practices

Well established, good laboratory practices (GLPs) should be followed. The following is a brief listing of recommended laboratory practices. A description of GLPs can be found in greater detail in ELAP (1988).

- Records on reagent preparation should be maintained in a log book. Prepared reagent containers should be labelled with the reagent, its date of preparation, expiry date, and the person responsible.
- Instruments should be maintained or serviced on a regular basis. Maintenance records should be kept in a log book.
- Written instructions should be available for all instruments.
- Standard procedures for cleaning glassware and containers should be followed.
- Routine checks of the purity of the distilled water should be conducted and documented. Distilled/deionized water should be checked on a conductivity meter at least daily.
- Chemical reagents should meet the purity requirements of each analytical method.
- Reagents and solvents should be stored according to the manufacturer's directions.
- Working standards and stock solutions should be checked to determine changes in concentration.
- Reagents should be prepared and standardized against primary reference standards.
- The temperatures of all refrigerators and incubators should be checked daily and temperature excursions should be recorded.

- Each oven should have a dedicated thermometer and the temperature should be checked prior to and following each use.
- Proper volumetric glassware should be used.
- Glassware should be cleaned according to specifications of the method.
- Gas cylinders should be replaced at 700-1400 kPa.
- Laboratory personnel should have appropriate training in analytical laboratory procedures, and in the particular analysis for which they are responsible.

5.4.7.2 Calibration Control

Statistical control over calibration can be confirmed between runs by means of two control standards, A and B, and within-run by means of blanks and midrange standards.

a) **Between-run Calibration Control** Two control standards, A and B, can be used to analyze and control between-run changes in calibration, once at the beginning of each analytical run. These standards are made up and maintained independently of the calibration standards and are normally chosen to be about 80% and 20% of full-scale, respectively. Results are accumulated over many runs and the sums (A + B) and differences (A - B) are plotted on control charts. During a specific run, a significant change in the sum (A + B) from the historical mean implies that a significant change in intercept has occurred, other factors remaining constant. A significant change in the difference (A - B) implies a significant change of slope, other factors remaining constant. Control and warning limits for A - B are calculated for the mean and the standard deviation of the population of differences:

Upper and Lower Warning Limits (UWL, LWL) = $X_{A-B} \pm 2\ SD_{A-B}$

Upper and Lower Control Limits (UCL, LCL) = $X_{A-B} \pm 3\ SD_{A-B}$

Control and Warning limits for A + B are similarly calculated using the same standard deviation:

UWL / LWL = $X_{A+B} \pm 2\ SD_{A-B}$
UCL / LCL = $X_{A+B} \pm 3\ SD_{A-B}$

The run should not proceed until it is shown that A + B and A - B are within control limits. Control limits should not exceed ± 5% of the average value for A+B and A-B.

b) **Within-run Calibration Control (Inorganic Analyses)** Within-run changes in calibration attributable to slope and baseline drift should be checked at regular intervals. This can be accomplished by use of a mid-range standard and reagent blank run after every 20 samples. Control limits should be established by each laboratory for each procedure. The drift should not exceed 10%. If a greater drift is detected, the analysis should be stopped, the instrument re-calibrated, and samples run after the last acceptable check sample and blank are reanalyzed.

c) **Within-run Calibration Control (Organic Analyses)** In organic analyses by GC, within-run changes in calibration should be checked by injection of a mid-level check standard at a frequency of 5% or every 12 hours. This injection is compared to the initial calibration by calculating the percent deviation in the response factor of each analyte in the check standard to the average response factor determined during the initial calibration. If the relative percent difference is greater than 25%, the calibration check should be repeated. If the repeated check standard still has a relative percent deviation greater than 25%, corrective action is recommended.

5.4.7.3 Precision

Precision is the degree of variation among individual measurements of the same variable using a specific analytical method and is usually expressed as the standard deviation of replicates (U.S. EPA 1990c). Statistical control of analytical precision is maintained by analyzing within-run duplicates at a frequency of at least 10%. Laboratory duplicates are separate aliquots split in the laboratory from a single sample.

The absolute difference between within-run duplicates is compared to a control limit determined from historical data. To obtain these control limits, the results of duplicate analyses are accumulated over many runs and sorted according to concentration ranges.

Convenient concentration ranges are 0 to 20%, 20 to 50%, and 50 to 100% of full scale (King 1976). Within each concentration range, control limits for the absolute difference between within-run duplicates is determined from the formula:

$$UCL = D_4 \times R$$

where D_4 is a statistical factor and R is the mean difference between duplicates, 3.267 (ASTM 1986; Taylor 1987).

If the difference between laboratory duplicate analyses exceeds the upper control limit, the situation should be evaluated to determine the most appropriate corrective action.

5.4.7.4 Accuracy and Bias

Accuracy is the degree of agreement between an observed value and the true value as determined by analysis of an accepted reference material (U.S. EPA 1990c). The converse of accuracy is the degree of systematic error in the analysis or bias. Accuracy is controlled by means of method blanks and certified reference materials.

a) **Method Blanks** A method blank is an aliquot of reagent water equivalent in volume to the samples being processed and run in exactly the same manner as the samples. The method blank quantifies the level of contamination introduced to the samples during sample processing and analysis. Method blanks should be analyzed at a frequency of 10% or 1/run, charted, and controlled at ± 2 SD (warning limits) and ± 3 SD (control limits). If a method blank is judged out of control and contaminated, those samples

processed with the blanks and greater than the detection limit should be repeated for the variable(s) affected. In general, a method blank is considered free of contamination if the analysis yields results less than the detection limit or less than 0.1 times the level found in all associated samples (CAEAL 1991).

b) **Standard Reference Materials** Standard reference materials (SRMs) are samples available in different matrices that have been extensively analyzed by several laboratories and have concentrations certified by standard-setting organizations such as the National Institute of Science and Technology, the U.S. EPA, the National Water Research Institute of Environment Canada and the National Research Council. When available, an SRM should be analyzed at a frequency of 5% or 1/run (Tables 5-10 and 5-11). The matrix and concentration of the SRM should be as close as possible to the samples being analyzed. The results of SRMs should be accumulated and control and warning limits determined as ±3 SD and ±2 SD, respectively.

5.4.7.5 Recovery

Recovery of the analyte over the entire analytical process is determined from matrix spikes, spiked blanks, and surrogate spikes.

a) **Matrix Spike** A matrix spike is a separate aliquot of a randomly chosen sample to which is added all the analytes of interest before processing of the sample. Analysis of a matrix spike gives an indication of the recovery efficiency obtained for the matrix particular to that sample. The sample should be spiked with all the analytes of interest at a concentration as close as possible to that concentration giving a response equal to the mid-level calibration standard. The spiking solution should be prepared from a stock source separate from that used for calibration. The recommended distribution of matrix spikes is 10% or 1/run (Tables 5-10 and 5-11). One method to calculate recovery is:

$$\%\ \text{Recovery} = \frac{\text{Measured Conc. - Unspiked Conc.}}{\text{Spike Amount}} \times 100$$

The results of matrix spikes should be plotted on separate control charts for each matrix. In-house limits should be set on the basis of ± 3 SD on a minimum of 10 data points. In multi-parameter analyses, at least 90% of the analytes should have recoveries within the specified limits. Recoveries for inorganic analytes should fall within 75 to 125%. Recoveries for organic variables should fall within the limits specified in Table 4 of CAEAL (1991). If a matrix spike does not meet these criteria, the spike should be repeated. If the recoveries do not meet the criteria in the repeat analysis and there are no indications of other problems with the analysis, a matrix effect should be noted and reported.

b) **Spiked Method Blank** The spiked method blank is a separate aliquot of the same reagent water used for the method blank that is spiked with the compound of interest at a concentration as close as possible to the concentration of the mid-level calibration standard. The spiked method blank gives an indication of the reliability of a method without the matrix effects of real samples. The spiked method blank should be processed

with and in the same manner as the samples. As with the matrix spike, the spiking solution should be prepared from stocks separate from those used for calibration. One method to calculate recovery is:

$$\% \text{ Recovery} = \frac{\text{SMB - MB}}{\text{Spike Amount}} \times 100$$

where: SMB = Concentration measured in spiked method blank
MB = Concentration measured in the method blank

In-house recovery limits should be calculated for the spiked method blank based on ± 3 SD and a minimum of 10 data points (Tables 5-9 and 5-10). Recoveries for inorganic analyses should fall between 75% and 125%. Recoveries for organic variables should fall within 70% and 120%. If a spiked blank recovery does not meet the criteria established, the spike should be repeated. If the spike still does not recover, the samples related to the spike should be repeated. If insufficient sample remains for a repeat analysis, the results should be reported and flagged as suspect with an explanation.

c) **Internal Standards (Organic Analyses)** All analyses using GC should be performed using internal standards, or properly validated methods using external standards. An internal standard is a compound that behaves similarly in an analytical system as the compounds of interest, but is unlikely to be found in the sample. Internal standards are added at the same level to all samples, standards, and control samples prior to measurement but after sample preparation. All analyte responses should be normalized for the internal standard response to correct for instrument variability in response to such factors as varying injection volumes, temperature fluctuations, and final extract volume. The response of the internal standard in the sample measurement should be within 20% of the internal response of a calibration standard analyzed within the same 12-hour period (Table 5-10). If this criterion is not met, the sample should be repeated. If upon re-analysis the criterion is still not met, the sample results should not be corrected for internal standard response and should be flagged with an explanation.

d) **Surrogate Spikes (Organic Analyses)** A surrogate standard is a compound not expected to be found in the sample, that behaves similarly to the analytes of interest during sample preparation and analysis. Where applicable, surrogates should be added to all samples (including QC samples) before sample preparation to indicate method performance and sample matrix effects. Analyses run by GC/MS should have at least two surrogates while, those run by GC should have at least one surrogate. The amount of surrogate added to all samples should be the same as that added to the calibration solutions. In-house control limits for surrogate recoveries are based on ±3 SD on a minimum of 10 data points. In-house control limits for surrogate recoveries should be within 60% to 120%. If any surrogate is outside the expected recovery range, the sample should be reanalyzed. If, upon reanalysis, the surrogate recovery is still outside the permissible range, the results should be reported with a flag and an explanation.

Table 5-10: Recommended quality control for inorganic analyses.

QC Sample	Frequency	Control Limits	Reference
Method Blank	1 per 10 samples	Less than Detection Limit or Less than 0.1 times sample levels	CAEAL (1991)
Laboratory Duplicates	1 per 10 samples	See Tables 6-1 and 6-2	CAEAL (1991)
Matrix Spikes	1 per 10 samples	75% to 125%	CAEAL (1991)
Spiked Method Blank	1 per batch or minimum 5%	75% to 125%	CAEAL (1991)
Standard Reference Materials	1 per batch or minimum 5%	See Tables 6-1 and 6-2	CAEAL (1991)
Calibration Control: • within run (blank and mid-range standard)	1 per 20 samples	10% drift max.	CAEAL (1991)
• between runs (20% and 80% full scale)	2 per run	± 5% of target value	King (1976)

Table 5-11: Recommended quality control for organic analyses.

QC Sample	Frequency	Control Limits	References
Method Blank	1 per 10 samples	Less than Detection Limit or Less than 0.1 times sample levels	CAEAL (1991)
Laboratory Duplicates	1 per 10 samples	See Tables 6-1 and 6-2	CAEAL (1991)
Matrix Spikes (Authentic Compounds)	1 per 10 samples	90% of compounds meet limits in Table 4 of CAEAL (1991)	CAEAL (1991)
Surrogate Spikes (for GC and GC/MS)	100%	60% to 120%	CAEAL (1991)
Spiked Method Blank	1 per batch or 5% minimum	70% to 120%	CAEAL (1991)
Standard Reference Materials	1 per batch or 5% minimum	See Tables 6-1 and 6-2	CAEAL (1991)
Internal Standards	100%	NA	CAEAL (1991)
Calibration Control: • within run (mid-run standard)	1 per 12 hours or 20 samples whichever is more frequent	± 25%	CAEAL (1991)

5.4.7.6 Detection Limits

Detection limits should be reported as the method detection limit (MDL) as described by U.S. EPA (1984). The MDL is defined as the minimum quantity of an analyte that should be observed to justify the claim to have detected the analyte with a specified risk (normally 5% or 1%) of making a false detection.

One method to calculate the MDL is from the standard deviation of the analysis at the lowest concentration range:

$$MDL = t_{0.05\ n-1} \times S \qquad (1)$$

where: $t_{0.05,\, n-1}$ is the one tailed value of Student's t for a 5% risk of false detection, n-1 degrees of freedom, and S is the standard deviation.

Ideally the standard deviation is calculated from low level replicate analysis on real samples having the same or similar sample matrix as the samples under consideration. This standard deviation can be calculated from a minimum of seven replicates in the same run using the standard statistical formula (U.S. EPA 1984). However, it is preferable to calculate S from between-within-run replicate pairs accumulated over many runs.

The standard deviation of low-level replicate pairs accumulated over a large number of analytical runs is:

$$S = \frac{\Sigma S D^2}{2n} \qquad (2)$$

where D is the individual replicate difference and n is the number of replicate pairs. A minimum of 40 replicate pairs is recommended (OMOE 1988). The value of either standard deviation is then entered in equation (1) to calculate the MDL.

5.4.7.7 Data Reporting Conventions

Established protocols for rounding-off analytical results should be followed. If too many figures are rounded-off before reporting, information is lost and real differences in the concentrations of samples from different locations or occasions may be concealed. Quality control procedures may be on a coarser basis than is desirable, or necessary, with the result that values of the mean, standard deviation, or other statistics of a set of results may be biased. Conversely, when too many significant figures are reported, relatively small, statistically insignificant differences may appear falsely large (Hunt and Wilson 1986).

The standard deviation of the analysis is the preferred criterion for deciding the number of significant figures (King 1989). The process of rounding-off should ensure retention of the digit that is in the same decimal position as the most significant digit in the calculated standard deviation. For example, if the analysis provides a value such as 12.345 and the calculated standard deviation based on within-run replicate analysis at this concentration level is 0.32, the result should be truncated to 12.3.

5.4.7.8 Analytical Precision and Accuracy

Precision is the degree of agreement among replicate analysis of a sample, usually expressed as the standard deviation. Reproducibility is the closeness of agreement between the results of measurement of the same parameter carried out under changed conditions of measurement. Reproducibility is the standard deviation obtained measuring the same sample in different analytical runs and is called between run precision. Between run precision includes variability due to calibration on different days, instrument drift and many other factors.

Precision is affected by random errors and is a measurable and controllable parameter. Precision should be estimated for all analyses by processing separate sample aliquots through the entire analytical method. A laboratory should monitor their precision and be able to report precision using several days of data. For most parameters the precision should be within 10%. For total suspended solids the precision should be within 15% at concentrations greater that 10 times the MDL. For pH, precision should be within ± 0.1 pH unit.

Accuracy is the combination of bias and precision of an analytical method, which reflects the closeness of a measured value to the true value of a sample. Bias is a systematic error caused by something in the measuring system resulting in the data being high or low. Bias can be caused by a number of factors including contamination, mechanical losses, blanks, spectral interference, calibration errors or the influence of different operators. Accuracy is measured as per cent recovery of known concentrations such as certified reference materials, spiked samples or reference samples prepared by the laboratory and analysed as samples.

Whether data is considered accurate or inaccurate is relative to the final use of the data. A laboratory should monitor their accuracy and be able to report it using several days of data.

5.4.7.9 Instrument Maintenance

ICP/MS Tuning and Performance: For analyses using mass spectrometry detection, instruments should be tuned to provide a mass calibration of the instrument (CAEAL 1991; U.S. EPA 1988). Instrument tuning is performed upon method set-up or as a corrective action. CAEAL (1991) recommends use of PFTBA (perfluorotributylamine, FC43) for tuning and has set specific performance criteria. Perfluorokerosene (PFK) is normally used to calibrate high resolution mass spectrometers. In addition, ICP/MS system performance checks using specific compounds should meet the performance requirements presented in CAEAL (1991).

For instrumental quality control the instrument check standard should be analyzed once per 10 samples to determine if significant instrument drift has occurred. If agreement is not within ±5% of the expected values (or within the established control limits) the analysis of samples should be discontinued, the problem corrected and the instrument recalibrated.

5.4.7.10 Organic Analytes Identification

Method principles for a variety of organic analytes by various analytical methods and for different sample types are presented in Tables 5-3 and 5-5. Acceptance criteria for GC/MS analyte identification and additional procedures for identification of analytes by gas chromatography and HPLC (High Pressure Liquid Chromatography) are outlined in CAEAL (1991).

5.4.7.11 Instrument Response Checks

a) **Instrument response** (absorption, counts, peak height, etc.) can be checked before calibration or analysis proceeds by comparing the response of a check sample used on an ongoing basis, to historical data. Instrument response can be charted in control charts with a warning limit set at ± 2 standard deviation and an out-of-control limit of ± 3 standard deviations.

b) **Organic Analyses** Instrument response checks can be conducted with organic analyses by daily comparison of the internal standard response or an analyte response of a mid-range standard to historical data. Typically, an analyte or analytes that are most sensitive to instrument response are chosen for this check. Warning and control limits are set at ±2 standard deviations and ±3 standard deviations (SD), respectively. Other standard external checks can be used depending on the type of instrumentation.

5.4.7.12 Instrument Calibration Requirements

a) **Inorganic Analyses** Calibration is recommended for all inorganic methods with a minimum of three concentration levels (5 recommended) of standards, plus a blank, so that all samples fall within the calibrated range (CAEAL 1991). In cases where instrument software limits the calibration to two points, the calibration range should not exceed the linear range of the instrument. Unless it is demonstrated that no bias is introduced, standards should be matched to the matrix of the samples.

b) **Organic Analyses** Calibration for analyses using GC/MS and GC is achieved with five concentration levels of standards to cover an expected linear range generally by using internal standards and by calculating an average response factor for each analyte over five concentration levels. These average response factors are then used to calculate the unknown concentrations in the samples. A calibration is considered valid if the relative percent standard deviation of a multiple calibration is less than or equal to 30% for all variables. The relative percent standard deviation is defined as:

$$\%\,RSD_A = \frac{SD}{Avg\ RRF\text{-}A} \times 100$$

where:

$\%\,RSD_A$	=	relative percent standard deviation of the response factor for variable A
SD	=	standard deviation of the response factor of variable A over the five concentration levels, and
$Avg\ RRF_A$	=	average response factor for variable A over the five concentration levels.

If this criterion is not met, corrective action should be taken and the initial calibration should be repeated. Analysis of samples should not proceed until a valid calibration is established.

5.4.8 Quality Assurance in the Laboratory

Quality assurance (QA) encompasses a wide range of internal and external management and technical practices designed to ensure data of known quality is commensurate with the intended use of the data.

External quality assurance activities include participation in relevant inter-laboratory comparisons and audits by outside agencies. Outside audits may be based on performance in analysis of standard reference materials, or on general review of practices as indicated by documentation of sampling, analytical and QA/QC procedures, test results, and supporting data.

5.4.9 Recording and Reporting of QA/QC Information

5.4.9.1 Documentation

Documentation of all aspects of the analysis is recommended to confirm the quality and reliability of the analytical results. Storage of sample results and data associated with the analyses in hard copy or on computer file (with back-up) is required for at least six years after analysis. Information for each sample or batch of samples is recommended on the following:

a) **Method Detection Limits (MDLs)** If MDLs are different from the laboratory-determined MDLs (due to interference, dilutions, etc.), this should be recorded.

b) **Sample Storage Times** Records should be kept on the sampling date, date of receipt, date of sample preparation, and date of analysis. This information is normally handled as part of the sample tracking process.

c) **Instrument Performance and Maintenance** A log should be kept of instrument performance including records of tuning and instrument response. Maintenance or service records should be kept for each instrument.

d) **Quality Control Samples** Records of duplicate analyses, blanks, spiked blank recoveries, surrogate recoveries, matrix spike recoveries and results from certified reference materials, and records of calibration and calibration checks should be maintained.

e) **Sample Reception, Preparation, and Analysis** All anomalies in delivery, storage, condition, preparation, and analysis of samples should be recorded. These include any deviations from standard operating procedures.

5.4.9.2 Reporting of QA/QC Information

Analytical results are reported as a test or analysis report and should include all relevant data needed to assess the validity of the data; including QA/QC components. Items that should

appear in the report include:

- The report should be accurate, clear, unambiguous and objective;
- Report needs a title (Test Report, Report of Analysis, Quality Report);
- Name, address and location of laboratory and location where tested;
- Unique identification of the report so it can be traced easily (serial number, group number);
- Name and address of client;
- Identification or description of the sample tested;
- Condition of the test item (unpreserved, leaking bottle, where relevant);
- Date of sample receipt; date of report;
- Identification of the analysis method and description of any non-standard tests;
- Reference to sample date and sampling method (grab sample, time proportioned composite sample etc.);
- Deviations from the usual test method (filtering, pH, adjustment, standard addition etc.);
- The analytical results with units clearly identified;
- Statement indicating whether or not the results were corrected for blanks;
- Quality control data;
- Identify if result is qualified (did not pass QC tests, sample size too small etc.);
- Signature of accountable person and date authorization;
- Subcontractors clearly identified; and
- Should notify clients if new information invalidates reports already issued.

5.4.10 Method Principles - Physical and Chemical

Table 5-3 provides a summary of recommended method principles for some variables for effluents and receiving waters, and recommended performance criteria for precision and accuracy. Table 5-5 presents corresponding information for sediments and tissues. The criteria for precision are based on the relative percent standard deviation of the analysis and are derived from historical data on replicate analyses of samples in the range of 20 to 50% of full scale. Under most circumstances, the analyst should expect duplicates to differ by less than the percentage indicated.

For inorganic analyses, the criteria for accuracy are presented at ± one standard deviation of the percent recovery of a standard reference material based on historical data. Under most circumstances, a reference material should fall within the range indicated.

For organic analyses, the performance criteria are presented as actual control limits on spikes added to each sample (Table 5-11). These limits should be calculated at three standard deviations from the historical mean recovery of each spike in the same matrix as the sample. In the event that these limits are not met in a particular sample, the sample should be repeated. If the repeated sample still does not meet the recovery criteria, the results should be flagged to indicate matrix effects in the absence of any other indications of problems with the analysis.

Comments specific to selected methods are presented below.

5.4.10.1 Resin and Fatty Acids in Effluents

While interlaboratory validation for the extraction and derivatization method for resin and fatty acids (RFA) in effluents in Voss and Rapsomatiotis (1985) has not been completed, the method is recommended for EEM. However, GC/MS in SIM mode is recommended as the preferred approach for instrumental analysis to avoid interferences. An o-methyl podocarpic acid surrogate is recommended as a method recovery check, while tricosanoic acid should be added immediately prior to diazomethane derivatization as a methylation check. A heneicosanoic acid internal standard should also be used in instrumental analysis. Quantitation ions are those presented in NCASI (1986).

5.4.10.2 Chlorinated Dioxins and Furans in Sediments

Extraction of sediment is different from that for water, but the extract should be cleaned and analyzed as described in the Environment Canada method for effluents (Environment Canada 1992a). For sediments, samples are air-dried, weighed, and then spiked with isotopically-labelled surrogates. Surrogates should be allowed to equilibrate with the sediments, preferably overnight prior to extraction, to ensure that surrogate recoveries are more representative of the sample matrix.

5.4.10.3 Chlorinated Phenols, Guaiacols, and Catechols

Procedures for the extraction and derivatization of chlorinated phenolics in effluents are recommended in Table 5-3. Surrogates, which should be added prior to extraction, are 2-fluorophenol, d6-phenol, 2,4,6-tribromophenol. Internal standards should be d4-1,4-dichlorobenzene, and hexachlorobenzene. Characteristic ions are presented in the work by Lee *et al.* (1989).

5.5 Chemical Tracers in Fish

Mills are recommended, where practical, to provide confirmation at the time of field sampling that the samples collected are representative of effluent from exposed and reference areas. In hydrologically dynamic receiving environments, or those receiving multiple discharges, it will likely be necessary to select a tracer, which will be accumulated in fish tissue. The purpose of using a tracer is to verify the exposure of fish to effluent in the near- and far-field areas (magnitude and geographic extent), and to verify the lack of exposure at reference areas.

This section provides guidance on the selection of tracers in fish, sampling, analysis and QA/QC procedures based on review of Cycle 1 data. A summary of the Tracer Expert Working Group's conclusions (Tracer Expert Working Group 1997) is also presented at the end of this section.

5.5.1 Applicability of Tracers

Based on the review of the Cycle 1 data, the application of tracers in the adult fish survey

was accepted in principle. An internal study of Cycle 2 results showed that resin acids in fish bile can be a useful tool to confirm that fish captured in the exposure area were exposed to mill effluent. A total of 15 mills used resin acid concentrations in fish biles as a tracer for effluent exposure for Cycle 2. For 10 of these mills the method was effective in confirming effluent exposure. The results varied for the remaining 5 mills and will require site-specific information and further investigation (Parker, personal communication, 2003).

It is recommended that site-specific decision making processes be followed to provide guidance for identifying mills where the probability of achieving the desired goal is high. Benefiting from the experiences gained in Cycle 2 at the national level, site specificity should be a primary consideration.

The decision tree provided in this section (Figure 5-5) should be followed to determine the applicability of fish tracers in subsequent cycles of EEM. The decision-making process considers factors such as whether fish at the study site can be captured in a local zone with some stability in effluent concentrations, if the mill under study uses a high percentage of softwood furnish, whether barriers separate reference and study sites and the effluent concentrations of resin acids.

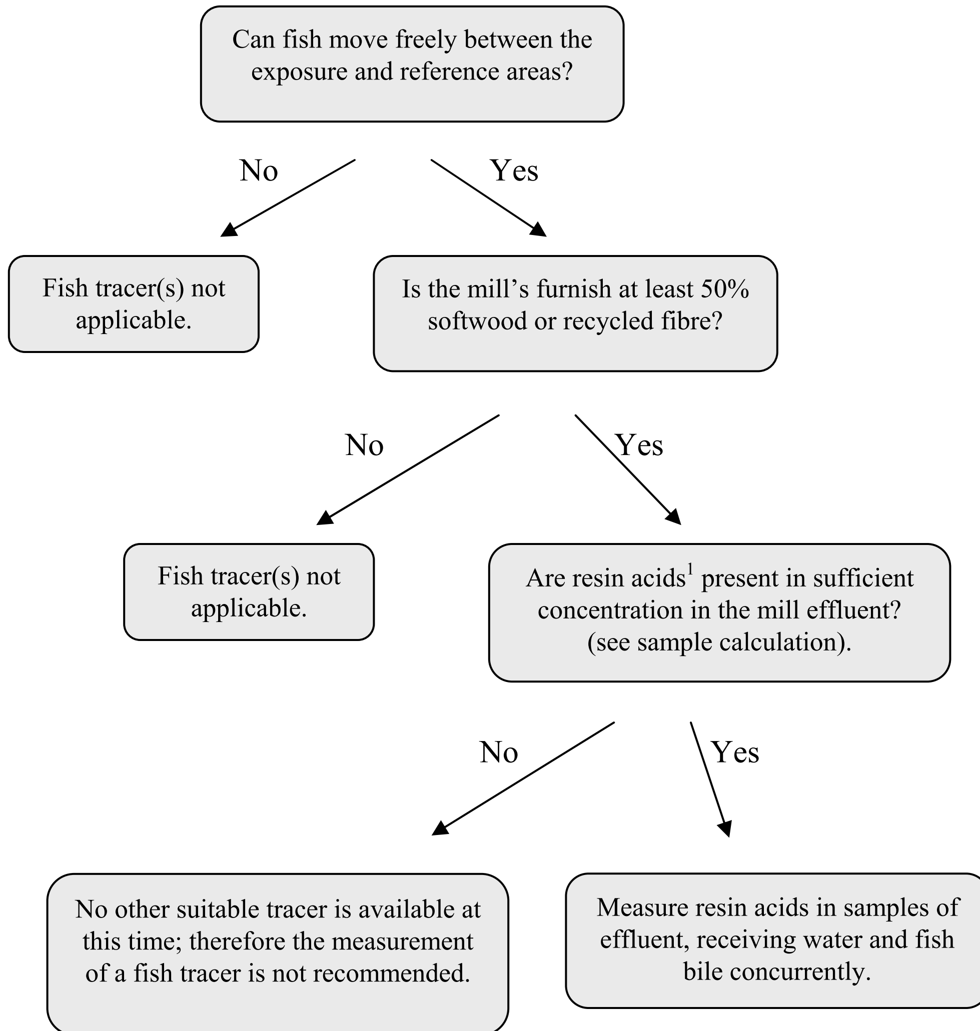
5.5.2 Selection of Tracers

The selected tracers should be specific for the effluent in question, should be taken up by the fish fairly rapidly, and retained from several days to several weeks in their original or only slightly modified form. Reliable analytical techniques for these compounds should be available and the compounds should be present in concentrations ranging from ng/g (ppb) to mg/g (ppm) to avoid very large errors normally encountered at lower concentrations.

Selection of the candidate chemical or biochemical tracer will be site-specific and depend upon several factors:

- the type of survey being conducted;
- the species of interest;
- the type of receiving environment (e.g. marine, freshwater, riverine, coastal);
- the characteristics of the effluent (e.g. process and treatment system);
- the presence of physical or biological constraints to movement; and
- the presence of other discharges to the receiving environment. For waters receiving discharges from many industries, a tracer specific to the effluent under examination should be selected.

Figure 5-5: Fish Tracer Decision Tree.



[1] Other tracers may be substituted if proven to be effective

Sample Calculation: To determine if the mill effluent contains sufficient concentrations of resin acid to use as a tracer.

Assumptions:

1) Detection limit for resin acids in fish bile = 0.5 µg/g
2) Detection limit for resin acid in water samples = 25 µg/L
3) Bioconcentration factor (BCF) of resin acids in fish bile = 1000
4) Exposure zone fish are captured within the 1% effluent plume

Equations: Tissue concentration = water concentration x BCF
Water concentration = effluent concentration x 0.01

Therefore: Effluent concentration = tissue concentration / (0.01 x BCF)

Effluent Concentration = 0.5 µg/g / (0.01 x 1000)
= 50 µg/L

Therefore if the effluent consistently contains 50 µg/L of resin acid, then there should be detectable concentrations of resin acid in the fish bile. This is a very conservative estimate. Detection limits for resin acids in bile can be as low as 0.1 µg/g and BCF for resin acids in fish bile have been reported in the 10^4 to the 10^6 range (Stuthridge, *et al.* 1995, Tracer Expert Working Group Final Report, 1997).

While the choice of a particular tracer may vary by site, some general characteristics apply. A tracer should:

- not be rapidly degraded in the environment or depurated in biota;
- be detectable in site effluent at a sufficient concentration to predict detectable levels in the receiving environment, for measurements in the water column;
- be detectable in site effluent or, alternatively, in sediments known to have been historically contaminated by site effluent for measurements in fish tissue or bile; and
- should be unique to the effluent in receiving environments receiving multiple discharges.

In simple riverine systems, where the biota are confined by physical or biological constraints (e.g. dams, sessile behaviour), a chemical tracer sampled from the water column at sampling sites, along with corresponding effluent samples, would likely be sufficient. However, many receiving environments will be considerably more complex than this and a different approach will be needed.

For certain industrial processes, it is possible that no products from the site effluent will accumulate in fish tissue to detectable levels. In these situations, it will only be possible to determine the relative position of the effluent plume at the time of field sampling, using a conservative tracer in the water column.

Elevated concentrations of a tracer with a relative short biological half-life could suggest

fish were exposed to the effluent. No defensible statement may be possible on the duration of time that the fish were in that zone because of the probability that a free swimming fish could pass through many concentration gradients. Indices such as fecundity and egg diameters would require many weeks to develop. In cases where fish are collected at a study site where tracer concentrations may be too low to serve its intended purpose, the significance of tracers is greatly reduced.

Another issue to be resolved is clarification on the significance of tracers found in fish from the reference site. Resin acids, fatty acids, phenols, and other natural chemicals are found in wood products; therefore, their ubiquitous distribution in fish from reference sites would not be unexpected.

Resin acids are naturally occurring carboxylic acids, which are found predominantly in softwood. They are released during the pulping process and discharged into mill effluent. Resin acids have been identified as a useful tracer in fish in some cases, but other tracers may be substituted if proven to be effective. Resin acids appear to be the most promising tracer for softwood mills; they are by-products of mills processing softwood and aspen, and cannot be tracers for mills whose furnish is primarily other hardwoods. The most common resin acids in mill effluent include abietic acid, isopimaric acid, dehydroabietic acid, sandraracopimaric acid and chlorinated forms of these. Dehydroabietic and abietic acids were the two most common tracers identified based on their presence in white sucker. Also, tracers in other media (e.g. sediment) may be useful as part of site-specific monitoring studies. No potential tracers have been identified for hardwood-based mills and further work is needed. It is also necessary to search for potential tracers that survive various forms of secondary treatment of the effluents. Data to date indicate that concentrations of resin and fatty acids and many of the chlorophenols were significantly reduced by secondary treatment or the reduction in the use of elemental chlorine in bleaching (> 80% for resin acids).

Mills considering resin acids as tracers are encouraged to identify laboratories capable of doing such analyses early in the design of the EEM study. Because only a limited number of laboratories are currently capable of doing these analyses, there could be shortages of analytical capacity and/or scheduling difficulties encountered as a result. Additionally, some laboratories may not have experience in these analyses and will require method development time to ensure adequate QA/QC. These factors, and the availability of alternative tracers, should all be considered in making the final selection of a tracer.

Research is currently being conducted on the use of stable isotopes to trace fish exposure to mill effluent (Dubé, Aquatic Toxicity Workshop, Whistler, BC, 2002). Preliminary results have shown that ä^{37}Cl may be a possible tracer of biotic exposure to mill effluent.

Chlorinated dioxins and furans are industrial by-products and can be distributed by long range atmospheric transport; therefore, their presence in fish from reference sites could be expected. The use of dioxins and furans as tracers should be discontinued. It should also be recognized that current mill practices have virtually eliminated, the discharge of dioxins and furans in effluents. Residual amounts that may be detected in fish are likely

attributable to sources deposited in sediments from previous mill practices rather than the quality of the mill effluent presently discharged.

Fatty acids cannot be used as tracers, since they are common contaminants and they are associated with soaps, which are used by laboratories in glassware washing. There is the possibility that analyzing for fatty acids may lead to false positives..

In cases where there are no suitable compounds in the effluent that could serve as a tracer in fish, a mill could use a water column tracer approach. There are a broader range of compounds or measurements (e.g. conductivity, colour, sodium) that can be measured in the receiving waters to confirm and possibly quantify the presence of the mill effluent. This approach could at least confirm that the fish were captured in an area where there was mill effluent present. However, this approach provides no indication of the duration of fish exposure to the effluent. Selection of tracers for plume delineation is discussed further in Chapter 2).

5.5.3 Sample Collection and Analysis

Samples will be collected in accordance with the quality assurance/quality control principles.

Many fish species are very mobile and can move between exposed and reference sites during the course of the year. Consequently, indicators of individual organisms may be needed to predict individual exposure. Species selection is determined by availability, and factors such as low mobility and prolonged residency time to the effluent exposure are important.

Fish or shellfish species should be readily available in the study and reference zones. Sampling protocol, such as the number of specimens taken, their size (age) and sex, and time of the year should be established. Information will be provided for sample storage and processing. It should be decided whether to analyze individual specimens or pooled samples and whether the analyses are to be done singly or in duplicate, and how to deal with unusual values.

The portion of fish sampled for a chemical tracer depends upon the industrial process of the site and the degree of effluent treatment. For example, for pulp mills (chlorine and non-chlorine bleaching) equipped with primary treatment, the preferred option is to measure the level of chemical tracer in tissue (e.g. muscle, liver, hepatopancreas) since this is representative of long-term exposure. For mills having secondary treatment, it may be necessary to determine tracer levels in bile, as levels in edible tissues may be below detection limits. Fish bile samples from fish should be placed on liquid nitrogen and kept at –80 °C until analyzed (Leppänen and Oikari 1999).

The use of single composite samples will be eliminated for tracer purposes to provide a statistical basis for data evaluation and decision making. Future sampling should include multiple individual samples or multiple pooled (composite) samples.

Fish should be analyzed for tracers if a practical method is available. It is recommended that 10-20% of fish collected be sampled.

Resin acids and their conjugates are magnified 1,000 to 100,000 times in bile and so make very good tracers. For this analysis, it is suggested that the technique described in Morales *et al.* (1992) be used. The following acids may be monitored: pimaric, sandaracopimaric, isopimaric, dehydroabietic, and abietic.

A QA/QC program for the measurement of tracers in samples of fish tissue is required. The analytical methods, and quality assurance/quality control measures, used for chlorinated dioxins and furans, resin and fatty acids, and chlorinated phenols are described in Table 5-5. The participation in round robin testing particularly for resin acids, chlorinated phenols, and other tracers that may be considered in the future, should be a routine practice, similar to those available for laboratories that analyze for dioxins and furans. Certified reference materials (CRMs) may not be available for many of these chemicals and, therefore, should be developed and become an integral part of the analytical validation process.

In terms of quality control for bile analysis, both resin acid and chlorophenol analyses of bile require hydrolysis of the bile prior to extraction, derivatization, and analysis. Either enzymatic or acid hydrolysis is acceptable (Söderström *et al*. 1994). A laboratory should show that the hydrolysis is effective, otherwise data will be reported which may be misleading. One suggested method is fortifying bile samples with either _-naphthyl-_-D-glucuronic acid or 6-bromo-2-naphyhyl-_-D-glucuronic acid. After hydrolysis, the recovery of _-naphthol and/or 6-bromo-2-naphthol is reported for each sample. This provides quality control data on the efficiency of the hydrolysis as well as for the efficiency of extraction and derivatization. Without this type of data the results are largely useless.

For quality control measures in resin acids and chlorophenols in bile, the lab should refer to Morales *et al.* (1992).

5.5.4 Tracers in Benthos

Cycle One data showed that sediment chlorinated guaiacols and catechols provided the best tracer information for the bleached kraft mills. The use of tracers in benthos has not been re-evaluated at this time, therefore additional information is not available. If the exposure of the benthos to the effluent is questionable it may be recommended that another plume delineation study be conducted.

Where benthic tracer studies are proposed, details should be discussed with the regional EEM contacts.

5.6 References

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