Environmental Technology Verification

General Test Protocol

Please note

This is the initial draft version of the General Test Protocol that has been distributed for general review. It has been submitted for peer review and any comments, suggestions, amendments, additions that are offered would be greatly appreciated. Please direct any comments to:

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Forward

The purpose of the General Test Protocol is to provide guidance to those who are involved in technology testing and demonstration. The Protocol provides a systematic framework for the demonstration testing of an environmental technology. Demonstration testing is a pre-requisite for entry into the Environmental Technology Verification (ETV) Program, a service which is delivered to technology vendors by ETV Canada Inc. under license to Environment Canada.

The General Test Protocol provides a technology vendor or test agency with specific guidelines to collect appropriate data that can be applied to the validation or verification of the performance of the technology. Two principle assumptions have been made with respect to the preparation and subsequent recommended use of this Protocol. Firstly, it is assumed that the technology is a developed process or system and requires sufficient data to demonstrate the performance of the technology. Secondly, it is assumed that acceptable quality data will be collected, using the guidelines of this protocol, in support of the validation of a performance claim under the Environmental Technology Verification Program.

Executive Summary

The General Test Protocol provides guidance to vendors and testing agencies in developing and executing a test program for the assessment of the performance of an environmental technology. The Protocol describes the relevance of each criteria that should be included in any experimental design, and where appropriate, baseline conditions are offered for these criteria. Where appropriate, specific requirements are specified for sampling of the three media: water, air and solids. Details are included for a number of criteria which specifies the minimum acceptable requirements for effective treatment or monitoring of a particular media.

Criteria required in an experimental plan include:

1. *Objectives*: Concise, relevant objectives should be specified that focus the test program on the technology performance.

2. *Experimental Design*: A properly designed program will clearly identify the scope of work and will include written operating procedures for all tasks associated with testing.

3. *Personne*l: Data collection should be directed and conducted by staff familiar with the technology and multi-media monitoring.

4. *Health, Safety & Training Requirements*: Safety procedures and a full understanding of the operation of the test equipment is essential for the protection of operators, the public and the environment.

5. *Sampling Methodology*: The selection of proper sampling methods is contingent on practicality and costs, among other criteria, which must provide acceptable, verifiable precision.

6. *Sampling Locations*: Samples must be collected from sites that offer representative data.

7. *Sample Type*: Grabs, composites, flow proportional composites and continuous online or inline monitoring represent the range of sample types available for testing technologies.

8. *Number of Samples*: An adequate number of samples are required to ensure that a meaningful understanding of the effects and results of the technology are developed.

9. *Sampling Times/Frequency*: Sampling times and frequency depend the requirements to monitor steady state operation and cyclic performance of the technology.

10. *Sampling Equipment*: A variety of sampling and flow monitoring equipment are available to effectively collect data.

11. *Sample Containers & Preservation*: Specific sample containers and preservation techniques are dictated by the contaminant types and the media monitored.

12. *Sample Handling*: Sample integrity and data reliability depend upon proper handling of samples following collection.

13. *Sample Quality Assurance/Quality Control*: A QA/QC program of at least 15% of duplicates, blanks and spikes provides confidence in the collected data.

14. *Sampling Records*: Accurate and legible record keeping will facilitate data interpretation.

15. *Sample Chain of Custody*: A number of criteria must be satisfied to ensure an effective “chain-of-custody” procedures are followed.

16. *Sample Disposal*: Proper procedures must be followed to dispose of used samples in a safe, effective manner.

17. *Analytical Laboratory Requirements*: Accredited laboratories ensure credible data.

18. *Analytical Procedures*: Recognized standard analytical procedures must be used to generate reliable data on contaminant types and concentrations.

19. *Quality Assurance Requirements*: Accredited laboratories are required to satisfy minimum quality assurance requirements to protect the integrity of chemical analyses.

20. *Operating Conditions*: Normal, or specified operating conditions, must be controlled and monitored during the entire test program.

21. *Process Control Equipment*: Field instrumentation and monitoring equipment must calibrated and be in good working order.

22. *Sample Security & Archival*: Allowable storage times for samples are dictated by the contaminant of interest, the media sampled and the precautions used to protect sample contents.

23. *Scheduling*: The schedule must reflect the cyclic nature of the technology.

24. *Experimental Plan Review*: Expect staff from a number of agencies can be “called upon” to provide a review and comment on the test program design, performance and completion.

25. *Auditing Program*: Independent third-party (unbiased) monitoring of the test program is essential to ensuring a credible program.

Additional information in appendices and selected references, listed in the bibliography, provides the user will sufficient information to develop an effective experimental program which will result in the collection of sound, high quality data.

Finally, the Protocol provides guidance in preparing a report that summarizes the results of the environmental technology testing. This report can also be used when applying to the ETV Program for a performance claim verification.

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Introduction

The General Test Protocol was designed to provide a systematic framework to guide vendors, test agencies, and other testing facilities through the process of demonstration testing of a technology, resulting in thorough, high quality, reliable, reproducible data which meets the quality requirements of the ETV program and provides accurate, meaningful data in support of the verification of a vendor's claim for a technology performance. The Test Protocol is generic in nature in order to provide appropriate guidance for vendors of a wide range of environmental technologies, applications, and/or associated contaminated media.

Data quality must be sufficient to demonstrate that the desired results have been achieved. This will depend on the quality of data generated, the desired level of confidence for the results, and the detection limits for the measured parameters. As a minimum, all of the criteria related to data quality (as detailed in Appendix A) must be met.

The quantity of data and the number of sampling runs required to achieve the desired level of confidence for the results must be identified during the planning stage. For example, for water or wastewater sampling, as a general guideline, a minimum of ten (10) data points must be collected to constitute an acceptable "data set". A preferred statistically sound data set requires a minimum of 30 data points. A minimum of three (3) data sets is preferred (i.e., three independent runs), where the technology is operated under identical steady state conditions. It is important to note that different guidelines are applied to the different media.

The number of samples which need to be collected may be greater or less than this guideline, depending on a number of factors including the specific technology being verified, the sample media, sample collection equipment, system operating cycles, and sampling costs. If the vendor wishes to deviate from the minimum of 10 samples repeated 3 times, he/she must provide justification for any deviation in the report on the demonstration testing. In such cases, best professional judgment will dictate the minimum number of samples to be collected.

Protocol Structure

The Test Protocol has been structured according to a 4-step process to facilitate collection of sound data for claim verification.

The four steps for Testing include:

1. Design of Test Program,
2. Data Collection,
3. Data Assessment, and
4. Reporting Results

The Protocol includes systematic instructions, examples, forms, and relevant references to assist the Test Agency (or vendor) in establishing, implementing, assessing, and reporting on their specific testing program and the results obtained.

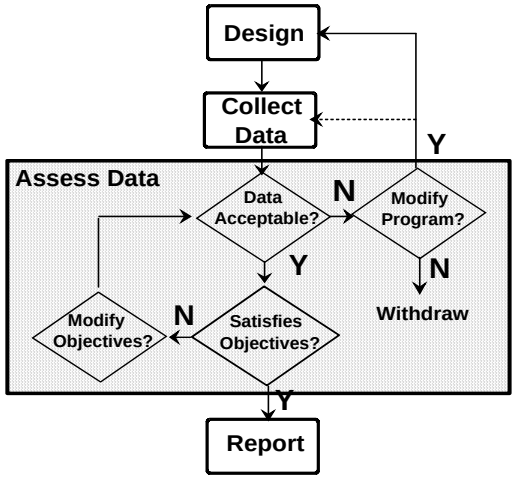


Figure 1. Test Protocol Concept

As shown in Figure 1, input may be sought from a

number of ETV Program participants during the design stage. Designing a suitable Testing Program is the most vital step in the process. Typically, an approved (unbiased) "Test Agency" would be responsible for developing the Testing Program on behalf of the vendor and possibly with general guidance from ETV Canada (or its' appointed expert). Alternatively, the vendor may choose to conduct his/her own testing as long as appropriate standard methods are used and documented and third party auditing of the test program is included. Note the data quality is usually more closely scrutinized when this option is selected, since the vendor has a vested interest in the outcome of the testing. The Testing Program is then implemented to collect all necessary data for verification. Finally, a report is generated which summarizes the results of the Testing Program and the data assessment process in support of claim verification.

Participants

The organizations and individuals that will participate in the Testing (e.g., sampling teams, analytical laboratories, Verification Entity) must be clearly specified by the vendor. Each participants role in planning, implementation and assessment activities must also be identified. A list of participating organizations and/or personnel and a brief statement identifying the role of each must be prepared. Participants may include the following:

- *Vendor Representative*
- *Test Agency Representative*
- *ETV Canada Expert or Verification Entity Representative*
- *Field Analyst*
- *Analytical Laboratory*
- *Testing site representative*
- *Government regulatory representative*

Proponent Responsibilities

Specific roles for each participant in the Testing Program are likely to be established on a case by case basis. However, in general terms the following roles apply.

- *Vendor*
  The vendor is responsible for ensuring that unbiased, quality data is obtained that validates the performance of his technology. The vendor may develop a suitable experimental program to acquire the quality data necessary for verification of the technology claim. If the vendor chooses to implement the test program using his own staff, then the data quality will be closely reviewed by the Verification Entity and ETV Canada in order to protect the integrity of the ETV Program. There will be a need to ensure third party involvement in this case, such as an independent auditor. Alternatively, the vendor may contract with a Test Agency to develop the test plan and conduct the data collection.

- *Test Agency*
  Although not mandatory, it is advisable that the vendor contracts the expertise of an independent, unbiased Test Agency. In addition to providing specific expertise, a Test Agency tends to lend a higher level of credibility to the Testing program and the data collected.

- *ETV Canada*

ETV Canada is responsible for the administration of the Environmental Technology Verification Program and, as such, is not directly involved in technology testing. However, ETV Canada is available for general advice regarding the development of the Test Program. It may be useful if the Test Agency (or vendor) discuss the planning phase with ETV Canada in the testing process, as the added insight may prove beneficial. ETV Canada can also identify an auditor for the Test Program undertaken.

- *CETACs*
  The Canadian Environmental Technology Advancement Corporations (CETACs) can assist the Vendor with preparation of applications, development of verification claims, and can coordinate with the Verification Entity, on behalf of the Vendor, during the Verification process. The CETACs can also provide general guidance on testing and the test program to help the Vendor be prepared for entry into ETV.

- *ETV Canada Appointed Expert*
  ETV Canada recognizes that specific technology expertise may not exist within ETV Canada directly and as such reserves the right to appoint an expert to act on their behalf. Again, it is to the vendor's benefit that ETV Canada (or an Appointed Expert) be included in the Testing Program. At the discretion of ETV Canada, the technology expert may also serve as the Testing Program auditor.

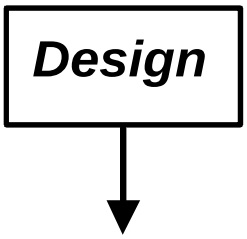
- *Verification Entity*
  The primary function of the Verification Entity lies within the verification process, more so than the actual testing process. However, since the data collected during the Testing Program is vital to the success of the verification process, it may prove beneficial to the vendor if a Verification Entity is involved at the planning and testing stages. Depending on the specific technology being evaluated, the vendor may request that ETV Canada select a Verification Entity to act as an independent 'Appointed Expert'. The Verification Entity can also function as the Testing Program auditor. This would enable a smoother transition from testing to verification by minimizing the number of participants involved in the performance evaluation. However, caution must be exercised, since the use of a Verification Entity during the Test Program may restrict their ability of this Verification Entity to be an "independent, unbiased" candidate to conduct the subsequent performance claim verification.

A brief description of the three steps Test Protocol is described in the following.

The process begins with the *Design* of a suitable testing program. The next step is *Implementation and Assessment, which* includes the data collection exercise including an ongoing assessment of the data to decide if sufficient quality data may be suitable for verifying the claim. If the data appears not to be suitable (due to quality or quantity of data) and the vendor wishes to continue, the Test Program can be altered and testing resumed. If the vendor does not feel that continued testing would meet satisfactory system performance requirements or the data quality requirements, he/she may decide to withdraw from testing at that time. However, should the vendor feel that the data are acceptable, then a formal submission to the ETV Program can be made. ETV Canada can provide guidance and advice on the claim verification process. If the data are deemed to support the claim, the Test Agency (or vendor) should continue to the *Reporting* stage. If the data do not appear to support the claim, the vendor may wish to modify the claim to suit the data before proceeding to the next stage. The modified claim may or may not require additional sample collection.

Each specific testing program will be unique based on the type of environmental technology, the specific application, the media impacted by implementation of the technology, and the actual claim being verified. As such, the General Test Protocol is to be used as a guidance document providing the necessary framework to establish a true testing program. In addition, it provides a list of references to more detailed information which should be used throughout the Testing Program, as appropriate.

Design Considerations



Introduction

For any Test Program, the design is the most critical step. It needs a lot of time and input from different sources which may include ETV Canada (or appointed expert), the Verification Entity, Test Agency, and most importantly, the vendor. Development of a suitable experimental design is essential and should be a cooperative effort to ensure that the plan is acceptable in terms of the technology capability and that quality data is generated in support of the vendor's claim.

The plan must consider a broad range of issues at the design stage including program objectives, participants, data requirements, sampling and equipment needs, health & safety issues, analytical requirements, and a strategy for data assessment.

Note, the General Test Protocol is intended to be a stand alone procedure. Although many of the references included in this document should be consulted in preparation of a detailed Testing Program, the Test Protocol is independent of the Verification Protocol. As such, the Testing Program designed by the Test Agency or vendor does not require ETV Canada approval or input. However, assistance is available from ETV Canada (or its designated expert) if the Test Agency or vendor desires. Again, it is advantageous for the vendor to obtain some level of acknowledgment from ETV Canada or a Verification Entity regarding the suitability of the Testing Program design before implementing an expensive sampling campaign, if the vendor intends to submit the data to the ETV Program.

A typical sequence of steps for the *Design* stage may be as follows:

- Test Agency (or vendor) develops DRAFT Experimental plan.
- DRAFT plan submitted to ETV Canada or Verification Entity for review.
- ETV Canada or Verification Entity acknowledges plan, or offers recommendations for revision to the vendor.
- Test Agency (or vendor) proceeds with implementation of the plan.

Testing Program Criteria

The design of the Testing Program is the most important step in the testing process and includes a number of considerations, which are vital to a successful testing campaign. Table 1. presents a "Testing Program Checklist" that should be used as a guide to ensure that all components of a demonstration test are identified. The sections following Table 1 provide detailed information regarding each of these considerations.

Table 1. Testing Program Checklist

ID Number	Demonstration Test Criterion	Minimum Standard Established	Criteria Addressed in Plan
1	Objectives	❑	❑
2	Experimental Design	❑	❑
3	Personnel	❑	❑
4	Health, Safety & Training Requirements	❑	❑
5	Sampling Methodology	❑	❑
6	Sampling Locations	❑	❑
7	Sample Type	❑	❑
8	Number of Samples	❑	❑
9	Sampling Times/Frequency	❑	❑
10	Sampling Equipment	❑	❑
11	Sample Containers & Preservation	❑	❑
12	Sample Handling	❑	❑
13	Sample Quality Assurance/Quality Control	❑	❑
14	Sampling Records	❑	❑
15	Sample Chain of Custody	❑	❑
16	Sample Disposal	❑	❑
17	Analytical Laboratory Requirements	❑	❑
18	Analytical Procedures	❑	❑
19	Quality Assurance Requirements	❑	❑
20	Operating Conditions	❑	❑
21	Process Control Equipment	❑	❑
22	Sample Security & Archival	❑	❑
23	Scheduling	❑	❑
24	Experimental Plan Review	❑	❑
25	Auditing Program	❑	❑

1. Objectives

The objective of most sampling programs is to produce a representative set of samples which are acceptable for analysis. The information (data) obtained will be used in the validation of performance claims made by clients concerning environmental technologies and processes operating under specified conditions.

The basis of the Testing Program is the selection of an appropriate experimental design. In order for an experimental design to be appropriate, it must ensure that data collected assesses the technology in terms of verification of the performance claim under specified conditions. This would include testing conducted at pre-defined process operating conditions and feed conditions that are consistent with the technology claim. The design must ensure that stable operating conditions are established since testing is designed to confirm successful operation of a technology. Testing, for verification purposes, is not intended to predict the performance of a technology under untested conditions, which is beyond the scope of the ETV program. Essentially, testing for verification purposes is the demonstration and evaluation of a technology under clearly defined conditions.

As part of the objectives, claims that are to be evaluated by the testing program must be identified along with the operating conditions to be used (i.e., the operating conditions under which the claims are professed valid).

2. Experimental Design

The experimental plan must clearly identify the scope of the work. Written instructions or Standard Operating Procedures (SOPs) for all sampling activities must be included. As much information as possible about the site or area of concern should be collected in order to formulate an effective workplan and sampling plan and also to determine safety requirements.

Most experimental programs are designed to evaluate a number of parameters and conditions (at some number of levels) which may affect the response of an environmental process. Typically, these designs are used to develop the technology and establish the normal operating conditions. For verification purposes, normal operating conditions are defined by the vendor and an appropriate sampling campaign is then limited to testing the response of the process under these operating conditions. For the ETV Test Protocol, the experimental program or sampling campaign must be designed to ensure that test data of all variables representing the specified operating ranges of the process are effectively and economically assessed. For completeness to the Test Protocol, a number of useful experimental designs that are typically used for identifying optimum conditions, but which will also be practical for verification purposes, are briefly described in Appendix C.

Simple experimental designs can be applied when operating conditions of the process are fixed at selected conditions. Complex designs are more practical when assessing the responses of processes that are operated over a range of conditions, and/or when a larger number of operating conditions dictate the process performance. In general, two basic types of experimental designs can be considered.

(1) Time series based design that assesses a batch process until the batch process reaches a conclusion. An example is monitoring the effluent from an ion exchange column until breakthrough of a contaminant is observed.

(2) Ongoing monitoring of a continuous process to determine the response over a representative period. An example is the monitoring of the effect of UV disinfection of treated effluent.

The design must be developed to cover all aspects related to the collection of quality data in support of the vendor's performance claim. To ensure effective, representative, unbiased data collection an acceptable experimental design must consist of randomly selected runs.

The choice of an appropriate experimental design (eg. completely randomized, Latin square, etc.) is not always easy, as more than one design can often be used to test a hypothesis. The "treatment design" refers to the types of treatments and controls to be used; treatments are defined as "the different procedures whose effects are to be measured and compared"[1]. The treatment design is extremely important to the overall study plan, as it determines the type of information available for providing strong justification for performance claims.

[1] Cochran and Cox, (1992)

When properly applied, experimental designs ensure minimum sample requirements for maximum information at minimal costs. One example is the simple 3X3 design, which is used to test 3 conditions at 3 levels for a total of 9 tests. A Greco Latin design[2] is structured to evaluate 3 parameters at 3 conditions at 3 levels, but still with only 9 tests. The alternative to this latter case is to use a simple 3X3X3 design, which would require 27 tests to collect about the same information.

Additional examples of experimental designs are provided in Appendix C.

In general, performance claims for environmental technologies require samples to be collected in a random fashion to eliminate biases. Regardless of the experimental design selected, a clear consistent measurement of 'treatment' and 'control' elements is usually required. The principles of randomness, treatment and control are the most important considerations regarding experimental design for ETV Testing purposes.

After a particular sampling design is developed, the Verification Entity (VE) will review the plan. The VE may then provide feedback to the vendor or Test Agency. The checklist, presented in Table 1, is designed to assist either the vendor (or Test Agency) and the VE in evaluating the test plan. The vendor and/or Test Agency should closely review this checklist to ensure compliance with, and an understanding of each criterion, prior to implementing the plan.

3. Personnel[3]

Personnel must be identified who will be responsible for collecting, preserving and shipping samples to the analytical laboratory. Personnel must have an acceptable level of knowledge and experience related to the environmental process and equipment, sampling techniques, the location(s) being sampled, and access to sampling tools, equipment, and procedures.

Careful consideration must be given to the personnel assigned to each task to insure effective, efficient and safe work. Sampling from sites containing hazardous materials requires effective administrative controls, and technical expertise and scientific support to ensure the collection of reliable data. Site sampling should include an individual or team with the expertise necessary for successful and safe sampling. Understanding the principles of analytical methods and its sensitivity will also directly influence the type of sample to be collected.

4. Health, Safety & Training Requirements

It is important to determine the level of safety requirements for the particular test site. Industries usually have strict safety procedures, require personnel entering the site to complete required safety training courses, and use all required safety equipment.

A list of all health and safety requirements including all personal protective equipment (PPE) must be compiled and distributed to all members of the sampling team. Product Material Safety Data Sheets (MSDS) must be consulted to offer guidance with respect to safety concerns and equipment requirements. A Health and Safety Action Plan and a Spill Response Action Plan (as appropriate) must be prepared and prominently displayed.

[2] Box, Hunter and Hunter (1978)
[3] Adapted from WTI, 1996.

A simple checklist can be prepared to ensure that the requirements for Health and Safety and Training have been satisfied by the testing agency and by each participant in the demonstration testing. An example of this checklist is presented in Table 2.

Table 2. System Operations, Health, Safety, and Training Requirements Checklist

Requirement	Acknowledged
User Manual(s) Provided	❒
Standard Operating Practices Available	❒
Operation & Maintenance Procedures Specified	❒
MSDS Available	❒
WHMIS Information Posted	❒
Safety Plan Developed	❒
Emergency Response Plan Prepared	❒
Protective Equipment Identified	❒
Off Site "Hands On" Training Provided	❒
On Site "Hands On" Training Provided	❒
Other:	❒
Other:	❒

5. Sampling Methodology

The selection of the proper sampling methods and equipment will be made based on a number of criteria, including: practicality, representativeness, cost, ease of operation, compatibility with analytical considerations, versatility and safety.

The methodology must have acceptable and verifiable precision, bias or accuracy, and sensitivity. Sampling protocols, which are acceptable, are described in the following. If an alternative protocol or methodology is used, the specific procedure, which was followed, must be documented including a succinct justification for using the method identified.

Water/Wastewater

For most water and wastewater treatment technologies, standard sampling protocols are well established. Sampling protocols identified in "Standard Methods for the Examination of Water and Wastewater", (APHA et al., 1995), should be followed. If this methodology is not used, the selected methods must be proven equivalent to the integrity of the methods identified in the Standard Methods text. Alternatively, Municipal/Industrial Strategy for Abatement (MISA) protocols may be used, as they are based on the Standard Methods.

In some cases, other sampling protocols may be acceptable depending on the nature of the technology being evaluated and the samples being collected. If an alternative sampling methodology is applied, documentation must be provided that confirms that the alternative methodology is at least equivalent to Standard Methods and ensures that the integrity of all of the criteria and specifications of this Test Protocol are maintained.

Standard Methods includes a description of sample collection and preservation techniques, safety considerations, a description of sample types, chain-of-custody procedures, containers, and recommended quantity of samples. The procedures described in Standard Methods are

intended for the examination of waters of a wide range of quality, including water suitable for domestic or industrial supplies, surface water, ground water, cooling or circulating water, boiler water, boiler feed water, treated and untreated municipal or industrial wastewater, and saline water.

Air Emissions

Air sampling procedures have been described in (MOEE, 1980; US EPA, 1996a; EC, 1993). These documents describe the acceptable practices for sampling locations, air emission guidelines and a variety of test methods used for air sampling. Regulatory jurisdictions often have similar versions of air sampling procedures.

A source sampling test is performed to measure the emissions of an air pollutant from an industrial operation. The rate and magnitude of these emissions vary with changes in the production rate and the process control and pollution abatement device operating parameters. It is crucial for the proper interpretation of the test results that all parameters affecting the emissions is closely monitored during the execution of a source sampling test.

The MOEE code (1980) describes the apparatus and techniques used to conduct source sampling tests. The first four methods - location of sampling site and sampling points, measurement of velocity and volumetric flow rate, determination of dry gas molecular weight and moisture content - are required, all or in part, to be performed in conjunction with subsequent methods which deal with measuring the concentrations of specific pollutants. These four methods are often performed simultaneously, e.g., in conducting a Method 5 particulate test, a velocity traverse and a moisture content determination are included as part of the procedure of that method.

Continuous emission monitors act as a long term continuous grab sample, either mechanically dawn through a filter or absorbent or chemically absorbed on a surface sensor. The period over which the sample is collected is important.

Solids (including Soil, Sediments and Sludges)

Solids sampling protocols (that include soil, sediments and sludges) have been effectively described in several protocols (US EPA, 1993 and US EPA 1986) and these protocols should be used. For the solid sample analysis, it is recommended that (CCME, 1993; US EPA, 1986; and ASA, 1986) be used. Other equivalent documents such as Carter (1993) may also be used. The EPA documents include description of sampling sites, sample types, sampling equipment and procedures. For the solid analysis, the references include a wide range of quality analysis and procedures for soil, sediments and sludges.

6. Sample Locations

Locations must be selected such that they are representative of typical process characteristics and mixing conditions. Typically, samples must be collected from the system input and output streams. Alternative sampling locations must be identified in the sampling design. Residual streams, which may include air streams, sludges/solids, and liquid wastes, should also be monitored. In this way, a much more accurate evaluation can be conducted by assessing the nature of residual waste streams and using mass balances to verify system performance.

Water/Wastewater

Samples must be collected from locations that are representative of the total water or wastewater stream. This location is typically at a point where full mixing occurs to ensure a homogenous sample; one, which ensures that, suspended material remains suspended. If sampling is not possible at an agitated point, then samples must be collected at a point in a pipe or stream which is located at a point downstream of at least 6 lengths from the last point of interjection.

Air Emissions[4]

The preferred location for the monitoring of an air emission from a stack is in a straight section of the stack or duct, close to the point of emission into the atmosphere, at least 8 stack or duct diameters downstream and 2 diameters upstream of any flow disturbance, such as a bend, expansion, contraction, visible lame, junction or stack exit. For rectangular stacks or ducts, an equivalent diameter for determining downstream and upstream distances is given by:

$$D = \frac{2LW}{(L+W)}$$

where *L* represents length, and *W* represents width.

For a circular stack or duct, at least two sampling ports with a 90° separation are required. Where applicable, the diameter passing through one port should be parallel to the centre line of an upstream flow disturbance and the other diameter should be perpendicular to this centre line. For a rectangular cross-section, ports are located on the most convenient face of the stack or duct.

Refer to Appendix E for alternatives when the criteria of eight and two diameters from disturbances cannot be met.

Soil, Sediment, Sludges (dispersed locations)[5]

To collect samples from materials dispersed over a large area, such as a pond, requires procedures that are more elaborate. Figure 2 is a systematic approach to sampling of soil or sediments from a pond or other large area.

Alternative sampling grids are presented in Appendix F.

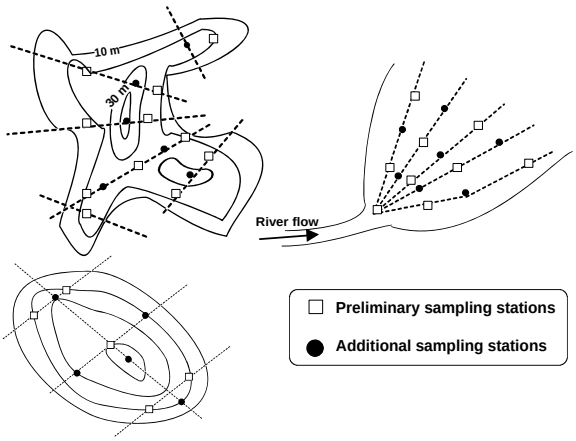


Figure 2. Example Sampling Grid

7. Sample Type

Three basic sampling approaches include random, systematic and judgmental. A combination of these approaches is usually the most feasible. These are accomplished using grab and composite samples. Exploratory sampling (screening) can establish the extent and variability in contaminant levels. Supplementary sampling can be used to confirm critical information and to clarify problem areas.

[4] Adapted from MOEE, 1980.
[5] Adapted from Carter, 1993

There are many variables involved in sampling process and waste streams: the composition of the waste streams themselves, the sampling locations (drums, pipes, tanks, pits, lagoons, soils, sediments, etc.) and the sampling equipment. Thus, professional judgment and common sense are very much required to ensure that a sample is truly representative of the process or waste stream being sampled. This will ultimately decide the type of sample, which is most appropriate for a given application.

A representative sample is one that encompasses all aspects of the waste, including particle size, concentration of constituents and effects of layering. The sample should be taken in such a way that it truly reflects the original material, since the quality of the analytical results generated from the samples is only as high as the quality of the sampling effort itself. While a laboratory will be able to test any sample submitted to it, an unrepresentative sample can lead to misconceptions about the technology, wasted resources to conduct the sampling effort and analyses, and ultimately failure of the technology to gain Verification.

Water/Wastewater

Sample types may include grab samples if feed conditions are relatively constant and the stream is well mixed, or composite samples where feed conditions may vary over time. A grab sample is meant to represent the sample stream at a given point in time as opposed to a composite sample, which represents the sample stream over a longer time (e.g., 24 hours). Another useful application of grab samples is for a situation where the source is known to vary with time. Grab samples collected at suitable intervals and analyzed separately can document the extent, frequency, and duration of these variations.

Grab samples can be collected by using an automated sampling device in the manual mode, or by dipping an appropriate container, bucket, bottle or vial, into the media stream using an appropriate retrieval device such as a chain, rope, or pole. Grab samples may be combined in a single large container and subdivided later, or they may be collected in several individual containers, each dedicated to a specific analysis.

Composite samples may be collected on either a flow-proportional or a time-proportional basis depending on the specific stream characteristics. Where the feed flow rate is relatively constant (less than 10% deviation from the mean for 90% of measured flow rates), a time-proportional sample is usually adequate. If the feed flow rate is quite variable (>10% deviation from the mean for 90% of measured flow rates), then a time-proportional sample is usually required. Automatic sampling equipment is usually used for composite sample collection.

For certain purposes, the information needed is provided best by analyzing mixtures of grab samples collected from different points simultaneously, or as nearly so as possible. An example of the need for integrated sampling occurs in a river or stream that varies in composition across its width and depth. To evaluate average composition or total loading, a mixture of samples representing various points in the cross-section must be used, in proportion to their relative flows. The need for integrated samples also may exist if combined treatment is proposed for several separate wastewater streams, the interaction of which may have a significant effect on treatability or even on composition.[6]

More detailed information has been included in Appendix D. For specific guidelines to be followed refer to MISA document.

[6] APHA et al., 1995

Air Emission[7]

The sample type is influenced by the target pollutant and the nature and consistency of the exhaust gases. Grab sampling is usually used if the stack gas flow is non-stratified and it's composition remains uniform over the sampling period. Integrated samples are a blend of grab samples collected simultaneously from a number of different points. If the stack gas flow is non-stratified but its composition varies with time or if the precision of single grab samples cannot be met, integrated sampling should be used.

Gas stratification in the stack may be present where there is an ambient air intake close to the sampling site, where there is mixing of exhausts from different processes, or possibly in horizontal ducts carrying a mixture of gases of different densities. Where stratification is suspected, choose a traverse such that a gas concentration profile across it would reveal any stratification. For example, the traverse should be parallel to the centre line down through the normal at the point of entry of the inlet gases into the duct or stack. In the case of horizontal inlet bends into the duct of stack, the traverse is usually horizontal, while in the case of vertical inlet bends, the traverse is usually vertical.

Soil[8]

Types of samples will include grab or composite samples for soils. A grab sample represents a single collection at a selected point or location. A composite sample will be comprised of a number of grabs from different points at the same location that are mixed to create a single "blended" sample.

Sampling the soil surface, especially for atmospheric depositions, necessitates a very shallow (< 5 cm) depth. Care must be taken to avoid unnecessary "dilution" with nonimpacted, deeper soils. Either grab or composite sampling can be used.

Depth sampling usually involves devices, such as an auger, to collect a core from the subsurface soil. Grab samples in this case involves the separation of segments or layers of the core into individual samples for subsequent analysis. A composite depth sample involves blending the core and collecting a subsample from the homogenized sample for analysis. If necessary, several cores can be collected and blended to provide a composite sample from a wide surface area or series of depths. Compositing cores provides average values of soil properties at a given site, however, discrete information about variability in the soil with depth is lost with compositing.

Sediment

Bottom sediments are typically variable, with their physical-chemical properties varying horizontally across a water body and vertically down the sediment profile. Sample types for sediments will be similar to those for soils. Grab samples may offer greater value in determining profiles both horizontally and vertically. Composite samples will be limited to providing only average values. Information describing sediment types has been reported by Mudroch and Azcue (1995).

Sludge

Due to the introduction within the last decade of regulations on the agricultural use of sewage sludge, increased emphasis has been placed on improving sampling methodologies in order to

[7] Adapted from MOEE, 1980.
[8] Adapted from Carter (1993).

obtain samples, which are, representative of the entire amount of sludge. Two references[9] provide background documents on this subject.

Fluid sludge[10]
In order to obtain an estimate of nutrients and metals in the sludge, which is being applied to the land, a representative sample must be provided for analysis. Samples should be taken from a composited mixture of a series of grab samples of the material being sampled that day. Clean non-metallic, acid cleaned containers for grabs and composites should be used. Sufficient sample volume to perform the required analyses must be collected. A 1L sample or a volume containing 1 gram dry weight for metals analysis and 1 L for pathogens and indicator organisms should be collected. Appropriate preservation techniques must be utilized for the various analyses. These are described in a later section.

Dried and Dewatered Sludge[11]
A composite mixture of grab samples of approximately 1 kg should be collected during a designated sampling period. The grab samples should be collected in strong, sealable plastic bags and immediately sealed after sampling to prevent moisture loss. The grabs are then emptied onto a flat non-metallic surface and mixed. Small subsamples from all sections of the sample, amounting to approximately 2 kg, are combined in a second plastic sealable bag. Alternately ASTM standards D346-75, D420-68, D1452-65 or D2234-76 may be employed.

8. Number of Samples[11]

Given the random variations in both an analytical procedure and the errors associated with sample retrieval, a single sample is usually insufficient for a desired level of uncertainty. If an overall standard deviation is known (or can be estimated), the required number of samples may be established by the following relationship:

$$N \geq \left(\frac{ts}{U}\right)^2$$

where:
N = number of samples,
t = Student-t statistic for a given confidence level,
s = overall standard deviation, and
U = acceptable level of uncertainty

For example, if s is 0.5 mg/L, U is $\pm$ 0.2 mg/L, and a 95% confidence level is desired, approximately 25 to 30 samples must be taken.

Note the process of identifying an appropriate number of samples is usually iterative in nature. As analytical results from the initial set of samples are made available, the standard deviation can be better estimated, resulting in a more accurate estimate of the number of samples required.

In general terms, the statistic discussed in the foregoing should be used to identify the number of samples required and is generally applicable to those situations where it is feasible to collect a large number of samples (e.g. water or wastewater). However, a number of media-specific

[9] Gomez et al., 1985; US EPA, 1994.
[10] Adapted from MOEE, 1996.
[11] APHA et al., 1995

guidelines have also been established to provide vendors with a "rule-of-thumb" type estimate, as explained in the following.

Water/Wastewater

A minimum of ten (10) data points is required for a given set of operating conditions. For a continuous process operating under steady state conditions a single ten-sample data set may be acceptable, however additional sample collection is preferred. For batch processes, a minimum of three (3) runs is required under identical operating conditions, again with a total of at least 10 data points for each run.

Air Emission[12]

The appropriate number of sample points (or traverse points) that make up a single air emission composite sample has been specified by EC (1993). It is important that the data describing the air emission control technology be statistically valid to confirm a Performance Claim verification. The minimum number of composites (made up of a sample at each traverse point) that would be acceptable for assessing an air emission point source is recommended to be three.

If samples can be collected at a location that is at least 8 stack or duct diameters downstream and 2 stack or duct diameters upstream of a flow disturbance, then the minimum number of traverse points for sampling is presented in Table 3. **If the criteria of eight and two diameters cannot be met, then the number of traverse points and their locations are given in Table E1 (Appendix E).**

Table 3. Minimum Number of Traverse Points for Sampling Sites
(where 8 & 2 diameter criteria are satisfied[13]).

	Minimum Number of Traverse Points	
Stack (Duct) Diameter (m)	Circular Duct	Rectangular Duct
> 0.61	12	12
0.30 to 0.61	8	9

Soil and Sediment[14]

Statistical concepts in soil sampling described by Mudroch & Azcue (1995) can be applied to the selection of the number of sampling stations in bottom sediment sampling. The cost of sampling and analyses of the sediment can be decreased by taking only as many samples as are needed for the given level of precision. The following example calculating the necessary number of sampling station. For example, unless a 5% chance of error occurs, we want the sample mean to be within $\pm$ 1.5 μg/g of the population mean. The following formula is used in calculating the number of needed sampling stations (n).

$$\eta = \frac{t^2 s^2}{D^2}$$

where:
t is a number chosen from a "Student t " statistics table for a chosen level of precision, (eg. 95%) and the degrees of freedom for t are first chosen arbitrarily, (i.e. 10), and then modified by reiteration. s^2 is the variance, known beforehand from other studies or estimated by $s^2 = (R/4)^2$, where R is the estimated range of concentration likely to be encountered in

[12] Adapted from MOEE, 1980.
[13] Taken from EC, 1993.
[14] From Mudroch and Azcue, 1995

sampling. *D* is the variability in mean concentration of contaminant we are willing to accept. (The formula is based on the assumption that the sample mean is normally distributed).

$$\eta = \frac{(2.23)^2 (3.25)^2}{(1.5)^2} = 23$$

where, O is the estimated number of sampling stations at 95% probability and within 1.5 μg/g of the true mean for sediment with a concentration of contaminant ranging from 0 to 13 μg/g.

$$\eta = \frac{(2.069)^2 (3.25)^2}{(1.5)^2} = 20$$

Since 23 sampling stations are considerably more than the 10 used to obtain a *t* value in the original iteration, we need to run the following reiteration using a *t* value representative of the new estimate.

A quantitative determination of a contaminant in twenty samples can still be expensive, but the estimated variance is high, i.e., a range from 0 to 13 μg/g of the contaminant in sediment. Any sampling scheme that reduces the variance will lower the number of needed sampling stations. The number can also be lowered by relaxing the probability from 95 to 90% or by allowing the confidence limits to increase to ± 2 μg/g or greater.

Sludge

Biosolids that are land applied are sampled on a quarterly basis. Biosolids that are not utilized are sampled on a yearly basis. These requirements apply only when a consistent historical record of all the parameters can be established.

For other installations, the following recommendations should be used. Sampling for all parameters should occur at a rate of twice per month during the period when biosolids are being applied to the land. Sampling should occur at least twice in the two months before land application. Changes in the quality of the biosolids due to process changes dictate that more frequent sampling should occur. Monteith (1978) suggested that digested sludge quality should be assessed one sampling day per two week interval. It was suggested that two samples per month for a 6 month period would be required to make statistically valid conclusions about the analytical data at any one site. These recommendations apply to fluid and dried samples.

A minimum number of samples collected over a reasonable time frame for the process (eg. digester) would be 3 grabs blended into 1 composite for each batch x 2 batches per month x 6 months providing 12 composites[15]. Using a similar logic, it is recommended that for a filter press with a much shorter cyclic period, 1 composite (of 3 grabs) x 3 batches per week x 4 weeks = 12 composites in a 1 month period would provide a sufficient sample number.

9. Sampling Times/Frequency

Sampling times or 'frequency' refers to exactly when during the test the samples are to be collected. This will depend on when steady-state is reached in the process, the existence of any diurnal or cyclic periods, how long it takes to acquire a sufficient amount of sample for collection. The type of stream or process being monitored will also impact on the sampling frequency. Examples of different types of processes include batch and continuous, each of which may be monitored differently. The effect of seasonal variation, equipment start up and changing feed conditions must also be taken into account. In general, sampling intervals should be chosen

[15] From MOEE, 1996

based on the expected frequency of changes. In practical applications, this may vary from as little as 5 minutes to as long as 1 hour or more. Seasonal variations in natural systems may necessitate sampling over months, depending on the specific claim(s) being made.

Although it is difficult to offer specific guidelines in a generic Test Protocol, as a minimum the sample frequency must provide a reasonable characterization of system performance under the operating conditions identified. In addition, sampling under such conditions must be repeated a number of times, where practical[16] such that the data may be verified by statistical analysis. Specifically, the data must prove that the technology meets the desired performance level within a 95% confidence level.

10. Sampling Equipment

Numerous measuring and sampling devices need to be carried into the field in order to generate and record the required information. In order to assure quality data, all sampling equipment and instrumentation must be in good working order and properly cleaned and calibrated prior to initiating the sampling campaign. Equipment (& instrumentation) may also have to be cleaned in between sample intervals and after sampling is complete. A lot of glassware is used in air emission source sampling trains. Depending on the target pollutant, glassware clean-up is required prior to sampling. In special cases, such as for dioxins and furans, proofing is also required before testing.

Materials in contact with the sample media must be resistant to environmental factors (such as corrosion, temperature, etc.) and must be compatible with the sample media itself. Collecting samples from different media will require special tools and equipment to ensure samples are representative of the bulk stream.

Additional information on Sampling Equipment for water and wastewater sampling is provided in Appendix D. Additional information on Sampling Equipment for air emission monitoring is provided in Appendix E. Additional information on Sampling Equipment for solids sampling is provided in Appendix F.

11. Sample Containers & Preservation

The laboratory performing the analyses should be consulted for information on required sample container type (glass or plastic, etc.), the minimum volume or weight of sample required, the preservative required, the permissible holding time and the required sample storage temperature.

Water and Wastewater[17]
Containers are typically made of plastic or glass for sample collection; however, one material may be preferable over the other depending on the contaminants of interest. For example, silica and sodium may be leached from glass but not from plastic; trace metals may adsorb on the surface of glass; and organic compounds cannot be collected in plastic containers except those made of fluorinated polymers. **Appendix D provides a summary of the types of containers and minimum sample volumes that should be applied to specific parameters.**

[16] For air monitoring, several repeat samples are not common due to the expense of sample collection.
[17] APHA et al., 1995

Methods of preservation are limited to retarding biological activity and chemical hydrolysis, to reducing volatile losses and to minimizing adsorption on sample container walls. Preservation methods are limited to pH control, chemical additions, use of amber or opaque glass, refrigeration, filtration or freezing. **Appendix D provides a table that summarizes the types of preservations that should be applied to specific parameters.**

Air
No preservatives are added to sampling canisters nor filter media used to capture particulates. Samples should be analyzed within 12 hours of collection. For air contaminants collected in aqueous traps, preservation techniques used in water and wastewater samples apply.

Soils and Sediments[18]
Preservation techniques are usually intended to retard microbial degradation, oxidation, and/or loss of volatile components. Methods are limited to pH control, poisoning, drying, refrigeration, freezing, and isolation from the atmosphere. No single preservation method is applicable to all constituents, so it is often necessary to preserve replicate samples or subsamples by different methods when a variety of parameters is required. In general, sample containers should be tightly sealed and headspace should be minimized as soon as the samples are taken. If acid digestion or chemical sequential extractions are required, these procedures should be carried out as soon as possible. Selection of the most appropriate methods should be based on the purpose of the study and the components to be determined.

Appendix F summarizes the preservation requirements for analyses of different parameters in sediment (and soil) samples.

12. Sample Handling

After a sample is collected, changes may occur that alters the sample's composition. Samples must be handled in a manner that minimizes these changes and prevents external contamination. Sample integrity and data reliability depends upon ensuring that samples are correctly managed. Samples will have a finite shelf life and chemical analyses must be conducted within the specified maximum storage period; storage period including sample collection and transportation times. It is important to ensure that proper storage facilities are provided at the sampling location (in the field), during transportation and at the laboratory prior to chemical analysis.

Appendices D and E provide a table that details the storage times for most parameters.

In addition, it is essential that every worker knows the potential hazards of the samples he/she is working with in order to take the necessary safety precautions to safeguard their own as well as their co-workers safety and health. The following are some issues that should be addressed when working with any hazardous materials:[19]

- Are containers used for dangerous substances free of leaks and do they otherwise appear to be adequate?
- Do the containers carry adequate and conspicuous warning labels or markings?

[18] Mudroch and Azcue, 1995
[19] From L Harrower, CFSSO, CCIW (27 Aug 97)

- Does the storage of material endanger the safety or health of employees because of unstable stacking or by concealing warning signs or symbols?
- Are proper storage cabinets available, and used, for any flammable, combustible or toxic substances?
- Are inter-reactive chemicals (e.g. acids, bases, corrosives, oxidizers, flammables) stored separately?
- Is ventilation adequate for the nature of the activities associated with the samples?

These are by no means the only questions that should be asked when working with hazardous materials but combined with the basics of the WHMIS system and proper field and lab discipline, should provide a safe, healthy testing environment.

13. Sample Quality Assurance/Quality Control

A description of Quality Assurance/Quality Control (QA/QC) is presented in a following section of this protocol (1.9. Quality Assurance Requirements). For the purposes of the ETV Program, it is recommended that a minimum of 15% of samples that are collected be submitted for QA/QC purposes. These QA/QC samples should include:

- field blanks;
- replicate samples (including split samples);
- spiked samples for recovery analysis.

14. Sampling Records

Records of sampling and equipment maintenance must be kept current and accessible for review. Records must include:

- date and time of all sampling activity including grab and toxicity samples and performance check samples for on-line analyzers, etc;
- temperature stability records;
- sample identifications
- sample collection method (i.e., autosampler, 24 hour composite, grab etc.);
- identification of sampling staff;
- malfunctions and corrective action taken;
- maintenance log including frequency and type of maintenance performed on equipment, etc.,
- calibration, cleaning, repair log for on-line analyzers
- any other relevant information.

Note, any sampling malfunctions/problems which may impact sample analysis must be reported, recorded and communicated to the laboratories performing the analysis.

15. Sample Chain of Custody[20]

It is essential to insure sample integrity from collection to data reporting. This includes the ability to trace possession and handling of the sample from the time of collection through analysis and final disposition. This process is referred to as chain of custody and is important in demonstrating sample control when litigation is involved. This will also prove useful when

[20] Ref. APHA et al., 1995.

justifying sample data quality for programs such as the Environmental Technology Verification process. A sample is considered to be under a person's custody if it is in the individual's physical possession, in the individual's sight, secured in a tamper-proof way by that individual, or secured in an area restricted to authorized personnel.

Records must be maintained regarding chain of custody of samples from collection through the analytical laboratory to reporting of the results. A chain-of-custody record must accompany each sample or group of samples. This record should include:

- Sample label, including sample number and description;
- Container type and size;
- Signature of collector;
- Date, time, and address of collection;
- Sample type;
- Sample analysis request sheet;
- Sample delivery to laboratory;
- Receipt at laboratory and logging of sample;
- Signature of persons involved in the chain of possession, including dates.

16. Sample Disposal[21]

The proper disposal of investigation-derived waste is important. Many questions need to be answered prior to disposing of waste material including:

1. Is the waste considered hazardous?
2. Does the volume of the waste generated require special notifications/permits from Federal/Provincial regulators?
3. How do we transport the waste?
4. Where do we store the waste?
5. What mechanisms are in place to dispose of the waste?

The difficulty in the disposition of investigation-derived wastes is typically dependent upon whether the site is inactive and/or abandoned, or active. At active sites it should be possible to arrange for proper disposal through combining sampling wastes with the routine site waste streams. If the site is inactive, or if there are signs that the waste storage area site is frequented by people (hunters, children on trail bikes), arrangements will have to be made to transport and dispose of the waste off-site. If off-site removal and disposal are required, then a mechanism must be established to procure the proper transport and disposal services.

17. Analytical Laboratory Requirements

For verification requirements, the laboratory that will be used to analyze the samples must be identified and recorded. This will include specifying:

- the laboratory that will analyze the samples (based on their accreditation and capabilities);
- requirements for laboratory QA/QC.

[21] Adapted from WTI Manual, 1996.

It is a mandatory requirement that samples be submitted to an accredited laboratory, one that has been certified for analyzing specific parameters by the Canadian Association for Environment and Analytical Laboratories (CAEAL) and is an accredited PALCAN member. The ISO/IEC Guide 25 (1990) details the general requirements for a laboratory to be recognized as competent to carry out specific calibrations or tests. The following summarizes the main points in the ISO/IEC Guide 25 :

1. Organization and management
2. Quality system, audit and review
3. Personnel qualifications and training.
4. Laboratory accommodation and environment.
5. Equipment and reference materials.
6. Measurement traceability and calibration.
7. Calibration and test methods.
8. Handling of calibration and test items
9. Laboratory records.
10. Certificates and reports.
11. Sub-contracting of testing
12. Outside support services and supplies.

Guidance on the general principles and protocols to be followed in sample preparation, clean-up and instrumental analysis was provided by MOEE (1992). Key requirements that must be met are:

1. Analysis must be carried out by competent laboratory personnel in a properly equipped and maintained laboratory environment;
2. Analytical procedures must meet general accepted principals of good laboratory practice and quality control.
3. Analytical techniques must be appropriate for the sample matrix and must lead to accurate identification of the compounds to be analyzed.
4. Recovery of the target parameters must be optimized;
5. Analytical procedures must be comply with the principles and protocols described in the Ministry documents;
6. The method detection limit (MDL) must be determined for each target parameter.

18. Analytical Procedures

Multiple analytical methods usually exist for many of the analytes of interest in a sampling program. A number of references provide the details for acceptable analytical procedures that should be used to produce reliable data. These include: Standard Methods (APHA et al., 1995), MOEE (1992), US EPA (1986b) and a number of ASTM documents. EC (1996) presents eight groups of major analytes including general variables, inorganic, monocyclic aromatic compounds, phenolic compounds, PAH's, chlorinated hydrocarbons, pesticides and miscellaneous organic parameters along with some recommended analytical methodologies.

Pollutants associated with seven common industries are presented in Table C 2 and Table C3 (Appendix C). Information contained in these tables may assist in the identification of target compounds and other potential areas of concern.

For verification requirements, the laboratory procedures that will be used in the analysis of the samples must be identified and recorded. This should include the methodology used and the inherent verifiable precision, accuracy, and sensitivity.

Where measurements are made using field analytical methods (e.g. HACH Field Test Kit), at least 15% of the total number of samples must be submitted to a certified analytical laboratory, using recognized standard analytical procedures, to be used to develop and confirm a direct correlation between the field analyses and the recognized standard method of analysis. As an example, HACH Field Kits are typically used as indicator analyses (with some level of accuracy

and precision), but the data generated from these analyses may not be of sufficient quality to be used in a statistical analysis unless an effective QA/QC program has been included.

19. Quality Assurance Requirements[22]

Quality control is defined as the procedures established and observed in the field and the lab to ensure that the end result of testing activities meet the intended data quality objectives. Quality assurance is defined as the management system that is in place to ensure that QC procedures are being performed correctly.

It is necessary to specify the QA/QC requirements used to establish the quality of the data generated in the field and laboratory. This will include detailing how precision, accuracy, and sensitivity will be presented. Precision (the agreement between repeated measurements of the same quantity) may be shown as relative percent differences between field duplicates. Accuracy (the agreement between a measurement and an accepted or known value) may be shown by the percent recovery of matrix spikes. Method sensitivity including detection levels, linearity, and blank levels should be adequate to verify the standard or specification.

Quality assurance (QA) is a set of operating principles that, if strictly followed during sample collection and analysis, will produce data of known and defensible quality, namely, the accuracy of the analytical result can be stated with a high level of confidence. Quality assurance planning includes the following:

- Cover sheet with plan approval;
- Staff organization and responsibilities;
- Sample control and documentation procedures;
- Standard operating procedure for each analytical method;
- Analyst training requirements;
- Equipment preventive maintenance procedures;
- Calibration procedures;
- Internal quality control activities;
- Data assessment procedures for accuracy and precision, and data reduction, validation, and reporting.

Quality control is a technical document that specifies activities required to achieve data quality objectives and describes how all data are assessed for precision, accuracy, completeness, comparability, and compatibility. A quality control program consists of the following:

- Statement of operator competence;
- Recovery of known additions as part of an analytical protocol;
- Analysis of externally supplied standards by using certified reference materials as laboratory control standards;
- Analysis of reagent blanks whenever new reagents are used;
- Calibration with standards;
- Analysis of replicates; (analysis of 10% or more of the samples in duplicate recommended);

[22] Adapted from APHA et al., 1995

- Control charts. (Three types of control charts are used in laboratories: (1) a mean chart for laboratory control standards (LCS) or calibration check standards (CCS); (2) a means chart for background or reagent blank results; and (3) a range chart for replicate analysis.)

20. Operating Conditions

The vendor must specify the operating conditions to be in effect during the test, and include the duration of testing. If the claim is to be validated over a range of operating conditions, specify the number of tests that are to be conducted and the operating conditions for each test. Two approaches can be used to evaluate relevant operating conditions that affect the performance of the technology: (1) systematic approach or (2) factorial design.

One systematic approach is to select average values for the operating conditions and measure the response of the technology at these conditions. Further testing is conducted after adjusting the operating conditions by an increase in the settings of (say) 33% and the technology responses measured. The next tests are run at after decreasing the settings by 33% of the average operating conditions. Continue with further testing by making adjustments to the operational set values by (say) ± 50%, ± 75%, ± 100%, ± 150%, etc., to the acceptable limitations of the operating conditions for the technology.

An alternative systematic approach would be to establish the minimum (or maximum) values from the operating conditions and measure the technology responses. The operating conditions would then be adjusted incrementally higher (or lower) and the technology responses measured again. This is continued to the acceptable limitations of the technology.
A factorial design can be used to minimize the number of tests required to identify the important operating conditions and the normal ranges for effective performance of the technology. Box et al (1978) describe the principles and present examples of experimental factorial designs. A factorial design should include randomly selected replicates to allow a determination of the expected allowable error and effective identification of significant operating conditions or ranges.

Typically, the data collected during an evaluation of operating conditions (using either approach) are used to establish the normal operating conditions. The technology should then be tested over an extended period to collect sufficient data that validates the technology performance.

As an alternative to the demonstration phase, during the testing of the technology over the incremental changes to the operating conditions, if the data from the technology responses are consistent with a measurable correlation and are of sufficient quantity, the results may be used to validate the technology performance over the range of operating conditions. The relationship of the effects (or responses) of the technology over any range of operating conditions must be statistically sound. Sufficient data are required to allow a statistical assessment and to establish an acceptable 95% confidence limit about the correlation.

21. Process Control Equipment

All field analytical instrumentation and monitoring equipment (for monitoring performance and control of process and operating conditions) required for testing must be listed along with verification of the condition of each piece of equipment. Equipment may include, but is not limited to, flow, pressure, and temperature monitoring equipment, and specific analytical monitoring equipment.

As a minimum, all equipment must be clean, in good working order, and calibrated according to manufacturer specifications, prior to the testing campaign.

22. Sample Security & Archival[23]

It is essential to ensure sample integrity from collection to data reporting. Many of the issues discussed in 15. Sample Chain of Custody can be used for general sample security. The following procedures summarize the major aspects of security:

1. Record every sample collected and identify every bottle by attaching appropriately inscribed tag or label. Record sufficient information to provide sample identification.
2. Use sample seals to detect unauthorized tampering with samples up to the time of analysis. Attach seal in such a way that it is necessary to break it to open the sample container.
3. Record all the information in a bound log book, including location, sampling procedure, type of sample, sample description, field observations and measurements, signatures of personnel responsible. Protect the log book.
4. The custodian receiving the sample must inspect its condition and seal. This person is responsible for assigning a lab number, registering the sample in the laboratory log book, and storing it in a secured storage room or cabinet until it is assigned to an analyst.

If required, samples may be retained to their maximum recommended storage time for the selected parameters for subsequent analysis as necessary. Appropriate procedures must be documented. In addition, data generated from samples which are stored, then subsequently analyzed, must so be defined. **Maximum storage times for most parameters are identified in Tables D3 and F2 in Appendices D and F.**

23. Scheduling

A suitable testing schedule should be established which ensures that system performance monitoring occurs during representative operating conditions. This also allows for tracking of results to maintain an efficient sampling campaign without exceeding the program budget and expected resource utilization.

The test schedule should encompass any routine cyclic changes in environmental feed conditions. As a minimum, 3 cycles should be covered (or 3 batches in the case of batch testing).

24. Experimental Plan Review

Prior to initiating testing, it is important that all parties understand the approach proposed for testing. Participants may include, but are not limited to, the vendor, the Verification Entity, an ETV Canada appointed expert, and an approved Test Agency.

25. Auditing Program

[23] Adapted from APHA et al., 1995.

To ensure testing integrity, an unbiased, independent auditor must monitor at least a portion of the test program and should review all data and test procedures used to evaluate the technology under assessment. Where practical, the independent auditor should be involved in the testing and data collection. The independent inspector can include regulatory personnel, for example. Although rarely, in some cases, the client may assume the role of an independent auditor, however caution must be exercised when using this approach since the client could be perceived to have a vested interest in the technology.

The Verification Entity could be considered as an agent responsible for auditing the testing program. Acting both as program auditor and as the technology verifier would ensure consistency throughout the process and aid the Verification Entity with a greater level of confidence when conducting the performance claim verification. However, a conflict of interest could be perceived with the verification entity undertaking both the auditing of the program and verification of the performance claim. To remedy this situation, an independent auditor could be retained to audit the final verification report.

Data Collection

Introduction

Prior to implementing the plan, the Test Agency (or vendor) must ensure that the application, operating conditions, and technology performance are at expected levels. At this point, the Test Agency (or vendor) may initiate testing in accordance with the methodology identified in the plan. Note, any deviations from the plan must be identified and written explanation provided.

Implementing the plan includes a number of considerations including scheduling, process monitoring, sampling and data collection, data storage and control, and auditing of the Testing program. A suitable data quality assessment must then follow.

Process Monitoring

It is imperative that the equipment is operated under representative conditions during testing. Representative operating conditions include:

- the equipment is operated in accordance with the manufacturer's established parameters,
- established maintenance practices are followed,
- testing occurs under the operating conditions specified in the test design, and
- safe operating practices are followed.

As stated under *Design*, all equipment must be calibrated before, during, and after testing to ensure compliance with the set operating conditions.

All important process variables must be monitored at regular intervals (e.g., hourly) and recorded in electronic format (i.e., spreadsheet).

All deviations from representative operating conditions must be recorded with the reason for the deviation clearly identified.

For cyclic operations, the sampling period should be planned to span at least three complete cycles. Cycles of extended duration can be broken into definable parts with sampling occurring in representative portions of these parts.

Data Collection

No testing program will result in the generation of a single data set. Rather, the data generated during testing will consist of several related data sets. Generally, the data which is collected can be categorized as either *performance parameters*, or *operating conditions*.

- *Performance Parameters*
  The performance parameters to be monitored in support of claim verification may include one or several analytical parameters or output variables. An account of all relevant residual streams must also be considered as part of the data collection exercise. Note, in most cases input and output values must be collected to evaluate the effectiveness of the technology.

- *Operating Conditions*

Any parameter, variable, or condition which has or could have a significant impact on system performance should be considered an operating condition. Some of the more common operating conditions related to environmental technologies include volume, flow, concentration, pressure, temperature, level, residence time, and chemical addition rate.

Note, system performance targets should have already been identified in the *Design* step. Also, expected operating conditions should also have been identified. However, it is during the *Implementation* process that actual measured values are compared with expected values to ensure that the system is performing suitably within an acceptable operating range. If not, system adjustments may have to be performed before testing is resumed. If the adjustments are significant, the test run must be restarted.

Data Control

Data may be recorded in either electronic or manual format. However, all data forwarded to the Verification Entity for verification purposes must by in spreadsheet format, preferably Microsoft Excel. Acceptance of any other data format will be at the discretion of the Verification Entity.

All raw data must be documented and assembled in a suitable format. Pertinent data must be organized in electronic spreadsheet format prior to being submitted to the verification entity for the data quality assessment.

Auditing of Performance Test

The importance and requirements for auditing have been described in a previous section (**25. Auditing Program**). The parties involved in the third party review of the testing and data validation must be identified. Included in their identification must be an explanation of their experience and expertise as the auditor of the data for the technology being under tested.

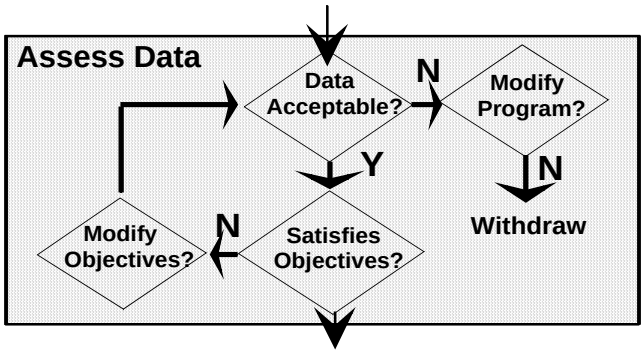
Table 5. provides a checklist for the Test Agency and/or vendor to use to ensure that data collected on the technology performance satisfies each of the criterion of the Test Protocol. If some information, or one or more criteria are not satisfied, it is at this point that additional data can be collected.

Table 5. Testing Program Checklist

ID Number	Demonstration Test Criterion	Achieves Minimum Standard	Fails Minimum Standard
1	Objectives	❑	❑
2	Experimental Design	❑	❑
3	Personnel	❑	❑
4	Health, Safety & Training Requirements	❑	❑
5	Sampling Methodology	❑	❑
6	Sampling Locations	❑	❑
7	Sample Type	❑	❑
8	Number of Samples	❑	❑
9	Sampling Times/Frequency	❑	❑
10	Sampling Equipment	❑	❑
11	Sample Containers & Preservation	❑	❑
12	Sample Handling	❑	❑
13	Sample Quality Assurance/Quality Control	❑	❑
14	Sampling Records	❑	❑
15	Sample Chain of Custody	❑	❑
16	Sample Disposal	❑	❑
17	Analytical Laboratory Requirements	❑	❑
18	Analytical Procedures	❑	❑
19	Quality Assurance Requirements	❑	❑
20	Operating Conditions	❑	❑
21	Process Control Equipment	❑	❑
22	Sample Security & Archival	❑	❑
23	Scheduling	❑	❑
24	Experimental Plan Review	❑	❑
25	Auditing Program	❑	❑

Data Assessment

Introduction



Data assessment is an iterative activity. Initial results should be evaluated and compared to expectations from the proposed experimental design. Deviations from expected results should be investigated to determine if the deviations are due to unusual operating conditions or unexpected feed conditions. If the deviations are actually unexpected responses, then changes to the experimental design, operating conditions or feed conditions can be made early in the program to continue with testing that satisfies the test objectives. It is important to note that these data represent a "start up" situation, but may not be acceptable for long term demonstration of the technology performance.

Although a detailed data assessment naturally follows the data collection process, it is important to at least identify how the data will be assessed for the specific application. The assessment strategy has a direct impact on the quantity and quality of data to be collected. As such, it warrants consideration during the design of the Testing program. The vendor should clearly identify the approach to be used during the data assessment stage. Specify the methodology that will be used to assess the data. This will include specification of:

- data interpretation and analysis needs, such as the use of specific statistical methods,
- requirements for data (and data base) security, archival & retention.

Data is to be assessed based on the principles of *relevance* and *quality*. A number of criteria must be met with regard to both of these principles, as identified in the initial stage: Design of Testing Program. Specifically, the criteria used to evaluate the relevance and quality of the data generated are described in Table 6. This checklist will be used by the Verification Entity (VE) during the Data Assessment process. The data assessment process which will be followed by the Verification Entity should be closely reviewed to ensure conformance.

To complement the *relevance* and *quality* criteria for assessing data, the following are examples of additional tools available for evaluating raw data generated during the Testing Program.

- Development and/or use of mathematical equations to describe relationships between key variables in a process. These equations could be used to compare predicted with observed results.
- Mass balances around a process to ensure that all major inputs and outputs are accounted.
- Statistical techniques to determine means, variances and confidence limits for measured data, and to test hypotheses (i.e., claims).

If applicable, all test results must be adjusted to standard conditions appropriate for the category of equipment and for the parameter measured. A number of Statistical Analysis Worksheets (SAW) have been developed to assist with the statistical analysis of data. These worksheets

are provided in Appendix B of the ETV General Verification Protocol. Similar statistical procedures are described in the US EPA Report "Guidance for Data Quality Assessment (1996).

The statistical procedures, described in these two documents, evaluate acceptability of the data sets that are being applied to the performance claim. Basically, the ETV Canada Protocol and the US EPA guidance document demonstarte the use of data quality assessment (scientific and statistical evaluation) procedures to ensure that "data obtained from environmental data operations are of the right type, quality and quantity to support their intended use."[24]

[24] US EPA (1996b)

Table 6. Data Assessment Final Checklist

Criterion	Yes	No
Relevance of Data		
Parameters measured in the process samples were appropriate to the claim being verified.	❑	❑
Samples were representative of typical process characteristics at the sampling locations.	❑	❑
Samples were collected under representative mixing conditions.	❑	❑
The appropriate type of sample was collected (eg. grab, composite, flow-proportional composite)	❑	❑
An adequate number of samples was collected to provide a representative data set.	❑	❑
The technology was operated within appropriate ranges of operating conditions during testing.	❑	❑
Quality of Data		
An acceptable experimental design was used for the testing program.	❑	❑
Site facilities for the test were adequate for generation of relevant data.	❑	❑
Operating conditions during the test were adequately monitored and documented.	❑	❑
Operating conditions were calibrated at an acceptable frequency.	❑	❑
Samples were collected according to acceptable sampling protocols.	❑	❑
Acceptable QA/QC procedures were followed during sample collection.	❑	❑
Samples were analyzed using acceptable analytical protocols.	❑	❑
The analytical laboratory was independent and appropriately accredited.	❑	❑
Acceptable QA/QC procedures were followed during laboratory analyses.	❑	❑
An acceptable chain-of-custody was used for sample handling and analysis.	❑	❑

Notes:

1. Instructions and explanations are provided in Appendix A.
2. Justification must be provided for a reject or not applicable selection.
3. *Reference to General Verification Protocol is temporary and will be excluded from final Test Protocol.

Reporting

The technology Testing Report shall include the following elements:

- Introduction
- Technology Description
- Objectives
- Testing Methodology
- Results
- Conclusions & Recommendations
- References
- Raw Data

These basic elements of the Test Report shall be identified during the test design phase. A brief description of each element to be included follows.

Introduction

Provide a background of the project, including the scope of testing and description of how the testing program was initiated.

Technology Description

Provide a brief description of the technology being tested, with a simple process flow chart. (The technology description should only describe the specific uses of the technology for which claims are being verified.) Include in the technology description, the following elements:

- The wastes (wastestreams) treated, measured or minimized by the process (include description of waste types, waste origin, concentration ranges, media);
- The intended application of the technology (what does it do & what does it do it to);
- List & description of documents that were reviewed to determine the unit processes or specific steps by which the process operates (e.g., design drawings, process flow diagrams, equipment specification sheets). Indicate which information is confidential.
- List & description of documents that were reviewed to determine methods for operating the technology to achieve the claims (Standard Operational Procedures, Users Manuals, Operational & Maintenance Manuals, Quality Assurance Procedures, etc.).

Objectives

Describe technology performance claims that were evaluated.

Testing Methodology

Include a description of how the following issues were addressed during the Testing program:

- equipment specifications;

- operating conditions (key operating variables, matrix of operating conditions selected for testing);

- sampling (locations, procedures, frequency, replicates, representivity of samples);

- sample analysis (parameters measured, analytical methods used, qualifications & accreditation of lab, QA/QC used)

Results

Provide summary tables and graphs of data (raw data are presented in the Appendix). Comment on the acceptability/soundness/consistency of sampling & analysis procedures used, what the analysis procedures can and cannot detect (accuracy & precision); the Quality Assurance Program and Quality Control procedures used. Include a description of the confidence with which it can be verified that the technology achieves what is claimed (statistical confidence of data; hypothesis testing to determine if claim was achieved). Describe any limitations of the technology that were noted during testing. Discuss deviations from pre-selected operating conditions or from pre-selected testing procedures.

Conclusions & Recommendations

Describe how test results support performance claim(s). Explain circumstances where data do not support claim(s). Recommend claims which should be acceptable for verification. Where appropriate, relate results to relevant regulatory requirements (eg. discharge or emission limits).

References

List all relevant technical literature and appropriate materials that were referenced during the testing design and/or planning phase.

Raw Data

Attach tables of all test data and electronic data files.

Appendix A

Bibliography

References

APHA ET AL., AWWA, WEF, (1995), Standard Methods for the Examination of Water and Wastewater, 19th Edition.

ASA, (1986a), (American Society of Agronomy) " Methods of Soil Analysis - Part I - Physical and Mineralogical" Klute, Ed.

ASA, (1986b), "Methods of Soil Analysis - Part II - Chemical and Microbiological Properties" Page, Miller, Keeney, Eds.

Box, G.E.P., Hunter, W.G. and Hunter, J.S., (1978), Statistics for Experimenters - An Introduction to Design, Data Analysis and Model Building, John Wylie & Sons, New York.

Carter, M.R., (1993), **Soil Sampling and Methods of Analysis**, Lewis Publishers.

CCME, (1993), (Canadian Council of Ministers of the Environment), Guidance Manual on Sampling, Analysis and Data Management for Contaminated Sites. Report CCME EPC-NCS62E.

Cochrane, W.G. and Cox, G.M. (1992), **Experimental Designs**, John Wiley & Sons.

Cooper, C.D. and Alley, F.C., (1990), " Air Pollution Control A Design Approach" Waveland Press Inc.

EC, (1993), (Environment Canada), "Reference Methods for Source Testing: Measurement of Releases of Particulates from Stationary Sources.", Reference Method EPS 1/RM/8.

EC, (1995), (Environment Canada), " The Inspector's Field Sampling Manual (A Sampling Manual and Reference Guide for Environment Canada Inspectors)" 1st Edition.

EC, (1996), "Multi-Media Sampling Training Course - Reference Manual", prepared for Environment Canada by Water Technology International Corporation.

Gomez, A. et al, (1985), **"Sampling Techniques for Sludge, Soil and Plants**" in Sampling Problems for the Chemical Analysis of Sludge, Soils and Plants, Elsevier Applied Science Publishers.

ISCO, "Open Channel Flow Measurement Handbook", first edition.

ISO Standards Handbook 16, (1983), "Measurement of Liquid Flow in Open Channels", first edition.

Lodge, J.P. Jr. (Editor), (1987), "**Methods of Air Sampling and Analysis**", 3rd Edition, Lewis Publishers.

MOEE, (1980), (Ministry of the Environment and Energy), Air Resources Branch, "Source Testing Code" Version #2, Report ARB-TDA-66-80.

MOEE, (1990), "Volatile Organic Compounds Monitoring Network Standard Operating Procedures and Technical Manual", Report No. ARB-224-89.

MOEE, (1992), "[MISA] Draft Protocol for the Sampling and Analysis of Industrial/Municipal Wastewater", Report: ISBN-07729-89709-2.

MOEE, (1996), & MAFRA (Ministry of Agriculture, Food and Rural Affairs), "Guidelines for the Utilization of Biosolids and Other Wastes on Agricultural Lands".

Monteith, H.D. and J.P. Stephenson, (1978), "Development of an Efficient Sampling Strategy to Characterize Digested Sludges", MOE Project No. 74-3-16, Research Report No. 71.

Mudroch, A and Azcue, JM., (1995), "**Manual on Aquatic Sediment Sampling**", Lewis Publishers.

UNEP, (1991) (United Nations Environment Program), "Audit and Reduction Manual for Industrial Emissions and Wastes", Technical Report Series Number 7, first edition.

US EPA, (1986a), "Permit Guidance Manual on Unsaturated Zone Monitoring for Hazardous Waste Land Treatment Units", Report EPA/530/SW-86-040.

US EPA, (1986b), "Test Methods for Evaluation of Solid Waste - Physical/Chemical Methods", EPA Report EPA-SW-846.

US EPA, (1991), "Description and Sampling of Contaminated Soils (A Field Pocket Guide)", Report EPA/625/12-91/002.

US EPA, (1993), "Subsurface Characterization and Monitoring Techniques: A Desk Reference Guide, Volume I: Solids and Ground Water, Appendices A and B", Report EPA/625/R-93/003a.

US EPA, (1994), "Land Application of Sewage Sludge", Report EPA/831-B-93-002b

US EPA, (1996a), (Environmental Protection Agency), "Code of Federal Regulations: Title 40, Part 60".

US EPA, (1996b), "Guidance for Data Quality Assessment - Practical Methods for Data Analysis, Report EPA QA/G-9, QA96 Version.", Report EPA/600/R-96/084.

Appendix B

Definitions & Glossary

Glossary of Terms for Environmental Technology Testing

Accreditation is recognition by an established (registered) organization for competence in performing high quality activities.

Air Emissions are airborne exhausts from industrial and municipal sources that result in gases, dusts and other contaminants contributing/discharging into the atmosphere. Ambient or atmospheric air is background air. Pure, clean air is a very rare commodity, if it actually exists. The availability of clean (or pure) air is compromised by pollutants from a variety of point sources and non point source locations that contribute gases, vapors and particulates.

Applicant (vendor) is the agent, supplier or manufacturer, who submits an environmental technology for verification through the ETV Program.

Assessment involves a review of data and information that describes the performance and integrity of an environmental technology or process. The effort applied to the assessment and the severity of the specifications in an assessment protocol dictate the merit of the result. In increasing order of rigor, the recognized products are: (1) peer review of data, (2) verification, (3) certification, (4) guarantee.

Audit involves a review of the performance and integrity of an environmental technology.

CAEAL = Canadian Association of Environmental Analytical Laboratories Inc., a partner in the SCC Program for the Accreditation of Laboratories (Canada), is an agency for certifying laboratories for the analyses of specific parameters. Some 87 labs have been certified under the Laboratory Certification Program. The most recent Directory is available at http://www.caeal.ca.

Certification involves the repeated or ongoing assessment of a technology performance by an independent third party, based on it meeting some established set of standards(s). Certification also normally includes liability.

Chain-of-Custody refers to the ability to trace the possession and handling of the sample from the time of collection through analysis and final disposition, to ensure sample integrity from collection to data reporting (Standard Methods, 1992).

Confidence Interval describes a range of values that contains the expected value of the target parameter with some defined associated level of probability or confidence. The confidence limits are the expected (probable) upper and lower (maximum and minimum) values for the data set.

Conformance is an affirmation or judgment that an activity, product or process has met the requirements of the relevant specifications or standards.

Contaminated soils are natural or artificial deposits of soil that have been contaminated with liquid and solid discharges resulting in an adverse impact on the use or value of the soil.

CSA = Canadian Standards Association.

Data set is a series of recorded observations that are specific to a single control or operating parameter or waste, feed or discharge characteristic.

Environmental Benefit is any significant alleviation of the detrimental effects that the creation, use or disposal of goods or services has on the environment and the health and welfare of humans and ecology.

Environmental Technology (product or process) is a system consisting of equipment and/or materials, the operating procedures and the skills and knowledge to fulfill specified requirements for environmental performance, reliability and safety. Included should be the associated quality control elements that apply to the manufacturer and to the user of the technology.

Equipment-based environmental service is a service that can make claims solely on measurable performance of the equipment or technology under specified conditions.

ETV Canada is responsible for the management and delivery of the ETV Program and oversees each verification and issues the verification certificates. ETV Canada uses approved Verification Entities to conduct independent assessments of the technology performance claims.

Hypothesis testing is a statistical technique used to select one conclusion from two possible choices (null hypothesis, alternative hypothesis). This method is used when a decision requires a high degree of confidence, such as in the verification of a performance claim. The **Null Hypothesis (H_o)** is a simple statement that a statistic is mathematically acceptable or correct, when the hypothesis is evaluated within an acceptable range of probability (eg. at the 95% confidence level.) If the null hypothesis is concluded to be false, then the **Alternative Hypothesis (H_A)** will be assumed to be true.

ISO/IEC = International Organization for Standardization/International Electrotechnical Commission

Mean Value is a single number used to represent the average of several related but distinct values. For example, if six temperature measurements are taken during a three-day test, then the mean temperature might be used to represent the average temperature for analysis and reporting. The most common average for most applications is the arithmetic mean. The geometric mean is sometimes used when the measured values are subject to very wide variations.

NSC = National Standard of Canada

NSS = National Standards System

Performance claim is a measurable, reproducible, verifiable, and specific technology result which describes the performance of the environmental technology.

Reference Laboratory is a laboratory owned and operated by a government regulatory agency for the principle purpose of analyzing samples referred to by other laboratories for confirmatory analysis. A reference laboratory [conducts] quality assurance functions relative

to other laboratories and may [perform] unusual, highly specialized, and difficult analyses not generally available through commercial laboratories.

Robust Procedures are statistical procedures which are insensitive to deviations from normality in the data.

Run (see Sample campaign)

Sample campaign (Run, Test) represents the complete number of data sets that are required to assess the performance of an environmental technology, including the control parameters and the feed and discharge characteristics.

Sample population is a representative data set for a particular parameter.

SCC = Standards Council of Canada

Sediments are deposits on the bottoms of rivers, lakes or oceans from natural or manmade sources that result in an impacted effect on the original natural bottom surface. For environmental purposes, sediments are those that have a detrimental impact on the bottom material or bottom dwelling organisms.

Sludge is the solid residues from water and wastewater treatment processes. Municipal sewage treatment results in biosolids, which are often contaminated with metals, toxic organics, etc. from industrial sources contributing to sanitary sewers. Industrial sludges result from solid separation processes in treatment processes that consist of concentrated amounts of inorganic or organic industrial wastes and/or byproducts from production processes. Sludges can be classified as fluid sludges which typically result from clarifiers, lagoons, settling basins, filters and other solid liquid separation devices. Dewatered sludges are the other general type of sludges resulting from unit processes which concentrate fluid sludges from concentrations as low as ½% solids to a dewatered sludge that is typically 10% or greater in solids content.

Soils (see Contaminated Soils)

Standard Deviation is a measure of the spread of the data, defined as the square root of the variance.

Test (see Sample campaign)

Testing Agency is an organization that has been contracted by the technology vendor, ETV Canada or the Verification Entity (at the technology vendor's request) to evaluate a technology. The Testing Agency will collect additional data, following appropriate ETV Test Protocols to provide adequate information to permit the completion of a performance claim verification. Where appropriate, accredited testing laboratories should be used.

Test Protocol is the detailed procedures for generating data that qualify a technology for verification.

Validation is the confirmation, by the examination and provision of objective evidence, that the particular requirements for a specified application are fulfilled.

Variance is a statistical measure of the dispersion of the data, showing how closely grouped or widely scattered the data are with respect to the mean value.

Vendor (see Applicant)

Verification is an examination of environmental performance claims made by suppliers, and of available supporting information, for the purpose of validating the performance claims. The purpose of verification is to substantiate that the performance and integrity of the environmental technology satisfies a standardized protocol as specified by Environment Canada's ETV Program. The verification must include the confirmation, by examination and provision of objective evidence, that specified requirements are achieved. These specifications must include that an environmental product or process is based on sound scientific and engineering principles, that it is effective, reliable and protective of health and environment, and that it performs in this manner under defined operating and environmental conditions.

Verification Certificate is a single page document that includes the ETV "Seal of Approval" which acknowledges that the performance claim has been verified. The Verification Certificate will definitively detail the performance claim and identify all relevant accompanying documentation that validates the technology claim.

Verification Entity is an approved independent organization or technical expert that conducts environmental technology perfromance claim assessments and activities to validate the claim. The Verification Entity must have independence and objectivity in terms of potential financial, fiduciary, procedural and/or technical relationships and must have the technical capability and/or engineering expertise to perform its roles and responsibilities as a Verification Entity. The Verification Entity will also be expected to provide expert technical advice to ETV Canada.

Wastewater is typically effluents or discharges from domestic, municipal and industrial sources which impart levels of contaminants (both soluble and particulate) into water that effectively render the water impractical for most subsequent uses without some form of wastewater treatment.

Water is the universal solvent and the essential compound for all life. Pure water is extremely difficult to obtain; condensation of water from a vapour, by the nature of the process requires a surface or nuclei. Pure water is extremely corrosive, and will quickly dissolve minerals. Clean (or basically clean) water are generally from surface and subsurface sources including lakes, rivers, wells and other groundwater sources. Typically, this quality of water requires minimal treatment for its effective use. The treatment of water to achieve the quality that is required is dependent upon the use of the water; the highest quality being distilled water and drinking or potable water.

Appendix C

General Supplemental Information on Testing Program Criteria

[25] Test Protocol criteria reference number

(2.) Experimental Design

The experimental plan must identify the scope of the work. Information about the site or area of concern must be collected in order to formulate the sampling plan and determine safety requirements. All chemical and physical characteristics of the substances under investigation must be clarified in order to evaluate human and environmental concerns. Other aspects of presampling assessment include identification of pollutant dispersal pathways, identification of media/receptors and characterization of site management practices.

A pre-sampling program can be used to assist in developing an effective experimental design to collect quality data for technology demonstration and performance validation. Issues[26] which should be considered when planning a pre-sampling project is shown as Table C1.

Table C1. Summary of Pre-Sampling Issues

Background Assessment	Information about the site should be collected to formulate a sampling plan. All chemical and physical characteristics of the substances under investigation should be identified. Other aspects of pre-sampling include identification of pollutant dispersal pathways, identification of media/receptors and characterization of site management practices.
Behavior of chemicals in the environment	Understanding the physical and chemical properties of a substance which is either added to a process or known to be an integral part of a process is required. Materials safety data sheets (MSDS) provide information which aid in determining how a chemical behaves in a specific environment. Additional information needed to determine dispersion pathways includes uses of nearby land, the physical and biological settings of the site and the climatic conditions in the area.
Regulatory requirements	An understanding of Federal and/or Provincial guidelines and regulations may have an effect on the sampling site and the determination of specific sampling procedures or standard reference methods that must be followed.
Mobilization phase	Site investigations run smoothly if a properly prepared and executed mobilization plan is in place. Some items which could be part of this phase include manpower allocations, organization of sampling personnel, determine the length of the project, decontamination and demobilization.
Site access	Ensure that key people are contacted when site access permission is required. Some people to include are health and safety people, community, neighbourhood contacts and owners/operators.
Screening Samples	Exploratory sampling can establish the extent and variability in contaminant concentrations. Supplementary sampling can be used to confirm critical information and to clarify problem areas. Data from field screening instruments can be used to refine sampling techniques, identify safety requirements, identify which samples must be sent for lab analyses and how samples will be handled.

[26] From EC, 1996.

Table C1. Summary of Pre-Sampling Issues	
Identify Target Compounds	For inorganic compounds identification (**qualitative** data collection), the use of various field kits along with traditional and state-of-the-art instrumentation is suggested. Examples of these kits includes the HACH Hazardous Materials Detection Laboratory, the HACH COD kit, the Atomic Adsorption Spectrophotometer, indiactor papers, portable wet chemistry test sets and packaged test kits. Examples of equipment for the screening of organic compounds, as well as specialty instruments, are documented in the "Multi-Media Sampling Training Course (EC, 1996). Included is information on physical parameter monitors, such as pH meters and dissolved oxygen meters.

Example Sampling Plan[27]

The following format may be useful in preparing your own plans:

1	Title	short, but easily indexed
2	References	legislation, regulations, interim orders, etc.
3	Introduction and objectives	describe issue and purpose of sampling
4	Scope (Time, budget)	breadth of coverage of the plan
5	Sample matrix and sampling site	Site location, hazards and timing
6	Method of sampling	e.g., grab, composite
7	Administrative arrangements health, safety, and security provisions	sampling personnel, other parties availability and training
8	Preliminary site inspection	if applicable
9	Sampling equipment ambient conditions, availability	proper tools, special considerations, etc.
10	Sample containers and packing • sample size • protocol and tools • preservation • identification/marking	what types of containers sample size requirements how and with what reagents, temperature how sample will be labelled
11	Precautions in transport and storage	
12	Sampling reports	additional information if necessary

Example Experimental Designs

Examples of experimental designs that have been used by commercial vendors are presented below. All of these treatment designs are "completely randomized designs" (CRDs). Examples 1 through 4 become progressively more complex. These types of experimental designs may be very useful in ensuring adequate data collection and provide a clear understanding of the effects of certain operating conditions.

[27] Adapted from EC, 1996.

Example 1

A simple experimental design may be performed to measure the effectiveness of adding a nutrient mixture for improving the biodegradability of a contaminated soil. The design uses a single treatment and control:

I) Contaminated soil + nutrients = (treatment)
II) Contaminated soil alone = (nutrient treatment control)

This design is very basic and as such, may be limited in its application.

Example 2

Typically, a more complex scenario exists and thus a more complex treatment design is used. A factorial design allows for evaluating the effects of one or more "factors" (i.e., a nutrient mixture, a chemical additive or surfactant, a microbial inoculum, etc.) at one or more levels. A 2^2 factorial design for evaluating the effects of two factors (a microbial inoculum and a surfactant), at one or more levels. A 2^2 factorial design for evaluating the effects of two factors (a microbial inoculum and a surfactant), at two levels each (either present or absent) for a bench-scale soil bioremediation treatability test may involve the following treatments/controls:

I)	Contaminated soil	no factors
ii)	Contaminated soil + inoculum	factor "a"
iii)	Contaminated soil + surfactant	factor "b"
iv)	Contaminated soil + inoculum + surfactant	factor "ab"

Such a design allows for testing of the main effects of the factors as well as interactions amongst the factors; a single two-way interaction exists (i.e., "ab").

Example 3

A complete 2^3 factorial design for evaluating the effects of three factors at two levels each (present/absent) for testing of a bioremediation technology could involve the following treatments/controls:

I)	Contaminated soil	no factors
ii)	Contaminated soil + nutrients	factor "a"
iii)	Contaminated soil + microbial inoculum	factor "b"
iv)	Contaminated soil + surfactant	factor "c"
v)	Contaminated soil + nutrients + inoculum	factors "ab"
vi)	Contaminated soil + nutrients + surfactant	factors "ac"
vii)	Contaminated soil + inoculum + surfactant	factors "bc"
viii)	Contaminated soil + nutrients + inoculum + surfactant	factors "abc"

Note, since the experimental design is selected based on the performance claim being made, complicated designs are often unnecessary. Detailed factorial design experiments are usually conducted at bench or pilot scale prior to full scale system design to obtain the necessary process development data. As such, although such experimental designs are very important throughout the developmental stages of environmental technologies, they are not necessarily required for the Testing program.

Example 4

To perform a general factorial design, an investigator selects a fixed number of levels for each of a selected number of variables (factors) and then runs experiments with all possible combinations. Depending on the number of factors and the number of levels, this can represent a very large number of experiments. An effective alternative to a full factorial design is a *fractional factorial design* that can be designed to use a minimum number of tests to evaluate several technology parameters (feed conditions, operating conditions). Factorial designs are often of great value at an early stage of an investigation, when it is frequently good practice to use a preliminary experimental effort to look at a large number of factors superficially rather than a small number thoroughly. These designs may be used as building blocks so that the degree of complexity of the finally constructed design can match the sophistication of the problem. Box et al. (1978) presents a number of examples of factorial designs.

(5.) Sampling Methodology[28]

Prior to any data collection activities, a detailed sampling plan must be developed. The first task is to identify a suitable sampling design. There are two primary types of sampling designs: authoritative (judgment) sampling and probability sampling.

With authoritative sampling, an expert having knowledge of the site (or process) designates where and when samples are to be taken. This type of sampling should only be considered when the objectives of the investigation are not of a statistical nature, for example, when the objective of a study is to identify specific locations of leaks, or when the study is focused solely on the sampling locations themselves. Generally, conclusions drawn from authoritative samples apply only to the individual samples and aggregation may result in severe bias and lead to highly erroneous conclusions.

When the study objectives involve estimation or decision making, some form of probability sampling is required. As described below, this does not preclude use of the expert's knowledge of the site or process in designing a probability-based sampling plan (in fact, use of this knowledge is essential); however, valid statistical inferences require that the plan incorporate some form of *randomization* in choosing sampling locations or sampling times. For example, to determine maximum SO_2 emission from a boiler, the sampling plan would reasonably focus, or put most of the weight on, periods of maximum or near-maximum boiler operation. Similarly, if a residential lot is being evaluated for contamination, then the sampling plan can take into consideration prior knowledge of contaminated areas, by weighting such areas more heavily in the sample selection and data analysis.

With probability samples, every member of the target population (i.e., every potential sampling unit) has a known probability of being included in the sample. Probability samples can be of various types, but in some way, they all make use of randomization, which allows valid probability statements to be made about the quality of estimates or hypothesis tests that are derived from the resultant data.

Simple Random Sampling

The simplest type of probability sample is the simple random sample where every possible sampling unit in the target population has an equal chance of being selected. Simple random samples, like the other samples, can be either samples in time and/or space and are often

[28] Adapted from US EPA, 1996b.

appropriate at an early stage of an investigation in which little is known about systematic variation within the site or process. All of the sampling units should have equal volume or mass, and ideally be of the same shape if applicable. With a simple random sample, the term "random" should not be interpreted to mean haphazard; rather, it has the explicit meaning of equiprobable selection. The advantage of random sampling is that the sampling error can be calculated because the probability of selecting a sample in the target population is known. The use of a random number table or generator to select the sampling locations will eliminate bias that would be introduced by the sampler.

Sequential Random Sampling

Simple random samples usually have a fixed sample size, but some alternative approaches are available, such as sequential random sampling, where the number of samples is not fixed. Rather, a statistical test is performed after each specimen's analysis (or after some minimum number have been analyzed). This strategy could be applicable when sampling and/or analysis is quite expensive, when information concerning sampling and/or measurement variability is lacking, when the characteristics of interest are stable over the time frame of the sampling effort, or when the objective of the sampling effort is to test a single specific hypothesis.

Systematic Random Sampling

In the case of spatial sampling, systematic sampling involves establishing a two-dimensional (or in some cases a three-dimensional) spatial grid and selecting a random starting location within one of the cells. Sampling points in the other cells are located in a deterministic way relative to that starting point. In addition, the orientation of the grid is sometimes chosen randomly and various types of systematic samples are possible. For example, points may be arranged in a pattern of squares (rectangular grid sampling) or a pattern of equilateral triangles (triangular grid sampling). The result of either approach is a simple pattern of equally spaced points at which sampling is to be performed.

Systematic sampling designs have several advantages over random sampling and some of the other types of probability sampling. They are generally easier to implement and they are preferred when one of the objectives is to locate "hot spots" within a site or map the pattern of concentrations over a site. Other advantages of this method include: (1) the number of samples to achieve a specified sampling error can be reduced, and (2) an unknown contaminant distribution has no impact on sample selection.

On the other hand, they should be used with caution whenever there is a possibility of some type of cyclical pattern in the waste site or process. Such a situation, combined with the uniform pattern of sampling points, could very readily lead to biased results. Not recognizing a trend may lead to biased results.

Stratified Random Sampling

Another type of probability sample is the stratified random sample, in which the site or process is divided into two or more nonoverlapping strata, sampling units are defined for each stratum, and separate simple random samples are employed to select the units in each stratum. Strata should be defined so that physical samples within a stratum are more similar to each other than to samples from other strata. Therefore, a stratified random sample should result in more precise estimates of the overall population parameter than those that would be obtained from a simple random sample with the same number of sampling units.

Stratification is an accepted way to incorporate prior knowledge and professional judgment into a probabilistic sampling design. Generally, units that are "alike" or anticipated to be "alike" are placed together in the same stratum. Units that are contiguous in space (e.g., similar depths) or time are often grouped together into the same stratum, but characteristics other than spatial or temporal proximity can also by employed. Media, terrain characteristics, concentration levels, etc., can also be used as the basis for creating strata.

Adaptive Sampling

Adaptive sampling involves taking a sample and using the resulting information to design the next stage of sampling. The process may continue through several additional rounds of sampling and analysis. A common application of adaptive sampling to environmental problems involves subdividing the region of interest into smaller units, taking a probability sample of these units, then sampling all units that border on any unit with a concentration level greater than some specified level C. This process is continued until all newly sampled units are below C. The field of adaptive sampling is undergoing active development and can be expected to have a significant impact on environmental sampling.

(18.) Analytical Procedures

Pollutants associated with seven common industries[29] are presented in Tables C2 and 3. Information contained in these tables may assist in the identification of target compounds and other potential areas of concern.

[29] From EC, 1996.

Table C2. List of Common Pollutants from Selected Industries

Rank[30]	Electroplating	Battery Recycling	Munitions Explosives	Leather Tanning
1	Sulfuric Acid	Lead	Acetone	Ammonium Sulfate (Solution)
2	Hydrochloric Acid	Sodium Sulfate (Solution)	Nitric Acid	Sulfuric Acid
3	Sodium Hydroxide (Solution)	Sodium Hydroxide (Solution)	Ammonium Nitrate Solution	Sodium Hydroxide (Solution)
4	1,1,1-Trichloroethane	Sulfuric Acid	Pentachlorophenol	Ammonia
5	Sodium Sulfate (Solution)	Ammonium Sulfate (Solution)	Sodium Sulfate (Solution)	Toluene
6	Nitric Acid	Manganese	Ammonia	Sodium Sulfate (Solution)
7	Dichloromethane	1,1,1-Trichloroethane	Sulfuric Acid	Methyl Ethyl Ketone
8	Nickel	Methanol	Methyl Ethyl Ketone	Xylene (Mixed Isomers)
9	Trichloroethylene	Freon 113	Cyclohexane	Chromium
10	Chromium	Trichloroethylene	Chlorine	Glycol Ethers
11	Tetrachloroethylene	Toluene	Nitroglycerin	Methyl Isobutyl Ketone
12	Methyl Ethyl Ketone	Zinc	Dichloromethane	2-Methoxyethanol
13	Zinc	Ammonia	Calcium Cyanamide	Acetone
14	Freon 113	Cadmium	Lead	2-Ethoxyethanol
15	Aluminum	Antimony	Ethylene Glycol	N-Butyl Alcohol
16	Copper	Barium	N-Butyl Alcohol	Tetrachloroethylene
17	Phosphoric Acid	Nickel	Tert-Butyl Alcohol	Cyclohexane
18	Toluene	Formaldehyde	m-Xylene	Ammonium Nitrate (Solution)
19	Lead	Acetone	Methanol	Manganese
20	Xylene (Mixed Isomers)	Xylene (Mixed Isomers)	Asbestos (Friable)	1,1,1-Trichloroethane
21	Acetone	Tetrachloroethylene	1,1,1-Trichloroethane	Dichloromethane
22	Cadmium	Dichloromethane	Polychlorinated Biphenyls	Diethanolamine
23	Ethylbenzene	Phenol	Copper	Methanol
24	Ethylene Glycol	Mercury	Aluminum	Isopropyl Alcohol
25	Cyanide Compounds	N-Butyl Alcohol	2,4-Dinitrotoluene	Phosphoric Acid
26	Ammonia	Methyl Ethyl Ketone	Glycol Ethers	Ethylene Glycol
27	Formaldehyde	Methyl Isobutyl Ketone	Benzene	Freon 113
28	Glycol Ethers	Hydrochloric Acid	Bis(2-Ethylhexyl) Adipate	Phenol
29	Chlorine	Nitric Acid	Zinc	Ethyl Acrylate
30	Methanol	1,1,1-Trichloroethane	Dibutyl Phthalate	
31	Ethylene Oxide	Cobalt	Sodium Hydroxide (Solution)	
32	Methyl Isobutyl Ketone	Arsenic	Diethyl Phthalate	
33	2-Methoxyethanol	Copper		
34	Hydrogen Fluoride	Silver		
35	Phenol	Acetonitrile		
36	1,2-Dichlorobenzene			
37	N-Butyl Alcohol			
38	Tert-Butyl Alcohol			
39	Barium			
40	Vinylidene Chloride			
41	2-Ethoxyethanol			
42	Isopropyl Alcohol			
43	Manganese			
44	Hydrogen Cyanide			
45	Styrene			
46	Tetrachlorvinphos			
47	Melamine			
48	N-Dioctyl Phthalate			
49	1,4-Dioxane			
50	Cobalt			
51	Naphthalene			
52	Ammonium Sulfate (Solution)			
53	Silver			
54	Propylene			

Table C3. List of Common Pollutants from Selected Industries

[30] Rank = order of Frequency of Occurance

Rank	Pesticide Manufacturing	Petroleum Refining	Wood Preservation
1	Sodium Sulfate (Solution)	Sodium Sulfate (Solution)	Chromium
2	Ammonia	Aluminum	Naphthalene
3	Toluene	Ammonia	Ammonia
4	Sodium Hydroxide (Solution)	Sodium Hydroxide (Solution)	Pentachlorophenol
5	Titanium Tetrachloride	Sulfuric Acid	Dibenzofuran
6	Methanol	Toluene	Anthracene
7	Dichloromethane	Xylene (Mixed Isomers)	Copper
8	Xylene (Mixed Isomers)	Benzene	Arsenic
9	Chlorobenzene	Methyl Ethyl Ketone	Formaldehyde
10	Hydrochloric Acid	Propylene	Biphenyl
11	Chlorophenols	Phenol	Benzene
12	Styrene	Diethanolamine	Dichloromethane
13	Acrylonitrile	Ethylene	1,1,1-Trichloroethane
14	Formaldehyde	Methanol	Ammonium Sulfate (Solution)
15	Carbon Tetrachloride	Cyclohexane	Quinoline
16	Chlorothalonil	1,2,4-Trimethylbenzene	Phenol
17	1,2-Dichloroethane	Ethylbenzene	Zinc
18	Acetone	Phosphoric Acid	Phosphoric Acid
19	Hexachlorobenzene	Chromium	O-Cresol
20	1,1,1-Trichloroethane	Methyl Tert-Butyl Ether	Hydrochloric Acid
21	Ethylene Glycol	Asbestos (Friable)	m-Cresol
22	Glycol Ethers	p-Xylene	
23	1,3-Butadiene	Ammonium Sulfate (Solution)	
24	Chloromethane	m-Xylene	
25	Captan	Cumene	
26	Tetrachloroethylene	Acetone	
27	Chlorine	Cresol (Mixed Isomers)	
28	Carbaryl	Hydrogen Fluoride	
29	Copper	o-Xylene	
30	Parathion	Naphthalene	
31	Zineb	Nickel	
32	Pyridine	Chlorine	
33	Ammonium Nitrate (Solution)	Lead	
34	Phosphoric Acid	Methyl Isobutyl Ketone	
35	Carbon Disulfide	Ethylene Glycol	
36	1,2,4-Trichlorobenzene	Molybdenum Trioxide	
37	Sulfuric Acid	Zinc	
38	Maleic Anhydride	Hydrochloric Acid	
39	Ethylbenzene	Glycol Ethers	
40	2,4-dichlorophenoxyacetic acid (2,4-D)	Barium	
41	Bromomethane	Copper	
42	Sec-Butyl Alcohol	1,1,1-Trichloroethane	
43	Lead	Antimony	
44	Cumene	1,3-Butadiene	
45	M-Xylene	N-Butyl Alcohol	
46	Asbestos (Friable)	Formaldehyde	
47	Freon 113	Epichlorohydrin	
48	Dichlorobenzene (Mixed Isomers)	Cobalt	
49	Cyclohexane	Vanadium (Fume or Dust)	
50	2,4-Dichlorophenol	Cumene Hydroperoxide	
51	1,4-Dichlorobenzene	Tert-Butyl Alcohol	
52	Dichlorobromomethane	4,4'-Isopropylidenediphenol	
53	Trifluralin	Butyraldehyde	
54	1,2,4-Trimethylbenzene	Biphenyl	
55	Methyl Isobutyl Ketone	Carbon Tetrachloride	
56	1,4-Dioxane	Styrene	
57	Nitric Acid	Trichloroethylene	
58	N-Butyl Alcohol	Manganese	
Rank	**Pesticide Manufacturing**	**Petroleum Refining**	

59	Fluometuron	Ethylene Oxide	
60	2-Methoxyethanol	Ammonium Nitrate (Solution)	
61	BIS (2-Ethylhexyl) Adipate	Carbon Disulfide	
62	Phenol	1,2-Dichloroethane	
63	Acrylic Acid	Polychlorinated Biphenyls	
64	Quintozene	Phosphorous (Yellow or White)	
65	Aluminum	Quinoline	
66	Benzoyl Peroxide	2-Methoxyethanol	
67	o-Xylene	1,2-Dibromoethane	
68	Chromium	Tetrachloroethylene	
69	2-Phenylphenol	Anthracene	
70	Hydrogen Cyanide	2,4-Dimethylphenol	
71	Zinc	Hydrogen Cyanide	
72	Hexachlorocyclopentadiene	Chloromethane	
73	Dicofol	Nitrobenzene	
74	Biphenyl	1,2-Dichloropropane	
75	4-Nitrophenol	Carbonyl Sulfide	
76	Methyl Ethyl Ketone	Acetonitrile	
77	Trichloroethylene	Silver	
78	m-Cresol	2-Ethoxyethanol	
79	Tetrachlorvinphos	Thallium	
80	DI(2-Ethylhexyl) Phthalate (DEHP)	Freon 113	
81	Terephthalic Acid	Selenium	
82	Dichlorvos	Dichloromethane	
83	Maneb	Mercury	
84	p-Xylene	Cadmium	
85	Methylene Bromide		
86	Chloramben		
87	Benzene		
88	Hydrogen Fluoride		
89	Ethylene		
90	C.I. Acid Blue 9, Disodium Salt		
91	Dimethyl Sulfate		
92	Isopropyl Alcohol		
93	Hydrazine		
94	Vinyl Chloride		
95	Methylenebis (Phenylisocyanate)		
96	Epichlorohydrin		
97	Propylene		
98	Nitrilotriacetic Acid		
99	Arsenic		
100	Naphthalene		
101	Vinylidene Chloride		
102	Trichlorfon		
103	Dibutyl Phthalate		
104	Aniline		
105	Methoxychlor		
106	Diethanolamine		
107	Nitrobenzene		
108	Cyanide Compounds		
109	Ammonium Sulfate (Solution)		
110	Lindane		
111	Polychlorinated Biphenyls		
112	Propylene Oxide		
113	2,4-Dinitrophenol		
114	Phosgene		
115	Hexachloroethane		
116	Cadmium		
117	Ethylene Oxide		
118	Benzyl Chloride		
119	4,6-Dinitro-o-Cresol		
120	Chlorobenzilate		

Appendix D

Supplemental Information on Water and Wastewater Sampling

[31] Test Protocol criteria reference number

(7.) Sample Type

Grab Sample

A grab sample is meant to represent the water/wastewater stream at a given point in time as opposed to a composite sample which represents the wastewater stream over a longer time period (24 hours). Grab samples can be collected by using an automated sampling device in the manual mode, or by dipping an appropriate container, bucket, bottle or vial, into the wastewater stream using an appropriate retrieval device such as a chain, rope, or pole. Grab samples may be combined in a single large container and subdivided later, or they may be collected in several individual containers, each dedicated to a specific analysis.
Grab samples can be of the following types:

1. wastewater is collected in a bucket or other container and immediately transferred to the appropriate laboratory container(s), preserved as necessary and capped.

2. the appropriate laboratory sample container is submerged in the wastewater stream on a chain or pole until it is full; it is retrieved, preserved as necessary and capped.

3. the wastewater is collected in a bucket as for GRAB 1 and the appropriate clean (outside as well) laboratory container (i.e., volatiles vial) is held at an angle and submerged into the liquid until it is full and air bubbles have been expelled at which time it is carefullly retrieved, preserved as necessary and capped. Care must be taken to avoid sample contamination from the outside of the laboratory container or the retrieval device.

Samples for oil and grease (O&G) must be collected directly into the laboratory container, unless direct retrieval is impossible, to minimize unavoidable losses during transfer.

Composite Sample

Composite samples can be collected by either automated or manual methods. Automated composite samples can be taken either proportional to the wastewater stream flow (in which cases there must be flow sensing devices connected to the sampler) or on an equal volume/equal time basis. Both of these approaches require fully automated, programmable sampling devices.

Manual composite samples are typically taken on an equal volume/equal time basis but can be combined in proportion to flow once all subsamples have been collected. This basically represents a compositing of grab samples.

In general, flow proportional composites should be taken from streams which vary considerably in flow. In cases where the process stream flow is typically non-variable, samples can be collected on an equal volume/equal time basis.

(10.) Sampling Equipment

Table D1: Summary of Equipment used in Sampling Water and Wastewater[32]	
Automatic Samplers	Automatic samplers can interface with computers for down loading information. Typically, with the addition of an external flowmeter, samplers can collect flow proportion samples.
Composite liquid waste sampler	This sampler is important for liquid hazardous wastes, allowing representative sampling of multiphase wastes with a wide range of viscosity, volatility, and solids content.
Depth Sampler	The sampler is used to collect water samples at different depths, in lakes, rivers or lagoons.
Extended bottle sampler	It is a grab sampler designed to sample subsurface liquids to a maximum depth of 1.5 m.
Dip Sampler	Dip sampler are used to collect liquid waste samples from disposal ponds, lagoons and effluent streams.
Vacuum Sampler	This sampling device uses a sample tube attached to a vacuum pump to transfer liquid waste from its original source to a sample container.
Weighted bottle sampler	This device can be used to sample liquids in storage tanks, wells, sumps, or other reservoirs.

Flow Measurement

In conjunction with sample collection it is essential to measure flow or volume. Flow rate (or total volume) information is needed not only to determine the make-up of composite samples but also to determine mass loadings of measured parameters. Removal efficiencies of environmental technologies should be based on the percent removal of the mass of contaminant entering the system. If an industrial waste discharge is subject to surcharges, volumetric measurements are necessary to calculate mass loading rates.

Liquid flow measurements procedures and equipment used in closed pipes, open pipes (with an outfall), open channels, lakes, streams and rivers need to be considered. Several types of flow conditions are found in the field. Open channel flow occurs when the flow is open to the atmosphere (free water surface). Pipeflow occurs in the conduit when atmospheric pressure in the pipe is less or greater than atmospheric pressure. A continuous flow measurement system is composed of a primary (flow device) and a secondary (flow sensor) device.

Table D2: Summary of Equipment used in Flow Monitoring of Water and Wastewater	
Closed Pipes Flow meters used is this situation include variable head (differential pressure) meters, variable area meters, propeller or turbine meters, magnetic meters, ultrasonic meters, etc.	
Propeller and turbine meters	The speed of rotation of the propeller is proportional to the velocity of the flow. A mechanical totalizer is used to obtain a reading of cumulative flow. An accuracy of +/- 2% is possible with these devices as long as the solids levels in the stream are not excessive and deposits do not build up on exposed surfaces.
Magnetic flow	Liquid passing through a magnetic field will generate a voltage in

[32] Adapted from Environment Canada (1995) and US EPA (1986).

Table D2: Summary of Equipment used in Flow Monitoring of Water and Wastewater	
meters	proportion to the flow rate. The line or pipe being measured must be flowing full to ensure that there is no interference from sedimentation or the entrapment of air. At a flow rate greater than 1 m/s, accuracy is +/- 1% over the full measurement range. Accuracy is reduced below 1 m/s. Tube magnetic meters are installed basically flush mounted and therefore have a wide range of applications. Insert type flow meters are sensitive to turbulence and suspended material. The flow is measured as: $E = kBL\,v$ where: E = magnitude of flowmeter voltage k = a constant B = field density L = path length v = average velocity of fluid
Variable head meters	These devices produce a constriction of a given size and shape in the flow causing a pressure drop. The flow is proportional to the square root of the pressure drop. Some examples of these meters include the venturi meter, flow tube, orifice meter, V-cone meter, elbow meters and flow nozzles. These devices tend to be used in clean water and gas applications. Their accuracy ranges between 0.25 to 5% depending on type, design and installation procedures.
Variable area meters	Usually referred to as rotameters, they are composed of a flow tube and a float. Accuracy of measurement is +/- 2 to 5% of maximum scale and it's use is limited to pipes of less than 60mm. Clean liquid applications are recommended.
Ultrasonic flow meters	Doppler meters send an ultrasonic pulse into the flow at a known beam angle. The return echo is detected and the shift in frequency between the emitted pulse and detected echo is proportional to the velocity of the flow. At velocities of flow greater than 30 cm/s, accuracy is +/- 2 to 5%. Transit type meters measure the time that an ultrasonic pulse takes to travel diagonally through the flow over a known distance. The time of travel is proportional to the velocity of liquid flow. Accuracy ranges from 1 to 2% for this type of meter. The flow is determined according to: $v_t = \frac{c^2(t_u - t_d)\tan\phi}{2D}$ where: v_t = time based flow velocity c = speed of sound in the fluid t_u = upstream transit time t_d = downstream transit time D = diameter of pipe ϕ = angle between sonic path and flow axis
OPEN CHANNEL FLOW Open channel flow conditions can be measured using primary devices such as weirs, parshall flumes, the palmer-bowlus flume and the parabolic nozzle.	
Weirs	A weir is an obstruction (dam) placed perpendicular to the direction of the flow. The weir shape can be rectangular, triangular, trapezoidal or

Table D2: Summary of Equipment used in Flow Monitoring of Water and Wastewater	
	straight. The flow over the weir is related to the head on the weir. The head is the height of the water level above the crest measured some distance upstream from the weir. To monitor flow continuously a secondary sensing device such as a mechanical float, a pressure transducer, a bubbler gauge, an ultrasonic meter or a capacitance probe can be employed. An accuracy is +/- 5% of the flow rate is produced by weirs. Flow depends upon the weir shape, and is given by: $Q = kH^{2.5}$ <u>V – notch weir</u>, where *Q* = flow rate *H* = head on the weir *k* = constant, based on notch dimensions $Q = k(L - 0.2H)H^{1.5}$ <u>Rectangular weir</u>, where *Q* = flow rate *H* = head on the weir *k* = constant, based on notch dimensions $Q = kLH^{1.5}$ <u>Cipolletti weir</u>, where *Q* = flow rate *H* = head on the weir *k* = constant, based on notch dimensions
Parshall flume	A flume is a device that does not dam the flow but merely reshapes it. The flow passes through a constriction (throat) area and its rate is increased. The flow depth is minimal and is known as the critical flow depth. The flow is proportional to the head raised to a power. Accuracy is usually +/- 5%. Due to its suitability for field application and the degree of accuracy attained, this device is the most commonly used device for wastewater flow measurement. Flow is described by: $Q = kH^n$ where *Q* = flow rate *H* = head measured at point H_a *k* = constant, based on flume dimensions *n* = power constant, based on throat width
Palmer-Bowlus flume	This device is installed in an existing channel and is sized by the dimensions of the channel. A depth measurement is taken one half of a pipe diameter upstream from the toe of the flume.
Parabolic nozzle	This device operates in a manner similar to the parshall flume, is self-scouring and handles solids in the liquid flow very well. Flow (Q) is proportional to H^2 (H = head).
Manning formula	In the “Isco Open Channel Flow Measurement Handbook” the use of

Table D2: Summary of Equipment used in Flow Monitoring of Water and Wastewater	
	the Manning formula for the calculation of gravity flow in an open channel is described. If the cross section of the conduit is uniform, the slope and the roughness of the conduit are known and the flow is by gravity, the rate of flow in the conduit can be calculated. A table showing typical values for the Manning roughness coefficient is also presented. $Q = \frac{1}{n} A r^{\frac{2}{3}} S^{\frac{1}{2}}$ where: Q = flow (m^3/s) n = roughness coefficient[33] A = cross sectional area (m^2) r = hydraulic radius (m) S = slope (m/m)
End of Pipe Discharge	
California pipe method	At the discharge end of a pipe (not flowing full) the flow rate can be calculated by measuring the depth of flow and diameter of the pipe. The values are substituted into the flow equation and the flow rate can be calculated. $Q = k(1 - \frac{a}{d})^{188} d^{2.48}$ where: *Q* = flow rate *a* = distance from the inside top of the pipe to the liquid *d* = pipe diameter *k* = constant
Other methods	
Measurement of flow velocity	If the velocity of flow and the cross-sectional area of flow are known, the product of these values produces a flow rate. Velocity can be measured using a float, a current meter or a velocity modified flow meter. The float method uses any floatable material to establish the time required to travel a known distance in the flow. A correction factor, depending on the material used as a float, is employed to calculate the average flow velocity. The current meter counts the revolutions of an impeller immersed parallel to the direction of flow. The number of revolutions per second of the propeller is used in a calibration equation to calculate the velocity of flow. Velocity modified flow meters sense both depth and velocity. The velocity is determined by an electromagnetic sensor while the head is measured with a bubbler or pressure sensor. The sensors are secured in a ring which is inserted into the pipe. This device is useful in clean water situations.
Dilution method	This method is applicable to steady flow conditions. A non-reactive chemical of known concentration is injected either in a batch dose or metered into the flow stream. The stream is sampled an appropriate distance downstream to allow for proper mixing. Knowing the two concentrations of the chemical and the injection rate, a mass balance calculation will give the stream flow rate. Some examples of tracers which might be used for different applications include sodium

[33] Common value for roughness coefficient is 0.013; see ISCO reference for other values

Table D2: Summary of Equipment used in Flow Monitoring of Water and Wastewater	
	dichromate, sodium chloride, rhodamine B, lithium chloride, fluorescien, sodium nitrite, magnesium sulphate and various radio-isotopes. Examples of the dilution technique are presented in "The Measurement of Liquid Flow in Open Channels" an ISO Standards Handbook 16, 1983. The methods and procedures used for the constant-rate injection method, the integration (sudden injection) method and the constant rate injection method and integration method using radioactive tracers are addressed. $Q_2 = \frac{c_1}{c_2 - c_o} Q_1$ where: Q_2 = waste stream flow (L/min) c_1 = concentration of feed solution (mg/L) c_2 = measured concentration in wastewater (mg/L) c_3 = background concentration in wastewater (mg/L) Q_1 = feed solution flow rate (L/min)
Volumetric flow measurement	An average flow rate can be calibrated by recording the time required to fill a calibrated tank. $Q = \frac{Vt}{1000}$ where: Q = Flow (L/min) V = tank volume (m^3) t = time (min)
Flow estimation	Verification of flow for a given industrial discharge can be done by using a mass balance equation. The discharge outflow is equal to the inflow volume less the volume used for production and the volume lost due to evaporation. Based on reasonable estimates, wastewater flow calculations can be achieved.

(11.) Sample Container & Preservation

Table D3. Summary of Sampling Handling Requirements[34]

Parameter	Container	Minimum Sample Size (mL)	Sample Type	Preservation	Maximum[35] Storage	QA/QC Option[36]
Acidity	P, G(B)	100	g	Refrigerate @ 4°C, in the dark	14 d	B, D, SB
Alcohol	G	40	g, c	Refrigerate @ 4°C	48 h	B, D
Alkalinity	P, G	200	g	Refrigerate	14 d	B, D
BOD	P, G	1000	g	Refrigerate	48 h	B, D
Boron	P	100	g, c	None required	6 months	B, D
Bromide	P, G	100	g, c	None required	28 d	B, D
Carbon, organic, total	G	100	g, c	Analyze immediately; or refrigerate and add H_3PO_4 or H_2SO_4 to pH<2	28 d	B, D
Carbon dioxide	P, G	100	g	Analyze immediately	N.S.	B, D
COD	P, G	100	g, c	Analyze as soon as possible, or add H_2SO_4 to ph<2; refrigerate	28 d	B, D
Chloride	P, G	50	g, c	None required	28 d	B, D
Chlorine, residual	P, G	500	g	Analyze immediately	stat	B, D
Chlorine dioxide	P, G	500	g	Analyze immediately	N.S.	B, D
Chlorophyll	P, G	500	g, c	30 d in dark	N.S.	B, D
Colour	P, G	500	g, c	Refrigerate	48 h	B, D
Conductivity	P, G	500	g, c	Refrigerate	28 d	B, D
Cyanide:						
Total	P, G	500	g, c	Add NaOH to pH>12, refrigerate in dark #	14 d; 24 h if sulfide present	B, D
Amenable to chlorination	P, G	500	g, c	Add 100 mg $Na_2S_2O_3$/L	14 d; 24 h if sulfide present	B, D
Fluoride	P	300	g, c	None required	28 d	B, D
Hardness	P, G	100	g, c	Add HNO_3 to pH<2	6 months	B, D
Iodine	P, G	500	g, c	Analyze immediately	N.S.	B, D
Metals, general	P(A), G(A)	500	g	For dissolved metals filter immediately, add HNO_3 to pH<2	6 months	B, D
Chromium VI	P(A), G(A)	300	g	Refrigerate	24 h	B, D
Copper by colorimetry*						B, D
Mercury	P(A), G(A)	500	g, c	Add HNO_3 to pH<2, 4°C, refrigerate	28 d	B, D
Nitrogen:						
Ammonia	P, G	500	g, c	Analyze as soon as possible or add H_2SO_4 to pH<2, refrigerate	28 d	B, D
Nitrate	P, G	100	g, c	Analyze as soon as possible, refrigerate	48 h (28 d for chlorinated samples)	B, D
Nitrate + nitrite	P, G	200	g, c	Add H_2SO_4 to pH<2, refrigerate	28 d	B, D
Nitrite	P, G	100	g, c	Analyze as soon as possible or refrigerate	48 h	B, D
Organic, Kjeldahl*	P, G	500	g, c	Refrigerate; add H_2SO_4 to pH<2	28 d	B, D
Odour	G	500	g	Analyze as soon as possible; refrigerate	N.S.	
Oil and Grease	G, wide-mouth calibrated	1000	g, c	Add HCl to pH<2, refrigerate	28 d	B, D

[34] Adapted from Standard Methods (1995) and WTI (1996)
P = polyethylene (or equivalent); G = glass; G(A) or P(A) = rinsed with 50% HNO_3; G(B) = glass, borosilicate;;
g = grab; c = composite; Refrigerate = storage at 4°C, in the dark; N.S. = not stated in cited reference;
stat = no storage allowed; analyze immediately
[35] Maximum **Recommended or Regulatory** Storage
[36] B = Blank; D = Duplicate; SB = Spiked Blank

Table D3. Summary of Sampling Handling Requirements[34]

Parameter	Container	Minimum Sample Size (mL)	Sample Type	Preservation	Maximum[35] Storage	QA/QC Option[36]
Organic compounds:						
MBAS	P, G	250	g, c	Refrigerate	48 h	B, D, SB
Pesticides*	G(S), TFE-lined cap	1000	g, c	Refrigerate; add 1000 mg ascorbic acid/L if residual chlorine present	7 d until extraction 40 d after extraction	B, D
Phenols	P, G	500	g, c	Refrigerate, add H_2SO_4 to pH<2	28 d	B, D
Purgeables* by purge and trap	G, TFE-lined cap	2 x 40	g	Refrigerate; add HCl to pH<2; add 1000 mg ascorbic acid/L if residual chlorine present	14 d	
Oxygen, dissolved:	G, BOD bottle	300	g			B, D
Electrode				Analyze immediately	stat	
Winkler				Titration may be delayed after acidification	8 h	
Ozone	G	1000	g	Analyze immediately	N.S.	B
pH	P, G	50	g	Analyze immediately	stat	B
Phosphate	G(A)	100	g	For dissolved phosphate filter immediately; refrigerate	N.S.	B, D
Salinity	G, wax seal	240	g	Analyze immediately or use wax seal	N.S.	B, D
Silica	P	200	g, c	Refrigerate, do not freeze	28 d	B, D
Sludge digester gas	G, gas bottle	-	g	-	N.S.	
Solids	P, G	200	g, c	Refrigerate	2-7 d	D
Sulfate	P, G	100	g, c	Refrigerate	28 d	B, D
Sulfide	P, G	100	g, c	Refrigerate; add 4 drops 2*N* zinc acetate/100 mL; add NaOH to pH>9	7 d	B, D
Taste	G	500	g	Analyze as soon as possible; refrigerate	N.S.	
Temperature	P, G	-	g	Analyze immediately	stat	
Turbidity	P, G	100	g, c	Analyze same day; store in dark up to 24 h, refrigerate	48 h	B, D
Volatile Acids	G, TFE - lined cap	2	g, c	pH > 2 with phosphoric acid, refrigerate with no headspace	14 d	B, D
Volatile Organics	G, TFE - lined cap	40	g, c	0.1% $CuSO_4$ by weight OR pH 2 with 1:1 HCl, refrigerate with no headspace	14 d	B, D, SB

Appendix E

Supplemental Information on Air Emissions Monitoring

[37] Test Protocol criteria reference number

(6.) Sample Location

Area sampling stations can be located in various places depending on project and site needs. Upwind locations establish background levels while downwind area sample indicate if any contaminants are leaving the site. The exclusion zone poses the greatest risk of exposure to chemicals and may require greater attention and additional sampling. The contamination reduction zone is sampled to establish the decontamination line for workers. Finally, the support zone is sampled to ensure that a clean area exists throughout the duration of the study. Information on wind speed and direction, temperature, barometric pressure and humidity assist in selecting air sampling locations, calculating air dispersion, calibrating instruments and determining exposure risks to the population or the environment.

For source testing of stacks or ducts with a circular cross section, locate the traverse points on two perpendicular lines according to Table E1.[38] For rectangular cross sections, divide the area into equal sections, the number of sections as described in Table E1.

Table E1. Location of Traverse Points in Circular Stacks[39]

Percent of Stack Diameter from Inside Wall to Traverse Point												
	Number of Traverse Points on a Diameter											
Traverse Point Number on a Diameter	2	4	6	8	10	12	14	16	18	20	22	24
1	14.6	6.7	4.4	3.3	2.5	2.1	1.8	1.6	1.4	1.3	1.1	1.1
2	85.4	25.0	14.7	10.5	8.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2
3		75.0	29.5	19.4	14.6	11.8	9.9	8.5	7.5	6.7	6.0	5.5
4		93.3	70.5	32.3	22.6	17.7	14.6	12.5	10.9	9.7	8.7	7.9
5			85.3	67.7	34.2	25.0	20.1	16.9	14.6	12.9	11.6	10.5
6			95.6	80.6	65.8	35.5	26.9	22.0	18.8	16.5	14.6	13.2
7				89.5	77.4	64.5	36.6	28.3	23.6	20.4	18.0	16.1
8				96.7	85.4	75.0	63.4	37.5	29.6	25.0	21.8	19.4
9					91.8	82.3	73.1	62.5	38.2	30.6	26.1	23.0
10					97.5	88.2	79.9	71.7	61.8	38.8	31.5	27.2
11						93.3	85.4	78.0	70.4	61.2	39.3	32.3
12						97.9	90.1	83.1	76.4	69.4	60.7	39.8
13							94.3	87.5	81.2	75.0	68.5	60.2
14							98.2	91.5	85.4	79.6	73.9	67.7
15								95.1	89.1	83.5	78.2	72.8
16								98.4	92.5	87.1	82.0	77.0
17									95.6	90.3	85.4	80.6
18									98.6	93.3	88.4	83.9
19										96.1	91.3	86.8
20										98.7	94.0	89.5
21											96.5	92.1
22											98.9	94.5
23												96.8
24												98.9

[38] Taken from EC, 1993.
[39] Taken from EC, 1993.

(8.) Number of Samples

For the ideal case, where the sampling site is located at least eight diameters downstream and two diameters upstream from a flow disturbance, the required minimum number of traverse points for a circular or rectangular duct is presented in TableE2.

TableE2. Minimum Number of Traverse Points for Sampling Sites
(where 8 & 2 diameter criteria are satisfied[40]).

	Minimum Number of Traverse Points	
Stack (Duct) Diameter (m)	Circular Duct	Rectangular Duct
> 0.61	12	12
0.30 to 0.61	8	9

However, when the 8 & 2 diameter criteria cannot be satisfied, the minimum number of traverse points are determined from Figures E1 or E2.

(10.) Sampling Equipment

Solid and liquid media along with colourimetric tubes are used to absorb gases or vapours, which need to be pumped through the media to ensure proper contact time. Solid sorbents are most widely used in site studies and are the media of choice for insoluble or non-reactive gases or vapours. They have high collection efficiencies, indefinite shelf lives (unopened), are easy to use, have improved tube design and have specific analytical procedures. Activated charcoal and silica gel are the two most widely used solid sorbents. Liquid absorbers tend to be contaminant-specific and have limited lives.

The components of the sampling device used to collect volatile organic compounds in ambient air include a sampling manifold, a sorbent cartridge with Carbotrap B and Carbosieve S, a particulate filter, a flow measuring device with flow controller and digital read-out, a metal bellows pump and a timer system (MOEE, 1990). A description of the operating procedures for set-up of the unit and for collection of volatile organic samples, as well as sample documentation and calibration of the sampling train are included in the MOEE (1990) document. The applicable method for stationary sources is Method 0031.[41]

Active sampling systems (electrical pumps) must be calibrated to a flow rate specified in standard analytical methods in order to interpret collected data correctly. The complete sampling set-up should be calibrated as a whole rather than just the pump. The soap bubble flow meter is the most popular calibration device and it represents a primary standard.

[40] Taken from EC, 1993.
[41] SW-846, Test Methods for Evaluating Solids Wastes.

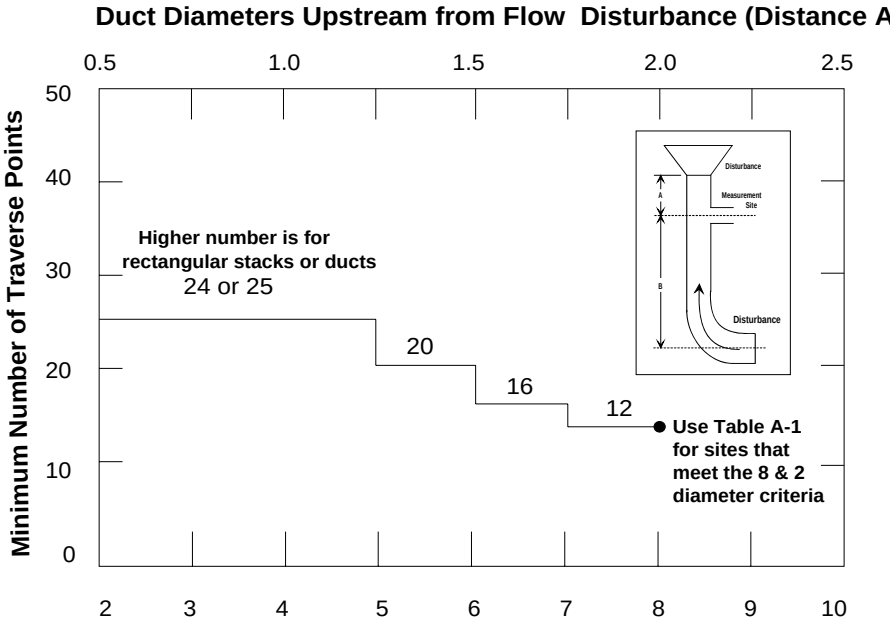


Figure E1. Minimum Number of Traverse Points for Particulate Sampling[42]

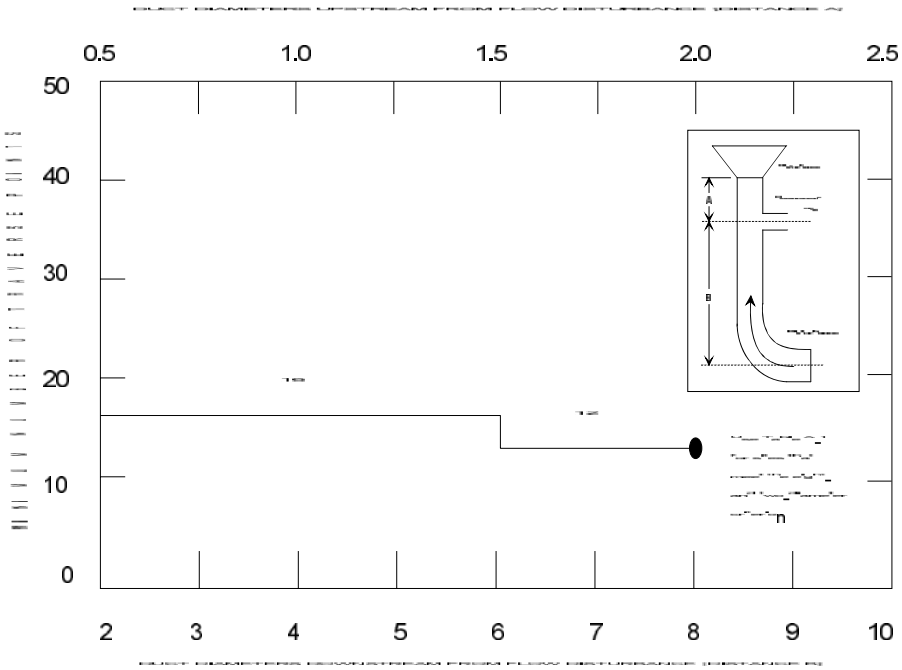


Figure E2. Minimum Number of Traverse Points for Velocity Measurement

[42] Taken from EC, 1993.

Table E1: Summary of Equipment used in Sampling Air Emissions[43]	
Passive dosimeters	The primary function of passive dosimeters is to act as monitors for personal exposure to gases and vapours. They are small, lightweight and simple devices, which do not require a pumping device. Calibration and maintenance requirements are reduced or eliminated. Based on design and operation, there are two main groups; namely, diffusion and permeation devices.
Gas Vapour Absorbers	Impingers and bubblers are used to collect gases and vapors by liquid absorption.
Respirable Dust Sampler	This device is a cylindrical collector consisting of a cyclone and filter. The particulate laden air is drawn along a tube at the center of the cyclone, where the particulates are collected on the filter. This device can be worn as a personal respirable dust monitor.
Air Sampling Canister	This unit is used to collect a grab sample of air over a short period of time or integrated sample over a specific time period (e.g. 24 hours).This is usually done by means of an evacuated chamber which, when opened, fills with the air to be analyzed
Sampling Bags	Typically used with a pump to collect an air sample in a special bag. Bags can be used for instantaneous or integrated sampling. Selection characteristics for sample bags include resistance to adsorption and permeation, tensile strength, performance under temperature extremes, construction features and service life.
Collection Media	Collects contaminants by drawing air through a specific solid media, (such as activated carbon, silica gel, and ion exchange resin) which trap the desired contaminant.
Air emission	Sampling train can be modified for each group of analytes to be sampled, which includes: condensable organic compounds, volatile organic compounds, aldehydes and ketones, inorganic gases, particles and multiple metals.
Particulate Sampler	The sampler contains a specialized filter material as part of an active sampling train to mechanically collect airborne particles by dry filtration. Cyclones are also used in cases of very high particulate loadings.
Integrated Sampling Train	Samples from a stack or a duct are collected using a sampling train, which mechanically collect samples on or into selected medium. The medium is then analyzed to identify the contaminants collected. The train consists of a pump to draw the contaminated air into the absorbers, a flow regulator to control the rate of movement, and a flow monitor to record air volume. The components of the sampling train vary widely with the analytes desired. Sample pumps are either electrically or battery operated. Several components of a pump could include a diaphragm, a flow regulator, a rotameter or stroke counter, a pulsation dampener, a pressure drop compensator, programmable timing and approval for explosive atmospheres. Samplers used for gas vapour absorption include impingers, fritted bubblers, glass bead columns, spiral and

[43] Adapted from Environment Canada (1995) and US EPA (1986).

Table E1: Summary of Equipment used in Sampling Air Emissions[43]	
	helical absorbers. Detailed descriptions of the sampling procedures and equipment are illustrated in CFR 40, part 60, (US EPA, 1996a), and in US EPA (1986b).

Flow Measurement

In conjunction with sample collection, it is essential to measure flow or volume. Flow rate (or total volume) information is needed not only to determine the make-up of composite samples but also to determine mass loadings of measured parameters. Removal efficiencies of environmental technologies should be based on the percent removal of the mass of contaminant entering the system. If an industrial waste discharge is subject to surcharges, volumetric measurements are necessary to calculate mass loading rates.

There are two common types of airflow measuring devices: (1) those that measure a cumulative volume of air, and (2) those that measure continuous rate of flow. With both types of instrument, the determination of the mass flow rate of gas depends on the temperature, pressure, humidity, and density of the gas.

Table E2: Summary of Equipment used in Flow Monitoring of Air Emissions	
Cumulative Volume Meters[44]	
Dry gas meter	A type of positive displacement meter, similar to a domestic gas meter, consisting of two bellows connected by valves and a counting mechanism. As air is drawn into the device, one bag fills and the other empties. The rate of this change is then measured by a dial.
Bubblemeter	Consists of a titration burette with a squeeze bulb full of soap solution at the bottom and a side entrance for the gas. When a measurement is started, the bulb is squeezed, forcing soap solution above the gas inlet. The time of travel of a soap bubble between two volume marks on the burette is then measured.
Calibration Devices	
Spirometer	Used as a primary calibration unit for the dry gas meter, this device is similar to a piston in a cylinder, in which the volume of air displaced in the unit is a precisely known engineering function of the distance traveled by the piston.
Wet test meter	Used as a secondary calibration unit for the dry gas meter, this device is a positive displacement meter, consisting of a partitioned drum that is half submerged in water. Air drawn in by the sampling train enters an opening at the drum and flows into individual compartments, which have openings at the edge of the drum. This causes the compartments to rise and the drum to rotate. The number of rotations is indicated on a dial on the face of the meter.
Continuous Rate Flow Meters	
Orifices or venturis	In the operation of the orifices or a venturis meter, the flow of the fluid through the device results in a decrease in static pressure between two points in the meter. The flow rate is then correlated with the pressure drop.

[44] Cooper and Alley (1990)

Table E2: Summary of Equipment used in Flow Monitoring of Air Emissions	
Pitot tubes	Stack gas volumetric flow rate is determined from measurements of stack gas velocity, temperature, absolute pressure, dry gas composition, moisture content and stack diameter. The pitot tube can be used under certain restrictions[45]. Details of the construction and use of S-type pitot tube are described in EC, 1993. The average stack gas volumetric flow rate is calculated as: $Q_s = 3600(U_s)_{avg} A_s (1 - B_{wo}) \frac{T_{ref} P_s}{(T_s)_{avg} P_{ref}}$ where: Q_s = volumetric stack gas flow rate on dry basis (m^3/h) $(U_s)_{avg}$ = average stack gas velocities (m/s) A_s = inside cross sectional area of stack (m^2) B_{wo} = proportion by volume of water vapour in stack gas T_{ref} = reference temperature (298 ^oK) P_s = absolute stack gas pressure (kPa) $(T_s)_{avg}$ = average stack gas temperature (^oK) P_{ref} = reference pressure (101.3 kPa)
Rotameters	The fluid flows upward through a vertical tapered tube and past a float, suspending it at a certain height, which is correlated with the flow rate.

Additional Air Monitoring Procedures

A number of procedures are described in Environment Canada's Reference Methods for Source Testing[46] including:

- Method C: Determination of Molecular Weight by Gas Analysis
  An integrated or grab sample is extracted from a single point in the gas stream and analyzed for its components using an Orsat analyzer, gas chromatograph or calibrated continuous analyzer.

- Method D: Determination of Moisture Content
  This method describes the equipment and procedures used to determine the moisture content from a single point in an enclosed gas stream being sampled.

- Method E: Determination of Particulate Releases
  This method describes the measurement of concentration and emission or release of particulate matter from enclosed gas streams of stationary sources.

- Method F: Calibration Procedure for S-Type Pitot Tube, Dry Gas Meter and Orifice Meter
  The S-Type pitot tube and/or probe assembly is calibrated in a wind tunnel against a standard tube having a known coefficient. The dry gas meter and the orifice meter are calibrated against a primary standard before each compliance test.

[45] EC, 1993.
[46] EC, 1993.

Appendix F

Supplemental Information on Solids (Sludge, Soils, Sediments) Sampling

[47] Test Protocol criteria reference number

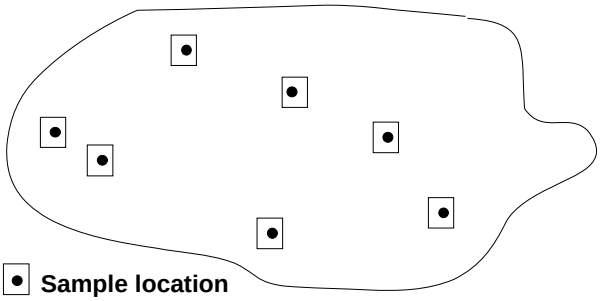
(5.) Sampling Methodology

The structural properties of a solid or semi-solid material add complexity to a sampling program. The balance, which exists in the soil with regard to, entrapped gases and moisture for example must be maintained during sampling procedures. Careful sampling methods and appropriate preservation techniques minimize any disturbances, which might occur due to sampling devices. An understanding of the physical properties of soil and the various types of soil at a sampling site provide valuable information to sampling personnel.

(6.) Sampling Locations

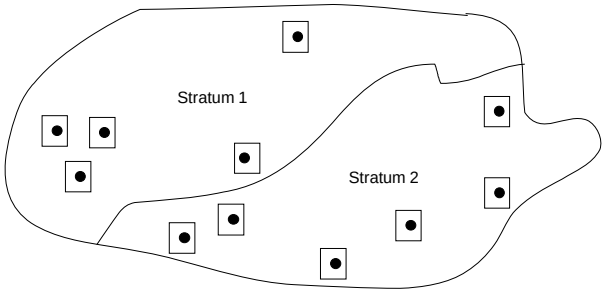
Sediment Sampling Grids

Soil, Sediment and Sludges (at dispersed locations)[48]
To collect samples from materials dispersed over a large area, such as a pond, requires procedures that are more elaborate. The following are approaches that can be applied to sampling of soil or sediments from a pond or other large area.



Simple Random Sampling
A simple random sample is one that allows every possible combination of sample units to be selected. The possible combinations are limited only by the sample size. Random sampling is accomplished by ensuring that at any stage of sampling the selection of a particular unit is not influenced by other units that have already been selected. On small sites (< 0.5 ha) with uniform conditions, as few as five to ten samples may be sufficient. Larger areas or ones that vary more may need up to 25 samples.

Random sampling provides estimates of a mean and confidence limits, but may not provide sufficient information on the pattern of disturbances. The simple random sampling plan is often used for: post-reclamation assessment of mine and gravel pit sites, land-farming operations, assessment of logging blocks, and soil storage piles. All of these tend to be uniform because the soil has been treated similarly within the disturbance type. Variability should be low, but a statistical analysis will confirm or refute that hypothesis.

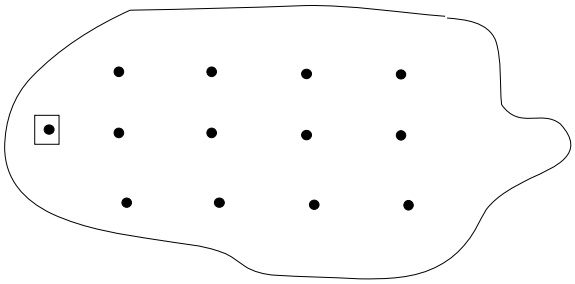


Stratified Random Sampling
In stratified random sampling, the total area is broken into a number of strata or subpopulations and a random sample is taken from each stratum.

This method is used: (1) to make statements about each stratum or subpopulation separately and (2) to increase the precision of estimates over the entire area. The basis of effective

[48] Adapted from Carter, 1993

stratification may be topography, type of vegetation cover, type of soil, estimated exposure to or concentration of contaminants, or the difference in type of clean-up procedure.



Systematic or Grid Sampling
Systematic sampling, a scheme in which selected units are at regular distances from each other attempts to guarantee complete coverage of a soil population. Sampling points are usually located at regular intervals on a grid as shown.

The sampling points follow a simple pattern, separated by a fixed distance. Although the sampling pattern is predetermined, the first sample location should be selected at random. All the sample sites follow the pattern from that point on. In some cases, however, there may be a need for stratified systematic sampling. This is encountered when the strata are well-defined entities, such as field research plots.

Composite Sampling
When only the average value of a soil property is needed, a substantial saving in analytical costs can be realized by compositing samples. A number of field samples representing the soil population under study is thoroughly mixed to form a composite, which is then sub-sampled for submission to the laboratory. This sampling plan can only be used for properties which are unaffected by physical disturbance (most biological and chemical properties).

(10.) Sampling Equipment

Table F1 provides some examples of sampling equipment for solid materials. Of particular note are methods for sampling soils for volatile organics analysis, which vary widely. Note that analyte recoveries have been highly variable. Loss through volatilization causes a lot of negative bias in the data. No standard procedures exist for sampling soils for VOC analyses. The selection of a sampling device is site specific. Samples should be removed from samplers and stored in glass jars or vials sealed with Teflon liners with no headspace. Target domains may include surface or subsurface environments, hot spots, a concentration greater or less than an action limit or the area above a leaking underground storage tank. Statistics from target domain data must be considered before a sample and analysis design is developed. Data must be of sufficiently high quality to meet the goals of the sampling activity. Samples of a size appropriate to the analytical method should be collected. As VOC concentration levels reach detection limits, the quantity and frequency of QA/QC samples must be increased or the number of samples must be increased. Trip blanks are a necessary element in VOC analysis. The trip blank soil matrix should have a sorptive capacity similar to the actual sample.

Table F1: Summary of Equipment used in Sampling Solids[49]	
Sediment	
Dredge	Dredges are grab samplers, used to collect surface sediments, have either a set of jaws which close when lowered to the surface of the sediment or a bucket which rotates into the sediment upon reaching the bottom.

[49] Adapted from Environment Canada (1995) and US EPA (1986).

Table F1: Summary of Equipment used in Sampling Solids[49]	
Single gravity corers	This device's main feature is a core barrel penetrating the sediment by gravity and collecting up to 2 m of sediment.
Piston corers	Piston corers feature a core barrel with a liner and piston for collecting bottom sediment cores up to 20 m in oceans or large, deep lakes.
Grain Sampler	The grain sampler is used for sampling powder or granular waste or materials of no greater than 0.6 cm in diameter, from bags, sacks, or similar containers.
Soil	
Spade, scoop and trowels	The simplest soil sample collection method is with the use of a spade or shovel to remove the surface layer and a stainless steel scoop to collect the sample at the required depth. This method is appropriate for shallow sampling. Very accurate, representative samples can be collected with this procedure.
Auger and thin-walled corer	The corer can be used manually or with power equipment to obtain an undisturbed variety of soils, sediment or sludge samples from the surface or to depths in excess of 6 m.
Split spoon sampler	The heavy steel sampling head can be split in two to release the sample. The split spoon is attached to a drill rod and pounded into the ground with a heavy casing driver or sledgehammer. Undisturbed soil samples can be collected from a variety of soil types and at greater depths than other soil equipment. Power equipment may be necessary due to the weight of this sampler.
Veihmeyer sampler	This device consists of a sampling tube, a drive head, a sampling head and a drop hammer. The sampler can be used for most types of soil to a depth of 4.9 meters.
Hollow stem auger	This device can be used for sampling from different types of soil including stony soils using mechanical power.

Volume Measurement

In conjunction with sample collection, it is essential to measure flow or volume. Flow rate (or total volume) information is needed not only to determine the make-up of composite samples but also to determine mass loadings of measured parameters. Removal efficiencies of environmental technologies should be based on the percent removal of the mass of contaminant entering the system. If an industrial waste discharge is subject to surcharges, volumetric measurements are necessary to calculate mass loading rates.

(11.) Sample Containers and Preservation

Table F2. Summary of Sample Handling Requirements

Parameter[50]	Container [51]	Preservation	Maximum Storage	Comments
Particle Size	P, G, or M	Wet, 4°C, tightly sealed	14 days	Drying, freezing, and thawing cause aggregation of particles
Stratigraphy	Core	Wet, 4°C	Several Months	Preserve original consistency
Bioassays	P or G	Sieved, 4°C, dark	Processed within 2 to 7 days	Mixing and sieving recommended before testing sediment toxicity
Bacteriological	Sterile G	Wet, 4°C	Processed within 6 hours	
pH, Eh, CEC	Bucket or core	Wet undisturbed and untreated	Determined in the field	Very difficult and problematic temperature corrections
P_{tot}, TKN	G	Freeze, -20°C	1 month	If possible, analyze in 24 hours
TOC	P or G	Freeze, -20°C	6 months, dark	Carbonates and bicarbonates can interfere
Oil and grease	M or G	Wet, 4°C	1 day	Wet sample can be stored for up to 1 month at -10°C with 1-2 mL concentrated H_2SO_4 per 80 g
Metals	P or T	Dry (60°C) or freeze (-20°C)	6 months	If samples are not analyzed within 48 hours, freeze dried -20°C up to 6 months
Mercury	G or T	Freeze, -20°C	1 month	Mercury analysis is performed with wet samples
Volatile organics	G vials with Teflon® septums	Freeze, -20°C	1 month	No preservatives should be added. Possible loss of some compounds
Cyanides	P	Freeze, -20°C	Up to 1 month	Sulfide interfere colorimetry
Pesticides and PCB	M or G covered with Al foil	Freeze, -20°C, dark	7 days until extraction	If samples are not analyzed within 48 hours, freeze dried -20°C up to 6 months

[50] CEC = cation exchange capacity; P_{tot} = total phosphorus; TKN = total Kjeldahl Nitrogen; TOC = total organic carbon
[51] P = polyethylene or polypropylene; G = glass; T = Teflon; M = metal