10.0 Sample Collection

Sample collection is a vital part of the composition of waters and wastewaters studies. It is often the major source of error while obtaining water quality information. In any study involving small samples of a material, inherent uncertainties exist related to the homogeneity of the sampled source, the number and frequency of the samples collected, the method of collection, and the size of the individual samples.

The most important factors affecting the ability to adequately determine the composition of water over a period of time are the methods and frequencies of sample collection.

10.1 SAMPLE COLLECTION METHODS

The three general types or methods of sample collection are:

A. The grab sample. This is an individual discrete sample collected over a period of time not exceeding 15 minutes.

B. The simple composite sample. It is collected by combining equal volumes of two or more grab samples collected at a fixed interval of time.

C. The proportioned composite sample. The volumes or collection frequencies of the grab samples combined vary with flow.

The choice of collection method is usually dictated by the circumstances surrounding the sample site and the objectives of the monitoring program. Some guidelines governing the selection of a sample collection method are:

1. A grab sample will adequately represent the flow at the time it is collected if it is known or can be determined that a source is uniform in composition (homogenous). For most dissolved constituents, some degree of homogeneity is common. For constituents that may be associated with suspended material, a single grab sample may be a very poor representation of the source being sampled.

2. A composite sample will accurately represent the water in a vertical cross section of a stream by combining appropriate volumes of samples taken at a series of points along the cross section, and will be used if the source is not known or not believed to be homogenous. For suspended sediment or associated constituents, a composite sample will better represent the quality of the water. The number of samples to be collected for compositing relates primarily to the representativeness of the composite sample and secondarily to the volume of the sample required for analysis.

3. Water stored in lakes and reservoirs is commonly not uniformly mixed. Thermal stratification and associated changes in water composition are among the most commonly observed effects. Single grab samples from lakes or reservoirs can be assumed to represent only the spot within the water body from which they came.

4. The collection of a grab sample is appropriate when the sample:

a) Characterizes water quality at a particular time;
b) Provides information about minimum and maximum concentrations;
c) Allows collection of variable sample volume;
d) Corroborates composite samples; and
e) Meets a requirement of a discharge permit.

5. Grab samples will be used when:

a) The stream does not flow continuously;
b) Water or waste characteristics ar e relatively constant;
c) Variables to be analyzed are likely to change with storage (dissolved gases, residual chlorine, soluble sulfide, oil and grease, microbiological parameters, organics, and pH);
d) Information on the maximum and minimum concentrations or variability of concentrations is desired;
e) The history of water quality is to be established based on relatively short-time intervals; and
f) Spatial variability is to be determined, for example, throughout the cross section and/or depth of a stream or a large body of water.

6. Composite samples will be used when:

a) Determining average concentrations; and
b) Calculating mass/unit time loading.

7. The method of sample collection used in DEQ Compliance Monitoring is usually specified in the permit. The DEQ Compliance Sampling Manual shows that sampling programs must include a minimum of a 24-hour operating day composite supplemented by two or more grab samples. With highly

variable wastewater characteristics or flow rate changes, additional sampling is required. A composite sample is defined as a minimum of eight discrete samples taken, proportional to flow, over the compositing period.

8. Composite samples from lagoons with long detention times may not be representative due to the tendency of lagoons to short circuit. Grab samples may be representative of lagoon discharges.

9. Agricultural discharges (concentrated animal waste or manure from a confined feedlot, runoff from an agricultural watershed, and irrigation return flows) are usually highly variable. A single grab sample may not be representative. A series of grab samples, or a flow-proportioned composite sample, would be best.

10. Biological samples (benthic macroinvertebrate and periphyton) may or may not be composited, depending on a study's objectives.

11. Composite samples will never be collected for microbiological examination. Data from individual samples show a range of values which composite samples will not display. Also, one or more portions that make up a composite sample may contain toxic or nutritive material and cause incorrect results.

10.2 SAMPLE COLLECTION FREQUENCY

When a sampling point has been selected and a procedure adopted that ensures that each sample adequately represents the water flowing at that instant, a decision is needed about how frequently samples or measurements must be obtained. The usefulness of water quality data and the ability to interpret water quality data is often tied directly to sampling frequency. A few of the more important factors to consider in determining sampling frequency are:

A. Types of variables to be measured. Flow dependent variables (suspended solids or associated constituents) might be sampled more frequently during periods of sediment transport than during low-flow periods. Some water quality variables (temperature, dissolved oxygen, and pH) may require diel sampling to define the expected ranges.

B. Expected seasonal changes. Seasonal changes are manifested by changes in flow, storm periods with attendant runoff, rising and falling water temperatures, increased or decreased biological growth, etc.

C. Influence of man-caused inputs. Anthropogenic activities may be characterized by daily cycles (quality of a wastewater discharge) or seasonal cycles (agricultural runoff).

D. Variances of water quality variables. Known variances computed from collected water quality data may be useful in computing future sampling frequencies. Variances within a site compared with variances between sites will be useful in optimizing sampling frequency to avoid collecting data that are repetitive and do not provide much water quality information.

E. Data interpretation. Data collection frequency ties directly to data interpretation. This does not mean that a great deal of data must be collected. It does mean that data must be collected at the correct time and location.

F. The expected budget, distance to and between sampling points, and available manpower will have an influence upon the frequency of sampling.

As a rule, it is much better to restrict the area of study or scope of the program if non-hydrological constraints such as budget or manpower force a reduction in the frequency of sampling. Also, if statistical evaluations of the data are planned, then a statistical strategy in the sample collection must be in place. An appropriate number of samples must be collected to ensure that the number of degrees of freedom is sufficient so that something might be said about the data collected. Significant as sampling

frequency is in detecting stream standard violations, maintaining effluent standards, estimating temporal changes in water quality, and defining natural water quality variations, very few quantitative criteria for designating appropriate sampling frequencies are available. However, a few guidelines can be used to determine the frequency of sample collection.

These guidelines are:

1. Samples will be collected or measurements made at such intervals that no important cycles of change in concentration could pass unnoticed between sampling times. For some streams where flow is completely controlled by large storage reservoirs, or is maintained at a nearly steady rate by large, constant groundwater inflows, a single sample may represent the composition accurately for days or weeks. For many streams, however, one sample cannot be safely assumed to represent the water composition for more than a few days.

2. Statistical analysis of water quality data requires that observations be independent, that is, there will be little or no seasonal or serial correlation in a data set of a water quality variable. Seasonal correlation can be removed statistically. Generally, sampling surface waters more often than monthly may introduce serial correlation into a data set; groundwater sampling more frequently than quarterly may also introduce serial correlation into a data set. However, sampling stream waters more frequently may be desirable than once a month, for example, during spring runoff, depending on a study's objectives.

10.3 SAMPLE COLLECTION QUALITY ASSURANCE

Quality assurance is a significant part of every sampling program. It is a broad management concept of maintaining the ability to furnish reliable information, and requires complete integration of field and laboratory systems for sample collection and measurement. Quality assurance incorporates all peripheral but essential operations such as survey design, equipment preparation, maintenance tasks, data handling, and personnel training. The objectives of quality assurance are to assure that the generated data are meaningful, representative, complete, precise, accurate, comparable, and scientifically defensible.

Quality assurance begins in the planning of a water quality monitoring project. Quality assurance aspects in this phase of a project are generally incorporated in a statement of Data Quality Objectives (DQOs), Section 6.0. DQOs specify the kinds of data needed to fulfill the objectives of a water quality monitoring project. They ensure that the data collected will provide adequate information for making a decision. They require careful consideration during the planning and design of a sampling program (sampling site selection, sampling frequency, duration of sampling, water quality variable selection, etc.).

The collection of water quality data is just as important as the planning and design aspects. Quality assurance procedures must be followed to ensure that the integrity of samples collected is not compromised, that is, those samples accurately represent the source at the time they were collected. This requires that some basic sample collection, handling, and analytical procedures be followed.

The quality assurance procedures are:

A. If several locations are to be sampled during one sampling run which include both clean and polluted sites, use separate collection equipment (buckets, automatic samplers, bailers, etc.) at each location if possible. Otherwise, sampling will progress from the clean areas to the polluted areas and the collection equipment will be rinsed several times with the water from the new source before the sample is collected.

B. Sampling equipment (buckets, funnels, bailers, etc.) will be rinsed several times with the water to be sampled. PCBs, oil and grease, phenols, and hazardous waste samples will be taken directly into the sample container. If collection equipment is needed for PCBs or hazardous waste, one-time-use equipment will be used, if possible. Otherwise, decontamination procedures will be followed where appropriate.

C. The sample container must be appropriate to the sampled variable (**Table 10.1**). Use special cleaning procedures, if necessary (i.e., acid soaked bottles for trace metals analyses). Sample containers will be rinsed three times with the source water to be collected.

D. All instruments used in the field must be calibrated before

use, and periodically afterwards, according to the manufacturers' recommendations.

E. Continuous sampling devices must be calibrated according to the manufacturers' specifications at the time of setup and checked as often as necessary. Sampler components (lines, collection bottles, etc.) must be cleaned, or replaced as necessary, before use.

F. Equipment will be checked before being taken into the field to make sure they are operating satisfactorily. To the extent possible and practical, backup equipment will be available.

G. Each instrument requiring calibration will have a logbook assigned to it in which all calibration information can be recorded. Information must include date and time of calibration, method of the calibration, person performing the calibration, and comments. All maintenance and repairs done will are logged with the name of the individual doing the work. All maintenance and repairs will be done as soon as possible after the need for such work is noted. The recording of the calibration data, maintenance, and repair work is necessary to counter challenges to the quality, integrity, and acceptability of the field data.

H. All samples must be preserved according to EPA requirements (**Table 10.1**). Use preservative ampules sized for the volume of the sample collected (do not over or under preserve). Samples that must be cooled at 4 °C are best preserved with chunks of ice. Samples will be collected so that as little time as possible lapses before they are preserved. Data from samples that have not been properly preserved or have exceeded maximum holding times will be reviewed, later flagged or discarded.

10.4 QUALITY CONTROL

Quality Control (QC) involves specific tasks undertaken to determine the reliability of the laboratory data. It is accomplished internally by routinely analyzing blanks, duplicates, and spikes in the day-to-day operation of a laboratory, or externally by incorporating field originated blanks, duplicates, and spikes into the set of the samples collected during a water quality survey.

The objectives of QC samples are to ensure that 1) the integrity of data generated in a monitoring effort is not compromised by extraneous sources of contamination (blanks); 2) the reported data are favorably comparable to the true values (accuracy); and 3) the results of a sample collection and measurement process (data generated by analytical procedures) are reproducible (precision).

Water quality monitoring programs commonly use QC samples at two points in the data generating process:

A. Laboratories routinely use duplicates and spikes to establish limits for precision and accuracy for each measurement parameter. These limits may change depending on the analytical method and concentration range under consideration. The limits allow the investigator or data user to calculate an interval within which a reported concentration is expected to occur (95% confidence internal). Also, the systemic errors inherent in the operation of a laboratory or analysis of a sample (variation in the preparation of standards, miscellaneous contamination, inaccurate balances, instrument drift, interferences, etc.) will be quantified.

B. The second point in the monitoring process where QC samples are commonly used is in documenting quality control associated with the collection of samples in the field. Field blanks, duplicates, and spikes are routinely incorporated into a monitoring program without a good understanding of their function. The purpose of these samples is to validate the precision and accuracy of laboratory data, and to determine the adequacy of preservation techniques, equipment cleaning and preparation, and sampling procedures. Field blanks (Sections 11.11.1 and 11.11.2) are used to measure and quantify the amount of contamination from extraneous sources (preservatives, sample bottles, sample handling, automatic samplers, etc.) which might compromise the integrity of a sample (alter its true value or concentration).

Duplicates and spikes reflect not only the errors and variations inherent in the laboratory analyses, but also the errors and variations inherent in the collection of duplicate samples and preparation of spiked samples. If the analyses of duplicate and spiked samples are unacceptable ("out of limits"), it is virtually impossible to tell whether the cause originates within the laboratory, the field collection, or the preparation of the samples. Duplicate and spiked sample analyses that are acceptable ("within limits") have the total error from the field collection and laboratory analyses that is not greater than the laboratory error alone.

QC samples (spikes, duplicates, blanks) will be an integral part of any water quality monitoring. The frequency of collection depends on the nature of the monitoring effort; the guidelines presented here will be applied on a case-by-case basis. QA project plans will provide more specific information on their use in specific project areas.

1. Duplicate samples are independent samples that are equally representative of the parameters of interest at a given point in space and time. Results of duplicate samples will, theoretically, be the same. Realistically, results may differ due to the non-homogeneity of the sample source, sampling and analytical errors. Duplicate samples document the technique and ability of the sampler and analyst to produce representative water quality data. In long-term, ongoing monitoring programs, duplicates will be submitted quarterly for those water quality variables of interest. Short-term monitoring programs with distinctly different objectives will include at least one set of duplicate samples for those variables of interest.

2. Spiked samples are prepared by mixing or diluting a given volume of a known standard or reference solution (spike) with a volume of ambient water (matrix). The analytical objective is to "recover" 100% of the spike concentration. The actual amount recovered is expressed as a percentage.

$$100 \times \frac{A - B}{D}$$

Where: A = concentration of the matrix and spike
B = concentration of the matrix
D = actual concentration of the spike

The percent recovered will be within some predetermined acceptance limits established by the laboratory for that parameter and measurement method. Spiked samples will help project managers in validating data and point to problem areas in laboratory analysis.

3. Field blanks are obtained by running distilled/deionized water through sample collection equipment (pumps, filters, etc.) after decontamination and collection in the appropriate sample containers. The analyses of these samples will determine if the decontamination procedures have been sufficient. They will be collected, stored, and shipped with the other samples. At least one field blank will be collected during each sampling episode. In addition, at least one field blank will be collected for each thirty samples collected during any one episode.

4. Trip blanks generally pertain to volatile organic samples only. They are prepared before the sampling event in appropriate sample containers and are kept with the other samples collected throughout the sampling event. They are then packaged for shipment with the other samples and sent for analysis. At no time after preparation, the samples are to be opened before reaching the laboratory. One trip blank will be included for each sampling episode.

5. Preservative blanks are prepared by preserving a sample of distilled/ deionized water in an appropriate sample container. The sample is analyzed for the variables of interest. The samples determine whether preservatives, preservative ampules, or sample containers are contributing detectable concentrations of an analyte to an environmental sample. One preservative blank will be submitted for each sampling episode. In addition, at least one preservative blank will be submitted for each thirty samples collected during a sampling episode.

In some situations, combining several QC samples into a "hybrid" blank may be desirable. For example, an acid soaked bottle for trace metals analysis may be filled with distilled or deionized water in the laboratory and preserved in the field. The sample would not only meet the objectives of a field blank (thoroughness of decontamination) and a preservative blank (preservative contamination) but it would also indicate if contamination is introduced by the sample handling and preservation technique. To summarize, employing QC/QA methods to ensure the integrity and accuracy of the water quality data is important.

10.5 PRESERVATION

Since few samples will be analyzed at a sampling site, they must be stored in a container with a preservative to maintain the integrity of a sample. Complete preservation of samples (wastewater or natural waters) is a practical impossibility because complete stability for every constituent can never be achieved. At best, preservation can only retard the chemical and biological changes that take place in a sample after it is collected.

Methods of preservation are generally limited to chemical addition, pH control, and refrigeration (icing). Preservation is intended to retard biological action, retard the hydrolysis of chemical compounds and complexes, and reduce volatility of constituents.

Also, these requirements are generally applicable to the Safe Drinking Water Act. Preservation of samples for other acts (CERCLA, RCRA, FIFRA, TSCA) is often refrigeration only, or no preservation at all.

Some guidelines will be followed when preserving samples. These include:

A. Grab samples must be preserved as soon as possible; the collection of grab samples must be timed so that little delay occurs in preserving the sample.

B. Be careful not to contaminate other samples with preservatives intended for a different type of sample analysis. Of particular concern is the contamination of samples intended for nitrogen analysis with nitric acid used for preserving samples for metals analysis.

C. For composite samples, each aliquot will be preserved at the time of collection. When use of an automatic sampler is impossible then samples may be preserved by refrigeration (or icing) until the samples are composited.

D. Holding times for various parameters will be regarded as maximum holding times; analysis will always be conducted as soon after collection as possible.

E. Samples for analysis of dissolved metals will be immediately filtered on-site before adding nitric acid.

F. Samples requiring icing (refrigeration) must be iced as soon as possible. Cubed ice will be used liberally and in contact with as much of the sample container as possible. Cubed ice chills samples better than block ice or synthetic ices (blue ice).

G. The collection and preservation of fish samples require special handling techniques. These are covered in Field Collection Method Section 12.1.4.

H. Macroinvertebrate samples are preserved with 99% ethanol. As much water will be removed (decanted) as possible from the sample container before adding ethanol. An ounce or two (jigger) of formalin may be added to ensure sample preservation under adverse conditions (hot weather).

I. Periphyton samples for taxonomic identification are preserved by adding several ml of Lugol's solution, followed by refrigeration.

10.6 SAMPLE IDENTIFICATION

The method of identification of a sample depends on the type of measurement or analysis. When field measurements are made, the data are recorded directly in logbooks or on field data sheets. Identifying information includes project name, station numbers, station locations, date, time and names of samplers. Field measurements, observations, and remarks are then recorded.

Preserved samples for laboratory analyses are identified by a sample tag or other appropriate identification.

Sample tags will contain, at a minimum, the following information : sample location, sample number, date, preservatives, and analyses to be performed (TSS/VSS, commons, metals, nutrients). More detailed information on requested analyses is entered on the data card (Section 21.1).

Sample tags will be filled out using waterproof or indelible ink. Identifying information may be recorded directly on the sample container if it is known that such documentation is resistant to water, ice, rubbing or smearing, and other sorts of physical or chemical abrasion.

QC samples (duplicates, blanks, spikes) will be clearly marked. If a sample is to be split, it is aliquoted into similar sample containers. Identical sample tags are completed and attached to each split and marked " Split ". The tag identifies the split sample for the appropriate government agency, facility, or laboratory.

When samples are received by a chemical laboratory, a unique identification number is affixed to all sample containers appropriate to that particular sampling event, and to the LIMS database and analysis sheet containing the pertinent identifying information (sample station, location, date and time of collection, etc.). In this manner, all submitted samples are permanently identified by a unique sample number for recording of field and laboratory measurements, and for permanent storage of data. Samples can also be archived up to the maximum recommended holding time and reanalyzed, if necessary, with little chance of misidentification.

10.7 FIELD FORMS

The DEQ has field forms specifically for the collection of surface waters and groundwater samples, evaluating macroinvertebrate habitat, stream inventory, stream discharge, Chain-of-Custody, wetland assessment, and wetland jurisdiction (Section 21.1).

Samplers must use the appropriate form and are required to fill-in all the information requested that is relevant. The information on these forms includes sample location, hydrologic and environmental condition, date and time the sampling took place. These forms also assist in the tracking process to provide quality assurance.

The forms are used to notify the chemical laboratory that analytes are requested to be tested or are used to assist in the interpretation of results. Much of the information on these forms is also required for entering into the DEQ-AREV database and STORET.