## 1.3 QUALITY ASSURANCE/CONTROL IN SAMPLING

Improper sampling techniques can lead to non-representative test results, which do not represent the media/matrix being sampled. Improper sampling techniques can lead to erroneous conclusions and management actions. Non-representative test results are also possible if adequate care and control is not taken during collection of the sample or the laboratory analysis of the sample.

A field quality assurance program is a systematic process, and together with a laboratory and data storage quality assurance program, ensures a specified degree of confidence in the data collected for an environmental survey.

The first step in ensuring proper sampling techniques is to provide staff with training for the sampling conditions they encounter. A sampling plan should also be established for each program or investigation. The sampling plan should outline such items as:

- when samples are to be collected (weekly, bi-weekly, monthly, quarterly, etc),
- where samples are to be collected,
- types of sample collection devices and containers to be used,
- what types of samples are to be collected at each site,
- which method to use,
- how these samples should be preserved,
- which field measurements (and notes) are to be made, and
- which laboratories the samples are to be shipped to.

Hard copies of sampling plans should be carried into the field with the contact name and information of the principal investigator to be contacted should questions arise in the field. A sampling plan ensures that all data are collected to the same standard using the same protocols. A sampling plan should contain enough detail for substitute field personnel to carry out the program/survey/investigation.

Sample bottles should be kept in a clean environment, away from dust, dirt, fumes and grime. As well, bottles must be capped at all times and stored in clean shipping containers (coolers) both before and after the collection of the sample. Vehicle cleanliness is an important factor in eliminating contamination problems (RISC 1994).

As stated previously samples must never be permitted to get warm and should be stored in a cool, dark place. Most samples must be cooled to 4 to 10°C during transit to the laboratory; ensure copious quantities of ice packs or dry ice are used to keep samples cool. Samples should be cooled as quickly as possible in order to reduce biological and chemical activity in the sample. Alternatively, during colder months, precautions must be taken to prevent samples from freezing. Collapsible jugs of warm water should be added to shipping containers to unsure the samples remain between 4 and 10 °C.

Sample collectors should keep their hands clean, wear gloves when sampling and refrain from eating or smoking while working with water samples. Exhaust fumes and cigarette smoke can contaminate samples with lead and other heavy metals. Air conditioning units are also a source of trace metal contamination.

Van Dorn bottles, dissolved oxygen samplers for grab samples and composite samplers need to be properly washed and rinsed. Hoses for composite samplers need to be cleaned as well since residual quantities can accumulate if the hoses are not properly maintained.

Field measurements should always be made *in-situ* or using a separate sub-sample, which is then discarded once the measurements have been made. They should never be made on a water sample that is returned to the analytical laboratory for further chemical analyses. For example, specific conductivity should never be measured in sample water that was first used for pH measurements. Potassium chloride diffusing from the pH probe alters the conductivity of the sample. Similarly, pH should not be measured from a sample that will be analyzed for phosphorus, as some pH buffers contain phosphorus. Use a separate bottle for water temperature if not *in-situ*. Dissolved oxygen measurements (by DO probe) should be made *in-situ* rather than in a separate container (Resource Inventory Standards Committee (RISC), 1994)

Often, sample containers provided by the laboratory for analyses will be "certified" as being contaminant-free. In some situations upon the advice from the laboratory, sample bottles need not be rinsed with the sample water being collected. Bottles must be supplied with cap in place. Cleaned re-used bottles are not suitable for some trace constituents.

## Types of Water Quality Sampling Quality Assurance/Quality Control (QA/QC) Samples

Quality control samples are used to verify the integrity of water samples. For example, blank samples (generally de-ionized water) can be used to determine if contamination might enter a water sample in the transport (trip blank) or the entire sampling process (field blank). **Blank** samples are used:

1) to test the purity of chemical preservatives;
2) to check for contamination of sample containers, filter papers, filtering equipment or any other equipment that is used in sample collection, handling or transportation;
3) to detect contamination that occurs during sampling, and
4) to detect other systematic and random errors occurring from the time of the sampling to the time of analysis.

**Trip blanks** are usually prepared in the laboratory and simply travel with the sample bottles from the laboratory to the sampler, to the sample site, and then back to the laboratory without ever being opened. These trip blanks indicate contamination within the bottle or from volatile compounds. Alberta Environment (2006b) recommends one per trip.

In contrast, **a field blank sample** is prepared in the same manner as a trip blank and makes the journey as a trip blank; however, the difference arises when sampling occurs. During the sampling process, the field blank sample is opened and the collection process is mimicked. These measure contamination from bottles, collection methods, the atmosphere, and preservatives. Alberta Environment (2006) recommends one for every ten regular samples. B.C. Environment (2003) recommends a minimum of one field blank per sample set, or one field blank per day per collection apparatus. A practical approach is to take a full suite of blanks but only initially

analyze the field blanks. If the field blanks don't indicate problems, the other blanks (e.g. travel, filtration, equipment) may be discarded or stored.

**Filtration blanks** should be used regularly or as a minimum, when contamination is suspected. These measure contamination from the filters, and the filtration apparatus.

**Bottle blanks** measure contamination from improper cleaning of bottles. Both filtration and bottle blanks should only be used on an as-needed basis.

In addition, more than one sample may be collected from the same sampling device (**replicate sample**) at the same time as the original sample to determine the precision (how close the results are to each other) of tests. Field replicates provide precision of field plus laboratory plus environmental heterogeneity. Environmental heterogeneity can be eliminated by collecting one sample which is then split. In some cases, it may be impossible to collect replicate samples at exactly the same time as the original sample. In such cases, these replicates are deemed to be co-located samples. For a true estimate of the temporal environmental heterogeneity, the co-located samples should be submitted at separate time intervals (if possible in time period). Generally, one duplicate should be collected per sample set (BC Environment 2003) or for every ten regular samples (Alberta Environment (2006b)).

Finally, **standard reference materials** or samples (where the actual value has been certified independently) are used to determine if the results are accurate (close to the true value). These are not often used by field staff; however, these can be used when special circumstances dictate (e.g., use of a new laboratory where one is uncertain of its analytical capabilities, beginning of the field season, new project, etc.). Values should be within the certified ranges for the standard reference material.

Typically the total number of QA/QC samples should represent a minimum of 10% of the total number of samples (Alberta Environment (2006b)) although others suggest higher levels in the order of 20%. They should include at a minimum, the collection and analysis of field duplicate samples and split samples. QA/QC samples may also include equipment blanks, field blanks, triplicate samples and field spikes.

The test laboratory itself usually will have similar processes in-place to ensure that results that were reported can be reproduced. These will include training plans for staff, analysis plans for each analyte to be tested, quality control samples to ensure that there is no contamination (analysis blanks) occurring in the laboratory, that the results are precise (replicates), and that the results are accurate (use of standard reference materials and percent recoveries). The amount of quality assurance provided by any laboratory should be available upon request. As well, the results of quality control samples analyzed at the same time as your samples should be available and should be obtained in order that the results can be interpreted later.

The initial amount of samples allocated to QA/QC depends on:

1. **Level of experience of the field staff and familiarity with the analyzing laboratory**. When both the laboratory and field staff are unfamiliar with the design of the program, funds directed towards QA/QC should be divided equally between the two. On the other

hand, if either has demonstrated consistency and reliability in the past, then funding requirements can be decreased for that component.

2. **The type of program**. Impact assessment and survey (or baseline) monitoring generally require more QA/QC funds than compliance and trend monitoring. Compliance monitoring is usually conducted as an extension of an existing monitoring program so that previous QA/QC efforts likely have established a satisfactory degree of accuracy and precision. For trend monitoring, there usually is more consistency in the field, personnel, and laboratory analytical techniques. Personnel and equipment techniques will be used at the same locations on a regular schedule during an extended period of time.
3. **State of water quality**. There is no need to invest significant funds for QA/QC when the values obtained for particular variables are consistently well above the minimum detectable limit (MDL). When values are well above the MDL, a false positive is highly unlikely, and therefore the funds might be of better use if directed elsewhere (e.g., towards more frequent monitoring). When values are well below the level of concern for protection of the designated water, a portion of the budget might be of better use when allocated to a separate program (i.e., a different watershed that is of higher priority).

## Types of Biological QA/QC Samples

**Replicate Samples:** Biological replicate samples can consist of multiple samples (grabs, tows, or whole fish) from the same general area (to measure how well a single sample represents the community or how many samples are necessary to achieve some level of sampling confidence), or portions of a single sample (i.e., sectioned grabs - to measure more localized invertebrate heterogeneity).

**Split Samples:** Split samples are aliquots taken from the same container and assumed to be identical. These samples can be sent to two or more laboratories for separate analysis and the results can be used to determine inter-laboratory variability or the consistency of results within one laboratory.

**Reference Samples:** Laboratory-tested and preserved reference materials are available for tissue samples. For example, the National Research Council of Canada (NRC) has dogfish liver and muscle tissue and lobster hepatopancreas tissue for the determination of trace elements and organo-mercury. These reference tissues have been subjected to a large number of analyses performed by independent laboratories using several different analytical techniques. Consequently, the NRC provides mean values and confidence intervals for these substances. Other reference tissues are available from other sources.

**Taxonomy Samples:** Basic taxonomic reference materials are available for taxonomy samples. The US EPA is a source for taxonomy samples in reference to algal taxonomy, chlorophyll-a and several bacterial species. These reference samples should be submitted to the analyzing laboratory along with the samples collected during a field trip. They should be transferred to a regular sample container and labeled with plausible site names and numbers (the codes used for identification must be documented in the field logbook).

As well, taxonomic reference materials can be created for various regions by generating a ‘reference collection’ or ‘voucher specimen’ collection that has been independently verified by

an external expert. There should be a minimum number of samples from the survey/study that are re-counted and re-identified by a second taxonomist to get an estimate of identification error and count error.

## Understanding QA Results

The QA data results should be evaluated for completeness. This includes providing a summary of the planned and actual QA procedures undertaken and a summary of the metadata on a variable-by-variable basis to indicate the success in obtaining and storing the data. This requires verification of a minimum of 10% of the laboratory results received via electronic transfer with results forwarded separately, usually in hard copy, within seven days of receiving the analytical results.

It should be determined if contamination is present in the samples. The general rule of thumb is that levels are acceptable if there are less than or equal to 5% of *blanks* with values greater than the detection limit (network-wide).

Precision is deemed to be acceptable if there is <25% relative difference or <18% coefficient of variation, when the mean of the *replicates* is ≥ 10 MDL, and results are ≥ 10 MDL if the analytical methods are different. The Relative % Difference is defined as:

$$\text{Relative \% difference} = \frac{(S_2-S_1)}{[(S_1+S_2)/2]} * 100\%$$

where $S_1$ and $S_2$ are the sample results

and for triplicates (or greater) use Relative Standard Deviation (RSD):

$$RSD = SD/(S_1+S_2 \ldots +S_n)/n$$

where $S_1$, $S_2$ and $S_n$ are the sample results
and SD is the standard deviation

The coefficient of variation is defined as:

$$\text{Coefficient of variation} = \frac{SD}{[(S_1+S_2)/2]}$$

where $S_1$, and $S_2$ are the sample results
and SD is the standard deviation

Detection Levels are considered to be good if ≥ 50% of values ≥ 3 MDL and MDL ≤ 0.1 of the lowest relevant water quality objective or guideline.

An example of the QA used in the Canada - British Columbia Water Quality Monitoring Agreement is shown below for one station (Table 3). It should be noted that 30 samples (26 + 2*2) are to be collected at the station each year, and that there are six rounds of QA samples submitted. This is a minimum 20% level of QA consisting of field replicates and field blanks (including filtration blanks and replicates where appropriate).

| Variable | Annual Frequency | QA Frequency |
|---|---|---|
| Alkalinity | 26 | 6 |
| Metals Trace | 26 | 6 |
| pH | 26 | 6 |
| Temperature | 26 | 6 |
| Turbidity | 26 | 6 |

Table 3 – An example of the level of QA required for one station under the B.C. – Canada Water Quality Monitoring Agreement