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Introduction

The objective of this manual is to outline a protocol that will ensure that collection of water quality data associated with the Environmental Water Quality Monitoring Program will be carried out using currently accepted methodologies, will be useful in terms of resource management and will be consistent with data collected by other organizations, both private and governmental.

Water Resource Monitoring - General

For riverine systems, the quality of water flowing past the sampling location is related to upstream conditions. Under ideal sampling conditions, a sample taken at any point in a stream cross section will be of identical concentration to any other taken in the same cross section. Similarly, a sample taken at point at a given time will yield an identical concentration of any constituent to a sample taken at any other time. Selection of a sampling location to maximize sample reproducibility is critical. Monitoring personnel must therefore not only be familiar with the system as a whole but also familiar with streamflow generation and routing mechanisms, channel mixing characteristics and fluvial sediment transport.

Water-quality sampling sites for purposes of the Environmental Water Quality Monitoring Program should be selected to clearly assess the condition of the water resource and to assure that comparisons can be made with subsequent samples. Because stream conditions are continually changing, a sampling scheme must have enough flexibility to provide comparable data over a wide range of physical and hydrologic conditions.

Although no single scheme can be considered the only correct approach for the selection of a water-quality sampling location, the location chosen must reflect the objectives of the program. In general, water quality monitoring locations are required for:

- the assessment of land use practices; either pre- or post land use or control treatment scenarios;
- compliance with water quality standards and criteria;
- long term changes in water quality due to regional changes in land use or climate.

The collection of water samples may seem a relatively simple task. However, more than the

simple dipping of a container into water is required to obtain representative water samples and to preserve their integrity for laboratory analysis. A representative sample can be easily obtained from rivers and lakes which are relatively homogeneous, whereas many bodies of water have significant spatial and temporal variations and the collection of a representative sample becomes much more complex. Chapter 2 includes procedures intended to aid investigators in the collection of representative water samples.

References to several types of water sampling equipment are not intended to be all-inclusive but rather to introduce common sampling equipment. Furthermore, instructions for operating sampling and field measurement equipment are not intended to replace those of the manufacturer but are to be considered as supplementary information. The sample containers, preservatives and sampling procedures described in this manual reflect those most widely used for physical, chemical and microbiological analyses.

Water Resource Monitoring Site Selection

The general approach of a water quality monitoring program is to establish water quality conditions for a given area. Subsequent water quality data are then compared statistically to these data and the conclusions are used to assess trends or differences in water quality. This approach provides information that can be used in land use management decisions and provides information regarding the general state of the riverine ecosystem.

Knowledge of the system to be monitored is critical to sample site selection. Site and study specific factors that should be included in the sample site determination:

- Prior planning with maps and preliminary water quality sampling and analysis

- Presence of tributaries - stream reaches immediately downstream of a tributary should be generally avoided. Typically, a distance of 5 stream widths below the influence of a tributary is adequate distance to ensure mixing.

- Degree of mixing - complete vertical and lateral mixing within the cross section is generally desirable. Presence of point or non-point discharges of contaminants to the stream should be considered in the determination of monitoring location.

- Accessibility - access to any sampling site is directly related to monitoring program cost. Bridges are frequently chosen for establishment of water quality monitoring stations due to access during most flows and they permit sampling at any point across

the stream width.

• Safety - monitoring of turbulent streams or during peak flows can be of safety concern for monitoring personnel. Monitoring locations should be chosen that allow sampling at peak flow with minimal risk to sampling personnel.

• Applicability for Discharge Measurement - established gaging stations should be used as sampling locations if practical. In locations where gaging stations are unavailable for discharge measurements, selection of sampling locations may be dictated by criteria recommended for selection of field discharge measurement (see Chapter 1). Since discharge is a calculated value based on velocity and cross sectional area, site location in an area of minimal channel complexity and uniform flow velocities will yield more accurate discharge determinations. In general, relatively straight stream reaches with uniform velocity are preferred.

The location of a water resource monitoring station and the frequency of monitoring needs to be identified in the water quality monitoring plan. Location and frequency are established from the project objectives, and the spatial and temporal variability of the system. It is the responsibility of the field investigator to locate all sampling stations accurately. It is important to take the sample at exactly the same location each time. Only if the same location is consistently sampled can temporal changes in the water quality parameter levels be interpreted with confidence. Therefore, accurate station location descriptions must be prepared on the first visit to every sampling site, and these must be carefully followed by investigators during subsequent sampling events.

Springs and seeps, when they occur, provide a means of assessing soil water and/or groundwater quality. Groundwater from springs should be identified as to the geologic strata from which the water discharges. Location and elevation should be noted. Collect samples from springs and seeps as near as possible to the point of discharge, before possible sample water changes (temperature and gasses) or surface contamination can occur.

Monitoring Frequency

Monitoring frequency is, in general, dictated by the program objectives, temporal variation in riverine conditions and program budget. In addition, field investigators are responsible for observing any unusual conditions which may indicate a need for additional water quality sampling outside a scheduled monitoring event. Upon observing an unusual condition, such as an unusual turbidity or odor of the water, excessive algal growth, indications that foreign

substances have entered the system (oil slicks, surface films, etc.) or fish kills, water quality samples should be taken to help identify the contaminant source or impacting land use. The type of samples and their preservation should be consistent with the type of analysis that the investigator thinks is warranted by the prevailing conditions. If additional samples are not collected at an established station, the new station location description should be accurately recorded.

Chapter 1

Stream Discharge Measurement

Introduction

Stream discharge is defined as the unit volume of water passing a given point on a stream or river over a given time. Stream discharge is typically expressed in cubic feet per second (cfs) or cubic meters per second (cms) and is based on the continuity equation or velocity-area method $Q = A \bullet V$, where A is the cross sectional area of the stream at the measurement point and V is the average velocity of water at that point.

Streamflow at any point in time is an integration of the streamflow generation and routing mechanisms in a watershed at that time. This integration also defines the water quality at that time, including land use activities, point source discharges and natural sources. Thus streamflow measurement should be considered an essential component of water quality monitoring. Streamflow measurements are useful for water quality data comparisons over time, interpretation of water quality data, and calculation of parameter loads.

Streamflow measurements will be made at each water quality location at the time of each water quality sampling. Streamflow measurements will be used to calibrate and reconfirm any stage-discharge relationship (rating curve). If the streamflow measurement differs by more than 10% of the predicted value and the measurement is considered good, the rating curve should be reevaluated (Rantz et al., 1982).

1.1. Equipment List for Stream Discharge Measurement

1. Flow meters - AA Price or Pygmy with wading rod, extra batteries, headphone, and copy of rating table, or direct reading instrument.

2. Tape measure - cloth or fiberglass tape is recommended.

3. Stakes - end stakes for anchoring tape measure to stream banks.

4. Stopwatch.

5. Waders - hip or chest.

6. Pencils, markers, and labels.

7. Discharge and sampling forms.

8. Calculator.

1.2. Gaging Site Selection

1. Purpose - have reasons for sampling at a particular location.

2. Access - near a road or trail.

3. Locatable - a distinctive feature nearby will help locate sampling point on the map.

4. Immediate stream reach - reasonably straight, narrow, free of rapids, pools, islands, and eddies; uniform, laminar flow.

5. Obstructions - free of large rocks, bottom debris, algae, weeds, and hanging plants from banks.

6. Bed material - avoid mud, large cobbles, and boulders.

1.3. Site Preparation

1. If necessary, move small obstructions and debris (before measurement only).

2. Set tape measure and stakes perpendicular to flow. If impossible, note the correction factor in field notes.

3. Calculate number and size of intervals; recommend 10 percent of flow in any one interval.

4. Find edge of water by looking straight down on the tape measure.

5. Prepare field notes by filling out appropriate blanks; always complete: observer name, date, time, stream name, and stage.

1.4. Stage Observation

The staff gages installed at specific water resource monitoring locations will be read at the time water samples are taken to determine the stage or elevation of the water surface at that location. Anchored in the stream bed, the gage will consist of a vertical scale that is permanently marked in increments of 0.01 feet and the stage reads directly from these markings to the nearest 0.01 feet. Stream stage is defined as the elevation of the water surface above an arbitrary zero datum at that specific point in the stream. Thus, the zero discharge point does not necessarily correspond to a stage of zero.

1.5. Field Measurement

The velocity measurements are made in the stream while wading when the depth and velocity of water permit safe crossing of the stream. The individual taking depth and velocity measurements will stand downstream of the measurement point and in a position that least affects the velocity of the water passing the current meter (obtained by standing behind the meter facing upstream). The wading rod is held at the tape in a vertical position with the meter parallel to the direction of flow while the velocity is being observed. The field procedure for determining flow by velocity is outlined in the following steps:

1. A tape will be suspended across the channel perpendicular to the direction of flow to measure the top width of flow.

2. The stage height will be read from the staff gage and recorded.

3. Suitable stream width increments to make velocity measurements will be determined.

4. The flow rate at each increment is measured using a top setting wading rod.

5. The velocity measurements will be taken by setting the current meter on the wading rod to the proper depth.

6. Repeat velocity measurement at each incremented cross-section.

7. After all velocity measurements are complete, the gage height (stream stage) will be read and recorded. The gage height will be compared to the initial gage height to determine if the gage height readings change more than 10% for depths of flow less

than 1 foot or 5% for depths greater than 1 foot occurred during the measurement. Should a change occur, the flow measurement will be repeated.

8. The discharge will be calculated and compared to staff gage discharge estimate from the rating curve. If there is a departure of more than ±10%, then discharge will be remeasured and/or stage-discharge curve recalibrated. The measurements will be taken at equal intervals across the stream. A minimum of five to ten measurements will be taken in the stream. For narrow streams, this may require measurements at 15 cm intervals or less. If the majority of flow is confined to one section of the stream, such as the center of the stream, the measurements should be taken at smaller increments in the majority of the flow and at larger intervals elsewhere across the stream. Usually no individual increment should contain more than ten percent of the total flow. However, it is not required that measurements always be taken at one or two foot intervals. The point at which the measurements ar taken is recorded according to the distance shown on the tape line suspended across the stream. For the streams in the area, it is recommended that depth and velocity measurements be taken at one foot intervals across the stream and at smaller intervals where the flow is concentrated.

The depth of flow is measured at each increment using the wading rod, as previously outlined. The rod is placed vertically in the stream at a specific interval along the tape line so the base plate of the rod rests on the streambed. The depth of water is read on the graduated rod to the nearest 0.01 feet. As previously indicated, the person holding the wading rod should stand downstream in a position that least effects the flow at the sensor.

Several different velocity methods can be used to determine the average flow velocity at a point. Two methods that are appropriate for measuring the average velocity for the streams in the area are the six-tenths depth method or the two-point method. Selection of the specific method depends on the depth of flow. The six-tenths depth method will be the primary method for measuring average velocity and is used whenever the depth of flow is less than 2.5 feet (USGS, 1977). All velocity measurements will be taken for a minimum of 45 seconds.

1. For each interval, read and record:

   (a) Distance - from reference point (note edge of water at beginning and end).

   (b) Width - distance halfway from previous to subsequent interval.

   (c) Depth - of water to normal stream bottom.

(d) Observation depth - distance from water surface to proper meter setting, 0.60 for one velocity measurement or 0.20 and 0.80 for two velocity measurements.

(e) Meter revolutions - if slow, count complete clicks; if fast count multiples or use direct reading instrument.

(f) Time - use a minimum of 40 seconds.

2. Edge effect - watch for partial intervals and calculate appropriately; do not count areas of zero velocity.

3. Calculate discharge - compare to past measurements and site familiarity for reasonableness.

1.6. Data Record

Data will be recorded on a standard form (Figure 1). The data recorded in the field includes the distance from initial point, depth, observation depth (the depth at which the velocity was measured), and velocity.

Discharge is calculated by the rational equation:

$$Q = \Sigma (VA)$$

Where: V = velocity
A = cross sectional area

The total discharge of the stream is the sum of the discharges in the partial sections:

$$Q = q_1 + q_2 + q_3 + \ldots q_n$$

Where: Q = total discharge of stream
q_1 = discharge of stream section 1
q_2 = discharge of stream section 2
q_n = discharge of last stream section.

Effluents or streams too small to be measured with a current meter may sometimes be accurately measured volumetrically with a bucket or other suitable container and timer. Measure volume or calibrate the container in liters and convert to appropriate units. There are 3.79 L per gallon and 7.47 gallons per cubic foot and 35.3 cubic feet per cubic meter.

Figure 1. STREAM DISCHARGE MEASUREMENT FIELD FORM

Station Location:							
Date:	**Party:**						
Stage:	**Current meter type and number:**						
Spin test (before):				**Spin test (after):**			
Distance	Depth	Velocity	Average Velocity	Average Depth	Area	Q	% total

Chapter 2

Sample Collection, Handling and Preservation

Introduction

A sample is intended to provide information regarding characteristics representative of a larger population. In the case of riverine environments, a single water quality sample may be intended to provide information regarding water quality associated with an entire drainage basin for a given discharge. Since the data is used to make inferences regarding the water quality over a large area, each step of the sampling process is critical. Sampling of waters can be difficult since contact with materials other than the sample container may result in sample alteration or contamination. Consistent sampling practices can minimize potential contamination and ensure that analytical information will be useful in the evaluation of the water resource. Knowledge of many water-quality sampling techniques will be useful since a variety of rivers and settings often must be sampled.

2.1. Sample Collection

The purpose of this section is to describe common water quality sampling techniques. The decision on what sampling method to use will be dictated by both the existing field conditions and the judgment of the sampling team. For purposes of the Environmental Water Quality Monitoring Program, priority should be given to recognized, accepted sampling practices to ensure valid data.

2.1.1. Guidelines for Representative Samples

For water quality sampling sites located on a homogeneous reach of a river or stream, the collection of depth-integrated samples in a single vertical may be adequate. For small streams a grab sample taken at the centroid of flow is usually adequate.

For sampling sites located on a nonhomogeneous reach of a river or stream, it is necessary to sample the channel cross section at the location at a specified number of points and depths. The number and type of samples taken will depend on the width, depth, discharge, the amount of suspended sediment being transported and aquatic life present. Generally, the more points that are sampled along the cross section, the more representative the composite sample will be. Three to five verticals are usually sufficient, and fewer are necessary for narrow and shallow streams.

2.2. Stream Sampling

Sample Container Immersion

An efficient method of collecting water samples is to use the sample container as the sampling device. Container immersion is generally used in shallow or wadable water bodies and can be used from fixed structures (e.g., bridges) or boats.

Using sample containers, water samples can be collected by the following procedure:

1. Select the appropriate sized precleaned and prelabeled sample container. Samples should be taken in a prearranged priority so that all sample handling and preservation can take place as rapidly as possible. Sample containers, sample size, and preservation requirements for water samples are presented by parameter in Chapters 3 and 4. Collect the sample where the water is well mixed, immediately downstream from a point of hydraulic turbulence such as a knickpoint or flume or where streamflow appears laminar.

2. Do not walk on, or in any way disturb, the stream bottom upstream from the sampling site.

3. Do not sample streams immediately below tributaries or other significant points of inflow. Sample far enough downstream for thorough mixing to have occurred (approximately 6 - 8 stream widths downstream), or sample both main stream and tributary just above the confluence.

4. Wide shallow streams should be sampled at several points. If sampled at several points, the samples can analyzed either as individual or composite samples.

5. Water quality can vary with depth; deep streams should be sampled with depth-integrating samplers, or samples should be taken at different depths for analysis as individual or composite samples.

6. Clear surface debris if present. Avoid water quality sampling in pools or standing water where floating solids tend to accumulate. Rinse sample containers with the water that is to be sampled three times prior to sampling.

7. Submerge the sample container below the water surface to the appropriate depth. To avoid contaminating the sample, collect samples with the mouth of the sample bottle or

collection container pointed upstream. Keep hands and other potential contaminants away from the mouth of the collection container. In a well-mixed stream, collect the sample in the center of the channel using depth integrated sampling techniques, avoiding the inadvertent collection of part of the stream bottom or top-floating materials.

8. Allow the container to fill to desired volume (e.g., leave about 1% of the container's capacity to allow for addition of preservatives (if necessary) and expansion if samples are to be shipped).

9. Collect sufficient sample volume to allow duplicate analyses and quality assurance testing. The required sample volume is the sum of the volume required for each analysis requested. Refer to later sections for minimum sample volumes required.

10. Remove the container from the water, filter if necessary, preserve sample as required. Secure the cap tightly.

11. Not all sample containers should be filled to the same level. Sample bottles should be filled completely if the samples are to be analyzed for dissolved oxygen, volatile organics, oil and grease, pH, NH_4^+, Fe^{2+} and alkalinity. Full bottles must be protected from freezing. When sampling for bacteria or suspended solids, it is desirable to leave an airspace in the sample container to facilitate mixing before subsampling in the laboratory.

12. Rinse the container's outside surface with clean water and dry with a paper towel. Verify the sample label is correct and complete.

13. Preserve the sample as required and place the labeled sample container in an appropriate carrying container. Complete chain-of-custody documents if required and record them in the field logbook.

14. Maintain an up-to-date field book in which to note setting, personnel, equipment used, environmental conditions, and problem areas.

15. Collect split and duplicate samples when required.

16. Rinse sampling and analytical equipment before leaving each sampling location.

17. Move to next sampling location and repeat procedures.

2.3. Springs, Seeps, and Very Shallow Streams

Unless pools are present, samples cannot be dipped in the normal way from springs, seeps, and very shallow streams. Water may be collected with a syringe from shallow water as long as it does not draw particulate matter from the bottom. It may be necessary to excavate a small pool or depression in order to collect adequate water volume for the sample. After disturbing the stream bed in any way it will be necessary to allow the flowing stream to clear of sediment and turbidity prior to sampling.

Scoops can be used to sample shallow water associated with seeps and springs where the surface contour intersects the water table. They can develop above the water table where infiltrated water percolates downward to a perching horizon and then migrates laterally to the intersection of that horizon and the surface contour. Biological activity effects on the oxygen content, pH, nutrient, and metals concentrations can be extensive. Water quality sampling should be as close to the surface expression as practical to minimize contact time with the atmosphere. Thus, the water that seeps from these areas may be substantially altered and may not represent subsurface conditions. However, seeps and springs can yield some pertinent information if the data are properly interpreted.

2.4. Sample Types

2.4.1. Grab Samples

A grab sample is defined as a discrete sample taken at a selected location, depth and time and analyzed for the constituents of interest. Grab samples are often used for small streams where depth integration is not possible.

2.4.2. Depth-Integrated Sample

A depth integrated sample is defined as a sample collected over a predetermined part or the entire depth of the water column at a selected location and time in a given water body and then analyzed for the constituents of interest.

2.4.3. Composite Samples

A composite sample is obtained by mixing several discrete samples of equal or weighted volumes in one bottle, an aliquot of which is then analyzed for the constituents of interest. The two main types of composite samples are:

1) Sequential or Time Composite
This composite is made up by:
(a) continuous, constant sample pumping or
(b) mixing equal water volumes collected at regular time intervals.

2) Flow Proportional Composite
This composite is obtained by:
(a) continuous pumping at a rate proportional to the flow,
(b) mixing equal volumes of water collected at time intervals which are inversely proportional to the volume of flow, or
(c) mixing volumes of water proportional to the flow collected during or at regular time intervals.

A composite sample provides an estimate of average water quality condition over the sampling period.

2.4.4. Pumping Samplers

2.4.4.1. Pumps

Three types of pumps - diaphragm, peristaltic and rotary - are available to collect water samples. In general, diaphragm pumps are hand-operated; the peristaltic and rotary pumps require a power source and consequently they have limited field utility in remote locations. Peristaltic pumps are not recommended for the collection of samples for chlorophyll analysis, as damage to algal cells may occur. All pumps must have an internal construction that does not contaminate the water sample. Input and output hoses must also be free from contaminants.

The in-field procedure is:

(a) Place the input hose at the water depth specified by the sampling program.

(b) Purge the pump and hoses with water from the station to be sampled before the actual water sampling begins.

(c) Each pump should be operated according to the instruction manual for that particular pump. Take care not to contaminate the pump system. Do not permit the hoses to drag on the ground when the system is being transported.

(d) Fill the type and number of sample bottles required at each station from the output hose.

2.5. Sample Handling

2.5.1. Sample Containers

Though there are few established rules that specify container size, shape, construction, or composition, the following should be considered:

- volume of sample
- stability of container in field
- storage convenience
- ease of sealing
- ease of labeling.

Do not use a sample container made of a material chemically similar to anything that is to be analytically determined. For example, samples to be analyzed for organic carbon should be collected in glass containers instead of plastic. Samples for boron analysis should be collected in a plastic container rather than a glass container. Make sure the sample container cap or lid will not contaminate the sample.

Disposable plastic bottles (polyethylene) serve as excellent sample containers for most routine analytical determinations. Depending upon laboratory requirements, 500 mL or 1000 mL (8 or 32 ounce) bottles will suffice for most samples. See Appendix for volume requirements by analysis. The most common container design is the modern cylindrical bottle. It is easy to label, fits conveniently into weighted sampling devices, and is disposable.

Collapsible plastic containers are also suitable. They are easy to store when empty, but they are difficult to inflate and label and will not conveniently fit weighted sampling devices.

Water samples may be collected in presterilized plastic bags. Six-ounce bags are adequate for most samples. The bags are easily labeled with a waterproof marker directly on the outer surface.

Glass milk bottles have been used for years to collect sediment samples with federal samplers. Milk bottles are easy to use in the field and in the laboratory, but they are subject to breakage and are heavy to transport. Because of their initial cost they are not considered disposable and, therefore, must be thoroughly washed and rinsed before reuse.

2.5.1.1. Sample Container Preparation

The water quality sample will be collected in a 1 liter narrow mouthed high density polyethylene (HDPE) sample collection bottle. Sample containers for required variables should be composed of high-density linear polyethylene. Containers to be used for pH, ANC (acid neutralizing capacity = alkalinity), and anion analyses shall be rinsed three times with deionized water, filled with deionized water, and allowed to stand for at least 48 hours, then emptied and rinsed with sample water in the field.

Soak the sample containers for cations and metals in 10% HCL for 12 hours, then rinse them 6 times with deionized water. Next, fill the containers with deionized water and allow them to stand for 48 hours, then empty and refill them with deionized water until they are used for collecting samples. The containers should not be allowed to dry between acid washing and sample collection, except when in storage.

At least 50% of the cleaned (selected randomly) containers must be given a conductivity check. Measure the conductivity of the deionized water in the container after the 48-hour period. If the conductivity is >2.0 μS/cm, rerinse all the containers in that batch. Record in the laboratory notebook the highest conductivity value for each batch. Since container contamination is random and is most likely to be caused by incomplete rinsing after acid washing, increasing the number of conductivity checks will give better assurance that each container has been thoroughly cleaned and rinsed prior to being used to collect samples.

2.5.2. Sample Filtration

Filtration of some water samples is recommended for some soluble constituents as a form of sample preservation. Filtration should be performed in the laboratory when and where conditions allow.

Water samples collected for dissolved inorganic chemical constituents (e.g., metals, alkalinity, and anionic species) should be filtered in the field immediately after collection if possible. The recommended method is an in-line filtration module that operates from sampling pump pressure.

These modules, which are commercially available, have tubing connectors on the inlet and outlet parts and range in diameter from 2.5 to 15 cm. Large diameter filter holders that can be rapidly disassembled for filter pad replacement are the most convenient and efficient. Gravity type filtering procedures can also be used.

Choice of filter media must be made on the basis of the analytical methods required for those samples (consult with an analyst prior to filtering). It is recommended that a 0.45 nm nominal-sized filter be used. Sampling personnel must be trained in proper procedures for replacing these filters because fine particles can easily be transferred to the outlet side of a disassembled filter module. Sloppy technique may result in contaminated samples. After a filter pad is changed, the initial 100 mL of fluid should be discarded as a rinse. Even if very careful procedures are followed, filter clogging by colloids and small particle breakthrough are problems that must be addressed on a case-by-case basis.

2.5.3. Sample Preservation

Sample preservation and holding times are parameter specific (Table 1). The preservation procedures for samples are pH adjustment or storage related:

pH Adjustment - Ultra-pure or metal grade nitric acid, suitable for trace metal analysis, will be used. Sufficient nitric acid (typically 2 mL/L) will be dispensed into the sample bottle to lower the pH to less than 2. The nitric acid will be used to preserve the samples to be analyzed for dissolved zinc. The nitric acid preservative will be added into the sample bottle prior to filling with the filtered water sample. H_2SO_4 and HCl are also used as preservatives. See Chapters 3 and 4 for analysis specific requirements.

Storage Temperature - All aliquots and samples will be stored in ice chests, other insulated container or under refrigeration at 4°C until filtration and preservation is performed and prior to and during delivery to the laboratory.

Table 1. Sample preservation and holding times for required measurements.

Variable	Sample Preservation	Maximum Holding Time
pH, field	closed container	measured on site
pH, lab	closed container	measured in lab upon return
Alkalinity, field	field titration	measured on site
Alkalinity, lab	store at 4°C	14 days
D.O., field	field titration	measured on site
E.C., field	field measurement	measured on site
Temperature, field	field measurement	measured on site
Conductivity	store at 4°C	14 days
SO_4^{2-} and Cl^-	filter through 0.45 μm, store at 4°C	28 days
NO_3^- and PO_4^{3-}	filter through 0.45 μm, store at 4°C	7 days
Total Nitrogen Total Phosphorous	freeze, -20°C	6 months
Metals	filter through 0.45 μm, store at 4° acidify with HNO_3 to pH 2.0	6 months

2.5.4. Recording Field Data and Sample Identification

Field notebooks, preferably containing water resistant paper, are used to record the chemical and physical parameters measured at the time of sample collection. These parameters include pH, temperature, specific conductivity (EC), dissolved oxygen (DO), and streamflow. This documentation should include the conditions for which the various instruments were calibrated and the conditions in which the measurements are made. Field data include:

1. Sample identification and location
2. Sample collection date and time
3. Sample party members
4. Weather conditions
5. Stream conditions
6. pH meter used and its calibration and measurements
7. Stream temperature
8. Specific conductance meter used, its calibration and measurement
9. The amount of sample collected and its relative location
10. If quality assurance samples were collected at this site (Quality assurance will be discussed in subsequent sections)
11. Any additional notes or observations pertinent to this sample or location for this sampling period

All entries should be made clearly and in ink. If an incorrect entry is made, a single heavy line should be drawn through the incorrect entry and the correction made. All corrections should be initialed and dated. The completed notebooks will be maintained by station in chronological order.

The field notebook should be used to record parameters for analysis; this is particularly true when parameters may change between stations.

2.5.4.1 Sample Labeling

A sample identification scheme should be developed that includes sample station identification and type of sample preservation. This type of labelling scheme is useful, as a control check, and invaluable if the field book is lost.

For example: BRB-A-6/94-07-jds
BRB - Belize River at Belmopan
A - anions - sample filtered, no preservative
6/94 - sampled June 1994, date and time may be included
07 - sample number 7, see field notebook
jds - initials of sampler

Common water sample identifiers:

	Description
T	total (raw)
TA	total acidified
A	anions
D	dissolved
DA	dissolved acidified

The sample container should be labeled with a waterproof marking pen on a pressure-sensitive label. The sample container label should contain:

1. Sample identification
2. Time (24 hour / military)
3. Date of collection
4. Name or initials of the person collecting the sample
5. Sample treatment (preservation)
6. Discharge (ft^3/s or gal./min.)
7. Remarks

Upon completion of sampling and field-data recording, the samples should be transferred to the laboratory under appropriate conditions. Samples should be shipped in an ice chest or other insulated container. The acid-preserved samples may also be stored in the ice chest as a matter of convenience. A chain of custody from (see Appendix) should be filled out by the individual doing the sampling and signed by each individual accepting custody of the sample if required. If sealing tape is used, the laboratory manager responsible for the analysis must sign the chain of custody form stating that there was no tampering with the tape sealing the container.

2.5.5. Field Quality Assurance

The Field Quality Assurance program is a systematic process which, together with the laboratory and data storage quality assurance programs, ensures a specified degree of confidence in the data collected for an environmental survey. The Field Quality Assurance program involves a series of steps, procedures and practices which are described in the following sections.

2.5.5.1. General Measures

(a) All equipment, apparatus and instruments should always be kept clean and in good working condition by means of the techniques and practices given elsewhere in this manual.

(b) Records should be kept of all repairs to the instruments and apparatus and of any irregular incidents or experiences which may affect operation.

(c) Conditions should be such that they encourage and maintain a safe work environment, both in the laboratory and field settings.

(d) It is essential that standardized and approved methodologies, such as those recommended in this manual, be used by field personnel. If any changes to the approved methods are made, they should be documented and experimental data obtained to ensure that the results are valid and comparable to the earlier data.

2.5.5.2. Prevention of Sample Contamination

The quality of data generated in a laboratory depends primarily on the quality of the samples received at the laboratory. Consequently, the field investigator must take the following precautions to protect samples from both contamination and deterioration (adapted from Environment Canada, 1983).

(a) Field measurements should always be made on a separate sub-sample, which is then discarded once the field measurements have been made. They should never be made on the same water sample which is returned to the laboratory for chemical analysis.

(b) Sample bottles, new or used, must be cleaned according to recommended methods.

(c) Only the recommended type of sample bottle for each parameter should be used.

(d) Water sample bottles should be employed for water samples only. Bottles that have been used for other purposes, such as storing concentrated reagents should not be used as sample containers.

(e) Recommended preservation methods must be used. All preservatives must be of analytical grade and included as field blanks for identification of potential contamination.

(f) When preserving samples, the possibility of adding the wrong preservative to a sample or cross-contaminating the preservative stocks should be minimized by preserving all the samples for a particular group of parameters together.

(g) The inner portion of sample bottles and caps should not be touched with bare hands, gloves, mitts, etc.

(h) Sample bottles must be kept in a clean environment, away from dust, dirt, fumes and grime. Vehicle cleanliness is an important factor in eliminating potential contamination of samples and equipment.

(i) Petroleum products (gasoline, oil, exhaust fumes) are prime sources of contamination. 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.

(j) Filter units and related apparatus must be kept clean, using procedures such as acid washes and soaking in special solutions, and should be protected from field contamination.

(k) Bottles or sample bags which have been sterilized must remain sterile until the sample is collected.

(l) All foreign and especially metal objects must be kept out of contact with acids and water samples.

(m) Specific conductance should never be measured in sample water that was first used for pH measurements.

(n) Samples must never be permitted to stand in the sun. Samples should be stored at 4°C in a cool place, ice chest or equivalent.

(o) Samples should be shipped to the laboratory without delay.

(p) The sample collector should keep his/her hands clean while working with water samples and field equipment.

2.6. Preparation for Field Trip

(a) Check and calibrate meters (pH, specific conductance, dissolved oxygen, turbidity) and thermometers.

(b) Replenish supplies of reagents for dissolved oxygen determinations as well as reagents for chemical preservation.

(c) Obtain fresh buffer solutions; pH values for the buffers should be close to the values expected in the field.

(d) Obtain road maps, station location descriptions, field sampling sheets, sampling bottles, labels, samplers, preservation reagents, pipettes, equipment manuals, etc.

(e) Obtain writing materials, extra rope and a comprehensive tool box.

(f) Obtain distilled water and clean beakers for pH, blanks and buffer measurements.

(g) If field filtering is required, obtain filtering apparatus.

(h) If microbiological sampling is to be done, obtain sterile bottles and ice chests. Ice

chests are recommended for all sample storage.

(i) Ensure that the laboratory is ready to receive water samples.

2.6.1. Sampling Equipment

Many varieties of field-testing equipment, sampling devices, and sample containers are in use. The purpose of this section is to describe these basic items. The following discussion is for identification purposes only. It does not imply endorsement nor does omission of certain brands imply that they are unsatisfactory.

2.6.1.1. General Equipment

- Insulated lab pack (cooler) and coolant
- Sample containers of adequate size, quantity and type
- Appropriate QA/QC components (trip blanks, field blanks, COC)
- Field information forms
- Field calibration forms
- Labeling equipment

2.6.1.2. Field Analysis Equipment

The instability of certain chemical and physical constituents in natural waters require that some measurements be made on site or shortly after sample collection. Water quality sampling personnel should know the operation and field use of these types of equipment:

- Discharge measurement equipment (Pygmy or Price AA, wading rod, tape, etc.)
- Field notebook
- pH meter and electrode(s)
- pH field testing kit (indicator only)
- Specific conductance meter

- Thermometer
- Alkalinity kit
- Acidity kit
- Dissolved oxygen meter
- Filtration equipment
- Chemical preservatives

These items must be transported and handled with care. Even though some have been designed for field use, they are subject to damage from shock, dust, and moisture. Use cushioned, waterproof carrying cases with all instruments.

2.6.1.3. Sampling Devices

Chemical constituents typically found in water under pristine conditions are present in both liquid and solid states. To be representative, a water sample must contain liquid water, dissolved solids, and undissolved solids in proportion to their occurrence. Undissolved solids may include both suspended solids, such as clay, and transported solids, such as sand. The devices described in this section will provide a practical means of obtaining a representative sample.

2.6.1.3.1. Suspended-Sediment Samplers

The Federal Inter-Agency Sedimentation Project of the Inter-Agency Committee on Water Resources, St. Anthony Falls Hydraulic Laboratory, has developed standard samplers and methods. The two depth-integrating samplers most likely to be used are the US-DH-48 and the US-DH-59.

The US-DH-48, which is suitable for wadable streams at least 3.5 inches deep, consists of an aluminum casting and glass or plastic bottle. The sample is collected through a brass or Teflon nozzle. The sampler weighs about 4 1/2 pounds and is held by a 3- or 4-foot rod.

In order for a sample from a deep stream, lake, or impoundment to be representative, it must

be depth-integrated. Samples for total suspended solids or other constituents, such as total iron and total manganese, may be collected with a US-DH-48 depth-integrating suspended-sediment sampler or similar sampler when water depth is adequate (>0.2 m). A Teflon nozzle and O-ring can be substituted in the DH-48 sampler, allowing for analysis of all constituents included in the inventory. If nozzles and fittings are of other materials - brass, aluminum, etc. - analysis may be somewhat restricted. More than one bottle of sampled water may be required, depending upon the laboratory determinations to be made and the preservation techniques used. The following procedure should be used when collecting samples for subsequent analyses:

1. Place a clean bottle in the US-DH-48 sampler.

2. Lower the sampler into the water and collect a small amount of sample.

3. Rinse bottle thoroughly and discard the water, making sure no solids remain.

4. Replace bottle, lower sampler at a uniform rate from the surface to the bottom, then raise it at a uniform rate. DO NOT STRIKE BOTTOM.

5. Repeat previous step at all verticals necessary for representative sample.

6. Fill the bottle no more than 3/4 full. If it is filled beyond that volume, all water must be discarded and a new sample collected.

High velocity, floating debris, very shallow water, or other conditions may preclude the use of a sediment sampler. In that case, grab samples should be collected in a clean, rinsed container. When grab samples are collected in wide, relatively shallow streams, it is important that several verticals be sampled due to the typically nonuniform distribution of suspended solids with depth. A single bottle may be filled through quick dips at several verticals, avoiding the necessity of compositing samples or collecting multiple samples.

The US-DH-59, which is used for larger streams that cannot be waded, is heavier and can be suspended by rope from a bridge or boat. The body consists of a bronze casting, weighing about 24 pounds. The DH-59 has a choice of nozzle sizes, depending upon flow velocity.

If Teflon nozzles and gaskets are used, both the DH-48 and DH-59 are suitable for collecting samples upon which most inorganic, organic, and physical tests can be made.

2.6.1.3.2. Bottles

Open-mouth bottle samples can be taken when stream velocities are low (less than approximately 2 feet per second) and the flow is non-turbulent, when only fine silt- and clay-sized particles are in suspension, and suspended-solids concentrations do not vary greatly either vertically or laterally. Standard suspended-sediment samplers do not fill properly at velocities less than about 1.5 ft/s.

Open-mouth bottle samples should be depth-integrated. A depth-integrated sample is one in which all depths accessible to the sampling device are uniformly represented. A narrow-mouth bottle, usually one liter or more in size, is commonly used. By equipping a sample bottle with tubing of the type shown in Figure 1 it is possible to control the rate of intake and thus facilitate the collection of a representative depth-integrated sample.

The sample bottle should be weighted so that it will sink readily to the bottom, taking sample on the trip from the surface to near the bottom and back to the surface. The trip must be at a uniform rate. Each point at which the sampling device is lowered to the bottom and hauled back is called a "vertical". The rate of lowering and raising the sampler must be such that the bottle is not more than three-fourths full, otherwise it will not contain a sample equally representative of all depths. If the bottle fills slowly or the stream is shallow, the sample bottle may be filled at more than one vertical or by lowering and raising several times at the same vertical.

Open-mouth bottle samples should be taken at several verticals in the cross-section to allow for the vertical and lateral variations in water quality that frequently exist in slowly moving waters. The number of verticals sampled is largely a matter of intuition; large variations in the water quality in the cross section will require sampling at more verticals than little variation.

A bottle is also acceptable for collecting samples from streams that are too shallow (less than 3.5 inches) to accommodate a suspended-sediment sampler. Where the stream or pond is very shallow, it may be necessary to "dip and pour" from one container into another. Be careful not to scoop up any bottom material with the sample and be careful to transfer all of any suspended matter that may tend to settle out.

2.6.1.4. Accessories

Other equipment required for sample identification, labeling, preservation, and shipping includes:

- acid preservative (nitric acid, hydrochloric acid)
- membrane filter, 0.45 micron
- filter holder
- syringe, plastic
- rope or nylon cord
- buffer solutions, pH 4, pH 7, pH 10
- specific conductance standards
- waterproof marker
- labels, pressure sensitive tape
- bottle caps
- bottles
- chain of custody form (if required)
- sample log book with: sample team identification, sample number, time, date, ambient temperature, weather conditions, refrigeration procedure, split sample identification, field blank identification

Chapter 3

Field Measured Parameters

Introduction

Certain constituents should be measured in the field whenever practical. These constituents can undergo chemical change during transport due to sensitivity to environmental conditions. The most common change in condition is water temperature (i.e. the stream temperature is often not at 4°C, the temperature required for sample preservation). Water temperature changes may affect pH, conductivity, alkalinity (pH endpoint), and dissolved oxygen. Other water quality constituents can be measured in the field, but the following are the most common:

- temperature
- pH
- conductivity
- dissolved oxygen
- turbidity
- alkalinity

Temperature

Definition: Thermal content of a solution on an absolute scale

Container: In-situ determination

Volume Required: Not applicable

Preservation: Not applicable

Holding Time: Not applicable

Field Procedure: Water temperature is important because it may indicate thermal pollution and it influences most physical, chemical, and biological processes. Gas-diffusion rates, chemical-reaction rates, and the settling velocity of particles are just a few of the many processes related to water temperature. In addition, temperature differences between water sources and seasonal variations of temperature make temperature useful in hydrologic investigations, particularly those that involve the mixing of groundwater and surface water.

For economy and ease of use, the liquid-in-glass thermometer is recommended for field use. A pocket-sized thermometer protected by a plastic or metal case is recommended. Mercury filled thermometers should be avoided since breakage may occur in the stream and the spilled mercury may be toxic. To eliminate the problem of column separation, it is best to use a thermometer with gas-filled capillary.

Most thermometers shipped from the manufacturer are not highly accurate. Before each new thermometer is issued for field use, it should be checked for accuracy. This is done by comparing the field thermometer to a precise instrument such as an ASTM calibration thermometer at three points. The comparison is usually made in a water bath to eliminate erratic readings. Any thermometer found to be off by more than 0.5°C should be rejected.

Temperature measurements should be made directly in the stream if possible. The following steps should be taken when making temperature measurements:

1. Check thermometer for liquid-column separation.

2. Immerse bulb into source.

3. Allow the reading to stabilize.

4. Read temperature with bulb immersed (removing the bulb from water can result in an erroneous temperature reading due to rapid thermometer response to changing conditions).

5. If temperature cannot be measured in the source, collect (at a minimum) an 8-ounce (500 mL) bottle or beaker of water and measure the temperature immediately. Shield the sample from the sun and wind while measuring.

6. Return thermometer to protective case.

Note: Temperature of the sample is required for accurate calibration of the instrumentation for dissolved oxygen, pH and conductivity. Temperatures should be recorded with results of these analyses. Air temperatures can be collected on-site, and provide useful information for site characterization as well.

Analytical Method: ASTM E1-58: Standard Specifications for ASTM Thermometers
APHA 2550: Temperature
STORET No : 00010
EPA Method : not available

Precision: $\pm$ 0.5 °C
Reporting: Report to nearest 0.5 °C

pH

Definition: pH is the negative logarithm of the hydrogen ion (H^+) activity in the water. Values may range from pH 1 to pH 14, with pH 7 neutral, less than 7 acidic and greater than 7 basic. Each pH unit represents a tenfold change in H^+ activity. pH is important in the toxicity and solubility of many constituents.

Container: Field determination (Polyethylene or teflon beaker)

Preservation: Refrigeration to 4°C

Holding Time: 6 hours

Field Procedure: Because the pH of some samples can change in a short time, it should be measured in the field with a reliable instrument or field test kit. Two different methods may be used to determine the pH of water.

Colorimetric Measurement: A wide variety of chemical reagents that display color changes over broad or narrow ranges of pH changes are used as indicators to show the approximate pH of the solution. Litmus type papers can be used to screen waters that may be extremely acidic or basic. Field kits can be used to estimate the pH of colorless, nonturbid, well-buffered water solutions, provided the reagents are fresh. Field data obtained with colorimetric kits can be used to screen waters and select appropriate buffers. Colorimetric measurements should be supported with a reliable pH meter or verified by laboratory analysis.

Electrometric: The pH meter used in conjunction with a glass electrode and reference electrode (or a combination glass plus reference electrode) develops a voltage potential in response to the hydrogen-ion activity without interference from most other ions. This method of measurement has become the standard for accurately determining pH in the field and laboratory.

It is important that maintenance and calibration be provided for all pH meters. If the pH meter is properly maintained and calibrated, field values may be more valid than lab values due to changes in pH with time and temperature fluctuation.

Calibration:

Calibrate meter and electrode according to manufacturer's instructions using two buffer solutions (for example 4 and 7, or 7 and 10). Use last the buffer having a pH nearest that anticipated for the sample. To avoid contamination of buffers, calibration and meter checks should be conducted in buffer solution in separate containers, such as small disposable paper cups. Buffer solutions should be discarded after use.

1. Check battery.

2. Expose electrode solution to atmosphere by uncovering filling port during measurements

3. Place function switch on "standby" or "ready".

4. Measure temperature of buffers.

5. Set temperature compensator to temperature of buffers.

6. Rinse electrode with deionized or distilled water thoroughly before placing it in a different buffer or into the sample.

7. If the approximate pH of sample is known (based on field- kit or multi-range pH paper results), place electrode in a buffer solution having pH near that anticipated for the sample. Turn function switch to "measure." Adjust meter to read pH of buffer by turning "standardize" knob.

8. Repeat this procedure using another buffer to closely "bracket" the anticipated pH of the sample, this time adjusting the meter reading with the "slope" knob (or equivalent) until the meter reads the pH of this second buffer.

9. If the pH range of the sample is not known, place electrode in pH 7 buffer. Turn function switch to "measure." Adjust meter to read pH 7 by turning "standardize" knob. Then, place electrode in the sample to determine an "anticipated" or "approximate" pH value for that sample.

10. Complete calibration by "bracketing" the approximate pH value of the sample.

When only occasional pH measurements are made, calibrate the instrument before each measurement. When frequent measurements are made, the meter calibration should be checked at least twice a day. If the meter is drifting appreciably it will need to be recalibrated more frequently - or it may need new electrodes. In all cases where readings indicate a violation, it is advisable to calibrate the instrument and double-check readings. If in-situ measurement is not possible, a water sample should be collected and analyzed immediately for pH. This sample is then discarded.

Measurement of Sample pH

1. Place electrode into sample.

2. Measure temperature.

3. Set temperature compensator to temperature of sample.

4. Turn function switch to "measure" or equivalent

5. Allow meter readout to stabilize (this may take several minutes if the solution is poorly buffered).

6. Record pH to nearest 0.1 pH unit.

7. Rinse electrode with deionized water.

8. Cover electrode with protective cap of deionized water or pH 7 buffer.

9. If the pH reading does not stabilize, record reading after 2 minutes.

Precautions

- Never remove electrode from buffer or sample unless meter is in

"standby" or "off" position. To do so may polarize the electrodes, permanently damaging them and resulting in unstable meter readings.

- Dirty connectors on pH electrodes may result in erroneous readings; do not handle the plug; if it is dirty, clean it with ethanol or isopropyl alcohol.

- Static electricity on meter face may be reduced by an antistatic cloth such as those used on phonograph records. If problem continues, check for broken or loose cable- shield wire.

- Keep electrode filled with the recommended solution to within 1/2 inch of filling opening. Do not substitute a filling solution of different chemical composition made for another electrode. Keep the fill hole closed when the electrode is not in use to prevent evaporation of the filling solution.

- Keep electrode tip moist by filling the provided rubber cap with either pH 7 buffer solution or deionized water. If the tip dries out, soak it in pH 7 buffer solution for 24 hours.

- Never immerse the electrode to such a depth that the surface of the filling solution is below that of the test solution.

- The temperature compensator on most meters must be set for the temperature of the sample that is being measured; however, on several brands of inexpensive meters the "temperature" compensation knob is also used as a "slope" knob to calibrate the meter to the second buffer. When these meters are used the buffers must be at the same temperature as the water being sampled. This can be accomplished by immersing the container of buffer in the stream being sampled until the temperatures are similar.

- Do not let the electrodes freeze.

- Avoid contamination of buffer. Use a separate container (cup) and discard it after use.

-Broken or scratched electrodes can give erroneous readings.

- Do not leave meter exposed to extreme weather conditions.

Note: Change in temperature will affect the ionic equilibrium of the solution resulting in an alteration of the pH measurement. Effort should be made to calibrate the instrument using buffer solutions within 5° C of the sample. The pH meter should include temperature compensation mechanism to minimize temperature effects on the electrode. Calibrate instrument at a maximum every 3 hours of use.

Analytical Method: ASTM D1293-84 : Standard Test Methods for pH of Water
APHA 4500-H^+ : pH Value
STORET No : 00400
EPA Method: 150.1
Electrometric - glass electrode in combination with reference potential (typical: saturated calomel) electrode.
pH measurement of waters of low conductivities: ASTM D5128-90.

Precision: $\pm$ 0.1 pH units
Reporting: Report to 0.1 pH unit

Conductivity (Specific Conductance)

Definition: The ability of a solution to carry an electric current. Conductivity can be used as an approximation of the dissolved solid content of the solution. Reported in micromhos/centimeter (μmhos/cm) or milliSiemens/meter (mS/m).

Container: in-situ determination

Volume Required: not applicable

Preservation: not applicable

Holding Time: not applicable

Field Procedure: Specific conductance is useful in estimating the concentration of dissolved solids in water. Rather precise field measurements of specific conductance can be made with a specific conductance meter. Most conductance meters are an adaptation of the Wheatstone resistor bridge with built-in circuitry capable of converting resistance values (ohms) to conductivity values (mhos). Most natural waters have a conductivity of much less than 1 mho, and to avoid decimals, values are usually reported in micromhos - the observed value in mhos times 1,000,000.

Conductance is dependent upon water temperature, and by convention, values are adjusted to 25°C (standard temperature and pressure). In most solutions an increase of 1°C will increase conductance by approximately 2 percent. Many field instruments have temperature compensation, either automatic or manual. If this feature is not built into the instrument and the water temperature is not 25°C, it is necessary to use a temperature-adjusted graph or the temperature factors given in Table 1 to adjust the values to 25°C.

Specific-conductance electrodes should be rinsed occasionally in a hydrogen peroxide solution or a weak acid solution (5 percent) to prevent debris and algae from accumulating. Maintenance and calibration of conductance meters should follow manufacturer's instructions.

Calibration and Measurement of Specific Conductance (manual temperature compensation):

1. Check battery
2. Measure temperature of standard.
3. Set temperature compensator to temperature of standard.
4. Check instrument against at least two known conductivity standards before every field trip.
5. Rinse electrode with sample water.
6. Return electrode to sample for temperature equilibration.
7. Measure temperature of sample.
8. Set temperature compensator to temperature of sample.
9. Read conductance according to manufacturer's instructions.
10. Remove probe from sample and rinse thoroughly with deionized or distilled water.
11. Record sample measurement

Precautions

- Gently agitate electrode in sample to eliminate air bubbles.
- Allow water temperature and electrode temperature to equalize.
- Make temperature correction (Automatic or manual compensator or by table).
- Make sure electrode is clean.
- Do not leave meter exposed to extreme weather conditions.

Table 1. Temperature factors for correcting conductivity data from meters without temperature compensating devices to the standard temperature of 25°C. Electrical conductivity @ 25°C = measured electrical conductivity x temperature factor for the temperature at which the conductance was measured.

°C	Temperature Factor	°C	Temperature Factor
0	1.87	16	1.25
1	1.82	17	1.19
2	1.76	18	1.16
3	1.71	19	1.14
4	1.66	20	1.11
5	1.61	21	1.09
6	1.57	22	1.06
7	1.53	23	1.04
8	1.49	24	1.02
9	1.45	25	1.00
10	1.41	26	0.98
11	1.37	27	0.96
12	1.34	28	0.94
13	1.31	29	0.92
14	1.28	30	0.91
15	1.25		

Analytical Method:	ASTM D1125-91 : Standard Test Methods for Electrical Conductivity and Resistivity of Water APHA 2510 : Conductivity STORET No : 00095 EPA Method: 120.1 Electrometric
Precision:	Standard deviation not to exceed 5% of measured value (National Handbook of Recommended methods for Water -Data Acquisition)
Reporting:	Record specific conductance in micromhos at 25°C to two significant figures. Examples: Measured value of 1926 is reported as 1900; measured value of 48.6 is reported as 49.

Dissolved Oxygen

Definition: Dissolved oxygen (DO) is a measure of the amount of oxygen in solution. Oxygen solubility is controlled by solution temperature and the partial pressure of oxygen within gasses in contact with the solution. Dissolved oxygen is influenced by photosynthetic and microbiologic activity and is therefore subject to significant daily variation. Water quality monitoring programs that include DO should consider these influences.

Container: in-situ determination

Volume Required: not applicable

Preservation: not applicable - immediate analysis

Holding Time: not applicable - immediate analysis

Field Procedure: Dissolved oxygen (DO) should be measured in-situ or in the field, as concentrations may show a large change in a short time if the sample is not adequately preserved. Even when the sample is preserved, as in a Winkler analysis, it is advisable to run the titrations within 3 to 6 h from the time the sample was taken. Dissolved oxygen concentrations may be determined directly with a DO meter or by a chemical method such as Winkler analysis. The method chosen will depend on a number of factors including the accuracy and precision required, convenience, equipment and personnel available and expected interferences. The methods discussed in this section are for DO meters, Winkler analysis and the Hach method. For very precise measurements the potentiometric method should be considered.

Sampling

Water samples for dissolved oxygen analysis should be collected using a specialized DO sampler or BOD model. Three samples should be taken. The recorded DO value will be the average of at least two readings that are within 0.5 mg/L of each other (or other predetermined error term).

Dissolved Oxygen Meters (Membrane Electrode Method)

Dissolved oxygen meters can be used to measure dissolved oxygen concentrations in-situ, in the field or in the laboratory. The procedure is as follows:

(i) calibrate the instrument by placing the probe in a water sample of known dissolved oxygen concentration, i.e., determined by the Winkler method, or in a freshly air-saturated water sample of known temperature. With the latter method calibration can be done by using a table listing the solubility of oxygen in water at different temperatures and pressures.

(ii) Place the probe in the solution to be measured and agitate the probe. Let the probe come to temperature.

Winkler Analysis

Remove stopper from the BOD bottle and add, using pipettes placed just below the water surface, 1.0 mL of manganous sulphate reagent followed immediately by 1.0 mL of alkaline-iodide-azide solution. Re-stopper the bottle at once and mix the contents by shaking vigorously for at least 20 seconds or until the precipitated manganous and manganic hydroxide is evenly dispersed. No air bubbles should be trapped in the bottle. Let stand for approximately 2 to 3 minutes, then shake the bottle again. Allow the precipitate in the sample to settle at least one third of the way down the bottle (approximately 10 to 20 minutes required).

Add 1.0 mL concentrated, reagent grade H_2SO_4 by permitting the acid to run down the neck of the bottle. Re-stopper the bottle and shake gently until the dissolution of the precipitate.

By means of a pipette transfer 100 mL of solution from the BOD bottle to an Erlenmeyer flask.

Titrate at once with thiosulfate solution to a very pale straw color.

Add 4 drops of starch solution. Continue the titration until the blue color just disappears.

Calculate the dissolved oxygen content of the sample as follows:

$$\text{mg/L DO} = \frac{N \times V \times 8 \times 100}{99.3}$$

where: N = normality of sodium thiosulfate solution,
V = volume of sodium thiosulfate solution used in the titration

This method is not applicable under the following conditions:

(i) Samples containing more than 1 mg/L of ferrous iron. However, if 1 mL fluoride solution is added before acidifying the sample and there is no delay in titration, the method can be used in the presence of up to 100-200 mg/L ferrous iron. The potassium fluoride solution is made by dissolving 40 g $KF_{*}2H_2O$ in distilled water and diluting to 100 mL.

(ii) Samples containing sulphite, thiosulfate, polythionate, free chlorine or hypochlorite.

(iii) Samples with high concentrations of suspended solids.

(iv) Samples containing other oxidizing or reducing materials.

In instances where this method is not applicable, a DO probe should be used.

Hach Method

The Hach method is used for determining dissolved oxygen concentrations in the field. It involves the same chemical reactions as Winkler titration. The reagents, except the titrant, which is PAO (phenylarsine oxide), not thiosulfate solution, are contained in individual "Powder Pillows" premeasured for the required concentrations.

This method can be used when results within $\pm$0.5 to 1.0 mg/L of the true value are sufficient for the purpose of the study.

The kit contains a Hach dissolved oxygen sampler, 300-mL BOD bottle, 60-mL BOD type bottle, a vial and a small dispensing bottle containing the PAO titrant, as well as pillows of reagents in the dry granular form. Starch, which is not supplied with the kit, must be obtained to assist in

the detection of the end point.

Sample Collection

(i) After the removal of the glass stopper, place the 60-mL DO sample bottle in the sampler.

(ii) Replace the sampler lid, with the sample inlet tube extending into the bottle.

(iii) Lower the sampler by the chain; then pull out the stopper at the desired depth.

(iv) When air bubbles stop rising from the sampler, raise the sampler by the chain and carefully remove the sample bottle.

(v) Add the contents of one pillow of Dissolved Oxygen 1 powder (manganous sulphate) and the contents of a Dissolved Oxygen II Powder (alkaline-iodide-azide) pillow. Stopper the bottle carefully so that air is not trapped in the bottle (see Note A below). Grip the bottle and shake vigorously (see Note B below). A flocculent precipitate will be formed. If oxygen is present, the precipitate will be brownish orange.

(vi) Let the sample stand until the floc has settled halfway and leaves the upper half of the bottle clear. Again shake the bottle and let stand until the upper half of the bottle is clear.

(vii) Remove the stopper and add the contents of one Dissolved Oxygen III Powder pillow (dry acid). Carefully re-stopper (see Note A) and shake to mix. The floc will dissolve and a yellow color will develop if oxygen is present. This is the prepared sample.

(viii) Pour off the contents of the DO bottle until the level just reaches the 30-mL mark on the bottle.

(ix) While swirling the sample to mix, quickly add PAO by drops, counting each drop until the samples change to a pale straw color. Add a few drops of starch solution. Continue adding PAO until the color changes from blue to colorless. Each drop is

equal to 0.2 mg/L dissolved oxygen.

Notes:

a. It is difficult to stopper the DO bottle without getting air bubbles trapped in the bottle. To avoid air bubbles, tip the DO bottle slightly and insert the stopper with a quick thrust. This will force air bubbles out. If air bubbles are trapped in the DO bottle in steps (v) or (vii), the sample should be discarded and the test started over.

b. A small amount of powdered reagent may remain stuck to the bottom of the DO bottle at this point, but this will not affect the test.

c. Do not permit the PAO solution to stand in direct sunlight, as it is decomposed by ultraviolet radiation.

d. When the water is saturated with dissolved oxygen, small bubbles of oxygen coming out of solution in the 60-mL bottle will cause an air bubble to form at the stopper. This is unavoidable; proceed with instructions as usual.

Analytical Method: ASTM D888-92 : Standard Test Methods for Dissolved Oxygen in Water
APHA 4500 - O : Oxygen Dissolved
STORET No : 00299
EPA Method: not available
Chemical - Modified Azide

Precision: ± 0.05 mg/L DO (APHA)

Reporting: Report to nearest 0.1 mg/L DO (0.5 mg/L for HACH method)

Turbidity

Definition: Capacity of a water sample to scatter light. A surrogate measure for clay, silt, organic matter, plankton, and other light reflecting debris. Whenever possible, turbidity should be measured in the field.

Container: Glass or Polyethylene

Volume Required: 100 mL

Preservation: Refrigeration to 4°C

Holding Time: 24 hours

Field Procedure: The field measurement is preferable, since some of the particulate matter will settle or adhere to the sample container wall during transportation. Furthermore, changes in the pH of the sample may cause the precipitation of carbonates and humic acids, affecting sample turbidity. When the analysis cannot be done immediately, the sample should be stored in the dark and for not more than 24 hours.

Turbidity can be measured by visual methods (in Jackson Turbidity Units or JTU) or nephelometric units (in Nephelometric Turbidity Units or NTU). Nephelometric methods are preferred on account of their greater precision, sensitivity and application over a wide turbidity range.

In-Field Procedure

(a) To operate the turbidity meter, follow the manual for the instrument.

(b) Prepare calibration curves for each range of the instrument by using appropriate standards.

(c) Test at least one standard in each range to be used.

(d) Make certain that the turbidity meter gives stable readings in all sensitivity ranges used.

(e) Keep sample tubes clean both inside and out; replace them when they become scratched or etched. Do not handle the tubes in the

region where the light beam enters them.

(f) Shake the sample vigorously before analysis. Readings should always be made after the same time period following the homogenizing of the sample (e.g., 10 s) to ensure uniform data.

(g) It is important to pour off the sample quickly and to measure the turbidity of the sample in triplicate.

Precision: not available

Reporting: Report as NTU's as follows (APHA):

Turbidity Range NTU	**Report to Nearest NTU**
0 - 1.0	0.05
1.0 - 10	0.1
10 - 40	0.5
40 - 100	5
100 - 400	10
400 - 1000	50
>1000	100

Alkalinity

Definition: Capacity of a water to neutralize an acid to a specified pH (typically pH 4.5). Generally, alkalinity is a measurement of carbonate, bicarbonate and hydroxide (can also include borates, phosphates or silicates) content of a water. Typically reported as mg/L $CaCO_3$ or milliequivalent/liter (meq/L) HCO_3^- -C.

Container: Glass or Polyethylene

Volume Required: 200 mL

Preservation: Refrigeration to 4°C

Holding Time: 24 hours/14 days

Field Procedure:

1. Add 0.1 mL (approximately 2 drops) of phenolphthalein indicator to sample of 100 mL. If the solution turns pink, titrate with acid.
2. titrate with 0.02 N H_2SO_4 over a white surface until the solution changes from pink to clear.
3. This endpoint represents pH 8.3 and is reported as phenolphthalein alkalinity.
4. Add 0.15 mL (approximately 3 drops) of bromcresol green - methyl red indicator to the above solution.
5. Titrate with 0.02 N H_2SO_4 until the solution turns light pink (pH = 4.6). This is reported as total alkalinity.

Calculation:

Phenolphthalein alkalinity:

$$\text{mg/L as } CaCO_3 = \frac{A * N * 5000}{\text{mL sample}}$$

Total alkalinity:

$$\text{mg/L as } CaCO_3 = \frac{B * N * 5000}{\text{mL sample}}$$

where:

A = mL titrant for sample to reach phenolphthalein endpoint. If no color develops, phenolphthalein alkalinity is zero.

B = mL of titrant for bromcresol green - methyl red endpoint.

N = normality of acid

Analytical Method: ASTM D1067-92 :Standard Test Methods for Acidity or Alkalinity of Water
APHA 2320 : Alkalinity
STORET No : 00410
EPA Method: 310.1
Automated Methyl Orange Titration

Precision: Due to high variability of sample characteristics a precision is not included.

Reporting: Report to $\pm$ 1 mg/L $CaCO_3$ (APHA)
to convert to meq/L HCO_3^- -C, divide by 50.

Chapter 4

Laboratory Measured Parameters

Introduction

Some water quality constituents cannot be measured in the field and thus require laboratory analysis. This section introduces the reader to some of these water quality parameters that are frequently used in non-point source pollution assessment and their laboratory analysis techniques. Constituents included in this section are:

alkalinity
acid neutralizing capacity
Biochemical Oxygen Demand (BOD)
Chemical Oxygen Demand (COD)
chloride ion, dissolved
chlorophyll a
clarity/turbidity
fecal coliform bacteria
hardness
herbicides
nitrogen, ammonia dissolved
nitrogen, nitrate, dissolved
nitrogen, Kjeldahl
oil and grease
pesticides
phosphorous (P), orthophosphate
phosphorous (P), total
solids, total dissolved
solids, total suspended
sulfate, dissolved
trace metals

Alkalinity

Definition: Capacity of a water to neutralize an acid to a specified pH (typically pH 4.5). Generally, alkalinity is a measurement of carbonate, bicarbonate and hydroxide (can also include borates, phosphates or silicates) content of a water. Typically reported as mg/L $CaCO_3$ or milliequivalent/liter (meq/L) HCO_3^- -C.

Container: Glass or Polyethylene

Volume Required: 200 mL

Preservation: Refrigeration to 4°C

Holding Time: 24 hours/14 days

Lab Procedure:

1. Add 0.1 mL (approximately 2 drops) of phenolphthalein indicator to sample of 100 mL. If the solution turns pink, titrate with acid.
2. titrate with 0.02 N H_2SO_4 over a white surface until the solution changes from pink to clear.
3. This endpoint represents pH 8.3 and is reported as phenolphthalein alkalinity.
4. Add 0.15 mL (approximately 3 drops) of bromcresol green - methyl red indicator to the above solution.
5. Titrate with 0.02 N H_2SO_4 until the solution turns light pink (pH = 4.6). This is reported as total alkalinity.

Calculation:

Phenolphthalein alkalinity:

$$\text{mg/L as } CaCO_3 = \frac{A * N * 5000}{\text{mL sample}}$$

Total alkalinity:

$$\text{mg/L as } CaCO_3 = \frac{B * N * 5000}{\text{mL sample}}$$

where:

A = mL titrant for sample to reach phenolphthalein endpoint. If no color develops, phenolphthalein alkalinity is zero.

B = mL of titrant for bromcresol green - methyl red endpoint.

N = normality of acid

Analytical Method: ASTM D1067-92 :Standard Test Methods for Acidity or Alkalinity of Water
APHA 2320 : Alkalinity
STORET No : 00410
EPA Method: 310.1
Automated Methyl Orange Titration

Precision: Due to high variability of sample characteristics a precision is not included.

Reporting: Report to ± 1 mg/L $CaCO_3$ (APHA)
to convert to meq/L HCO_3^- -C, divide by 50.

Acid Neutralizing Capacity

Definition:	Capacity of a water to neutralize an acid to a specified pH endpoint. ANC differs from alkalinity since the pH equivalence point is determined analytically rather than fixed (i.e. pH 4.5) in order to more accurately describe the capacity of a water to neutralize the H^+ ion. Typically quantified using the Gran titration.
Container:	HDPE
Volume Required:	100 mL
Preservation:	Refrigeration to 4°C
Holding Time:	24 hours
Lab Procedure:	Waters of low alkalinity (< 100 μeq/L) may require a Gran titration since the equivalence pH is often higher than 4.3 and conventional titration tends to overestimate solution alkalinity. The Gran titration uses a microburette and endpoint inflection determined by plotting the change in pH per mL of acid added over pH. Once the equivalence (H_2CO_3 - HCO_3^-) pH is determined, the mLs of acid added to that point are used to calculate solution alkalinity (Gran, 1956).
Analytical Method:	Gran Titration
Precision:	not available
Reporting:	Report as mg/L $CaCO_3$ or milliequivalent/liter (meq/L) HCO_3^- -C

Biochemical Oxygen Demand (BOD)

Definition: The biochemical oxygen demand (BOD) determination is an empirical test in which standardized laboratory procedures are used to determine the relative oxygen requirements of wastewater, effluents, and polluted waters.

Container: Amber glass

Volume Required: 50 mL (or more depending on BOD)

Preservation: Refrigerate to 4°C or colder

Holding Time: No more than 6 hours preferred, not to exceed 24 hours

Lab Procedure: Manometric (from Hach, 1993)

Principle

A measured sample of wastewater is placed in one of the bottles on the Hach BOD apparatus. The bottle is connected to a closed end mercury manometer. In the airspace above the wastewater sample is a quantity of air which contains 21% oxygen (atmospheric). Over a period of time, bacteria in the wastewater utilize oxygen to oxidize organic matter present in the sample, consuming dissolved oxygen from the sample. The air in the closed sample bottle replenishes the utilized oxygen resulting in a decrease in pressure in the airspace in the sample bottle. this pressure decrease is measured on the mercury manometer and is measured directly as mg/L BOD. During the test period (typically 5 days), the sample is continuously agitated by a magnetic stirring bar driven by the magnetic platform of the BOD apparatus. Carbon dioxide is produced by the oxidation of organic matter and must be removed from the system so that the pressure difference observed is proportional to the amount of oxygen consumed. This is accomplished by the addition of potassium hydroxide solution to each sample bottle.

Initial Setup:

Installing Seal Cups

Remove the sample bottle caps and insert a seal cup in the neck of each

of the bottles

Filling Manometers with Mercury

Caution: Mercury is poisonous and should be handled with extreme care. If spilled, clean and dispose of waste according to MSDS instructions.

Remove the screw cap from each manometer body and carefully pour the contents of one mercury bottle furnished with the BOD apparatus. After all 5 manometers contain mercury, add 10 to 20 drops of water to each. this ensures adequate water vapor pressure in the space above the mercury during a test run. Before manometer caps are replaced, lightly grease each manometer O-ring with lubri-seal grease (or equivalent). Check the water level above the mercury in the reservoir and add as necessary.

General Procedure:

1. accurately measure the desired sample volume (typically 157 mL for direct scale reading) into the amber glass liter bottle. The sample should be temperature adjusted to within 2-3°C of the incubation temperature before measuring (typically 20°C);

2. place a 4 cm (1.5 inch) magnetic stirring bar in each bottle;

3. remove the sample bottle caps and place 2 drops of 45% potassium hydroxide solution into each of the seal cups. Do not allow any of the solution to leak into the sample. If leakage of potassium hydroxide to the sample occurs, discard sample, clean the contaminated glassware and prepare a fresh sample;

4. place the bottles on the BOD apparatus base and start the stirring bar by connecting the electrical plug. Check to ensure that all stir bars are functioning. Check bottles and pulley if stirrer bars are not functioning. With the manometer caps open, screw the sample bottle caps loosely in place (do not tighten). After approximately 30 minutes (approximate thermal equilibrium), tighten both sample bottle and manometer caps. If the sample is not at thermal equilibrium, an extremely rapid initial negative reading will result. This indicates that the sample is too cold and

is releasing oxygen. If this occurs, loosen both the sample bottle and the manometer cap briefly and reclose. Proceed to step 5 immediately;

5. loosen the set screws on the manometer scale and set the zero mark adjacent to the top of the mercury column. If the scale cannot be zeroed, loosen the bottle cap and manometer cap briefly, then tighten and reset the scale. Record the time and composition of each sample bottle. Manometer readings can be periodically recorded and plotted (mg/L BOD vs. time). An approximation of final BOD can be determined from this plot.

Cleaning the apparatus:

Cleaning the apparatus after each operation is essential for accurate BOD determination. The following procedure is recommended:

1. Sample Bottles

After each test, rinse the sample bottles with hot water. Clean thoroughly with a laboratory detergent and triple rinse with deionized water (Note: detergents can produce a BOD, thorough rinse is necessary). Air dry. Cap if stored.

2. Stirring magnets

Clean using same procedure as sample bottles.

3. Seal Cups

Clean thoroughly with a laboratory detergent and triple rinse with deionized water. Air dry.

Results:

A 5-day, 20°C BOD test, if carried out as described above, should provide the following information:

1. the daily BOD reading should be higher for each successive day of the test;

2. the difference in readings between each successive day's reading

should be decreasing, at least for the first 5 days.

Standard Samples:

Although the Hach BOD apparatus has been shown to produce results equivalent to the dilution method, the occasional analysis of a standard BOD sample will provide quality assurance in both apparatus operation and procedure. A procedure for the standard BOD sample follows:

1. Prepare a solution of deionized water containing the nutrient solution indicated on pg 489-490 Standard Methods for the Examination of Water and Wastewater.

2. Using the solution prepared in step 1, prepare a solution containing 150 mg/L glucose and 159 mg/L glutamic acid. This solution must be freshly prepared as it will deteriorate upon standing.

3. Seed a selected volume of solution from step 2 with 10% by volume of the seed (e.g. 180 mL plus 20 mL of seed), Mix thoroughly.

4. Use 157 mL of the seeded standard for the test run following the general procedure for the BOD test.

5. Perform a BOD test on the seed (full strength) used at the same time as the sample.

6. Correct the BOD result obtained

7. the corrected BOD of the standard solution should be 220 ± 11 mg/L

Analytical Method: ASTM: not available
APHA: 5210B Biochemical Oxygen Demand
STORET No.: not available
EPA Method: not available

Precision: not available

Reporting: Report as mg/L

Chemical Oxygen Demand (COD)

Definition:	The chemical oxygen demand (COD) is used as a measure of the oxygen equivalent of the organic matter content of a water sample that is susceptible to oxidation by a strong chemical oxidant. COD can be related empirically to BOD, organic carbon or organic matter.
Container:	Amber glass
Volume Required:	sufficient volume
Preservation:	Acidify to pH <2 with H_2SO_4
Holding Time:	24 hours
Lab Procedure:	Open reflux or closed reflux method - Refer to Standard Methods for the Examination of Water and Wastewater.
Analytical Method:	ASTM: not available APHA: 5220B, 5220C Chemical Oxygen Demand STORET No.: not available EPA Method: not available
Precision:	at 200 mg O_2/L $\pm$ 13 mg/L at 100 mg O_2/L $\pm$ 14 mg/L
Reporting:	report as mg O_2/L COD

Chloride ion, dissolved

Definition: General category including the chloride specie of several cations (typically Na, K, Ca). Significant due to high corrosivity.

Container: HDPE

Volume Required: 50 mL

Preservation: Refrigerate to 4°C

Holding Time: 28 days

Lab Procedure: Chloride concentration is generally determined using titrimetric techniques. The argenometric method is outlined as follows:

1. Pour 100 mL sample into a 250 mL beaker;
2. Adjust the pH of sample to between 7 and 10 using either NaOH (1 N) or H_2SO_4 (1 N), if necessary;
3. Add 1 mL K_2CrO_4 indicator solution. Place beaker with sample onto magnetic stirrer and stir throughout titration;
4. Titrate with $AgNO_3$ until red color appears as titrant is added. Continue titrating slowly until a pinkish-yellow endpoint is reached. the endpoint is somewhat arbitrary and consistency between samples is required.
5. Repeat procedure for a blank (100 mL analytical grade water)

Calculation:

$$\text{mg/L Cl} = \frac{(A - B) * N * 35450}{\text{mL of sample}}$$

where:
A = mL titrant required for sample
B = mL titrant required for blank
N = normality of $AgNO_3$ (0.0141)

Analytical Method:	ASTM: D 512 - 89 Standard Test Method for Chloride Ion in Water APHA: 4500 - Cl^- Chloride STORET No.: EPA Method: 300.0, 325
Precision:	1 % full scale
Reporting:	Report as mg/L Chloride ion (Cl), dissolved $<$ 10 mg/L report to one decimal $\geq$ 10 mg/L report 3 significant figures (National Handbook)

Chlorophyll a

Definition: The concentration of photosynthetic pigments is used to estimate phytoplankton biomass. All green plants contain chlorophyll a which constitutes 1 to 2 % of the dry weight of planktonic algae (APHA, 1992). Other pigments that occur in phytoplankton include chlorophylls b and c.

Container: Glass (opaque), or HDPE covered in aluminum foil

Volume Required: 500 mL

Preservation: Refrigerate to 4°C in dark

Holding Time: 30 days

Lab Procedure: The three methods for determination of chlorophyll a in phytoplankton are: spectrophotometric, fluorometric and high-performance liquid chromatography (HPLC). Fluorometry is more sensitive than spectrophotometry requires less sample and can be used for in-vivo measurements. These optical methods can significantly under- or overestimate chlorophyll a concentration due to overlapping absorption and fluorescent bands (APHA, 1992).

1. Pigment extraction:
   Concentrate the sample by centrifuging or filtering (use glass fiber filters) as soon as possible following sample collection. If delayed, hold samples at 4°C in dark. Chlorophyll a concentration within the sample will change if exposed to light even briefly. Samples on filters taken from water having pH 7 or higher may be placed in air-tight plastic bags and stored frozen for 3 weeks. Samples from acidic waters must be processed promptly to avoid chlorophyll degradation. All sampling and analytical equipment should be acid free (APHA, 1992).

2. Fluorometric determination:
   Optimum sensitivity for chlorophyll a extract measurements is obtained at an excitation wavelength of 430 nm and an emission wavelength of 663 nm (APHA, 1992). Calibrate the fluorometer spectrophotometrically with source water and a known chlorophyll concentration.

Analytical Method:	APHA 10200 H Fluorometric
Precision:	not available
Reporting:	Fluorometer and spectrophotometer values are typically μg/L chlorophyll a. Refer to manufacturer's instructions for conversion to mg/m^3.

Clarity/Turbidity

Definition: Capacity of a water sample to scatter light. A surrogate measure for clay, silt, organic matter, plankton, and other light reflecting debris. Whenever possible, turbidity should be measured in the field. Typically reported in Nephelometric Turbidity Units (NTU).

Container: HDPE

Volume Required: 100 mL

Preservation: Refrigerate to 4°C

Holding Time: 24 hrs/48 hours

Lab Procedure: **Calibration**

1. Zero the meter according to manufacturer's specifications;

2. switch power on (for maximum accuracy, instrument should remain on for a minimum of 12 hours prior to calibration and analysis);

3. focus instrument by viewing template in the cell holder. The lamp image should fill the inside circle of the viewing port. Adjust if necessary according to manufacturer's specifications;

4. Calibrate the instrument with standard cells prepared using Standard Methods or with commercially available standard cells. Replace cells if flocculent is present. Standardize the instrument according to manufacturer's specifications;

Operation

1. Fill clean, undamaged cell with 25 mL of sample. Dry outside surface of cell. Since the analytical method is photometric, a clean unscratched cell is essential to the analysis. Air bubbles or trapped air should not be present in the sample;

2. Place the cell in the holder according to manufacturer's

specifications, and close cell holder cover;

3. Select sensing range according to manufacturer's specifications;

4. Read turbidity from scale and record in NTUs. At very low turbidity (0.2 NTU scale), subtract 0.04 NTU from the reading due to stray light which is significant only at very low turbidities;

5. Dilution of the sample may be required for samples of very high turbidity. Dilution factors should be recorded and multiplied to the instrument reading to determine actual turbidity. Multiple dilutions may be required to achieve a measurable scale;

6. Remove the sample cell, close the cell holder cover and return the range selection switch to the 100 - or 1000 - NTU position; discard sample and thoroughly clean the sample cell;

7. The instrument should remain running continuously to avoid the 12 hour warmup period.

Analytical Method: ASTM: D1889-88a Standard Test Method for Turbidity of Water
APHA: 212
STORET No : 00070, 00076, 00078
EPA Method: 180.1
Nephelometer - measures quantity of light scattering

Precision: not available

Reporting: Report turbidity as follows (APHA):

Turbidity Range NTU	**Report to Nearest NTU**
0 - 1.0	0.05
1.0 - 10	0.1
10 - 40	0.5
40 - 100	5
100 - 400	10
400 - 1000	50
> 1000	100

Fecal coliform bacteria

Definition: Number of bacterial colonies per 100 mL. Fecal bacteria generally indicative of waterborne pathogens.

Container: HDPE

Volume Required: 100 mL

Preservation: 0.008% $Na_2S_2O_3$, Refrigerate to 4°C,

Holding Time: 6 hours

Lab Procedure: Several procedures exist for the determination of fecal coliform bacteria. The general procedure is outlined below:

1. A minimum of three replications should be conducted for each sample and should be conducted concurrently;
2. Place a sterile absorbent pad in a 47 mm petri dish (sterility of all equipment used in this procedure is critical to the integrity of the sample);
3. Add 2 mL growth medium to each petri dish using a sterile pipette;
4. Close each petri dish and store until Step 12;
5. Autoclave filtration apparatus according to manufacturer's specifications;
6. Insert a membrane filter into filtration apparatus, grid side up (handle filter with sterilized forceps only);
7. Add approximately 20 mL sterile buffer to the filtration apparatus;
8. Pass the sample through the filtration apparatus, using a vacuum pump or other vacuum source;
9. Rinse the filtration apparatus thoroughly with sterile buffer

solution (the volume used should, at a minimum, equal the volume of the sample), and apply vacuum;

10. Repeat rinse procedure;

11. Remove the filter from filtration apparatus using sterilized forceps;

12. Place the filter (grid side up) on the absorbent pad in a petri dish prepared as described in Steps 1 - 4. Placement of the filter on the pad should avoid trapping of air beneath the filter. Replace petri dish cover;

13. Incubate petri dishes within 30 minutes of filtration;

14. Following incubation remove the petri dish and count the colonies using a stereomicroscope (10 - 20 x magnification).

*ALL SAMPLING AND ANALYTICAL EQUIPMENT REQUIRES STERILIZATION

Calculation:

$$\frac{N}{100 \text{ mL of sample}} = \frac{(N \text{ counted}) * 100}{\text{mL of sample}}$$

Analytical Method: ASTM: D4454-85 Standard Test Method for Simultaneous Enumeration of Total and Respiring Bacteria in Aquatic Systems by Microscopy; D3508-78 Standard Method for Evaluating Water Testing Membrane Filters for Fecal Coliform Recovery
APHA: 909
STORET No.: not available
EPA Method: 9221, 9222
MPN - Most Probable Number

Precision: not available

Reporting: Report as number of colonies per 100 mL.
Report to nearest whole number.

Hardness

Definition: Defined as the capacity of a water to precipitate or waste soap. Generally associated with the concentration of Ca and Mg in a water but includes any polyvalent cation. Typically reported in mg/L $CaCO_3$.

Container: HDPE

Volume Required: 100 mL

Preservation: pH < 2 with HNO_3 or H_2SO_4, Refrigerate to 4°C

Holding Time: 24 hrs/48 hours

Lab Procedure: There are currently two methods used for the determine of hardness in water, titrimetric and by calculation. The calculation method includes analysis of all polyvalent cations and summing the concentrations. The calculation method is considered very accurate but time consuming and cost prohibitive. The EDTA titrimetric method gives a determination of only Ca^{2+} and Mg^{2+} and is subject to interference (APHA, 1985). The EDTA is generally adequate for most purposes since the contribution of polyvalent cations other than Ca^{2+} and Mg^{2+} to hardness is usually insignificant.

EDTA Titration:

1. The sample to be titrated should not require more than 15 mL EDTA titrant or a titration time of greater than 5 minutes (beginning with buffer addition);

2. Dilute 25 mL of sample with approximately 50 mL analytical grade water. Add 1 - 2 mL buffer solution to yield a solution pH of 10.0 - 10.1. Addition of an inhibitor may be required if a sharp titration endpoint cannot be determined in Step 4 (below). If required the inhibitor should be added prior to addition of the indicator solution ;

3. Add 1 - 2 mL indicator solution;

4. Add EDTA titrant slowly, stirring continuously. The last drops of titrant should be added at 3 - 5 second intervals until the

solution color changes to the blue endpoint indicator. Caution is required as incandescent lighting may alter the appearance of the solution at the titration endpoint (a reddish color may be present);

5. Record the quantity of EDTA titrant required;

6. For waters of low hardness (< 5 mg/L), use a higher sample volume and proportionately higher buffer, inhibitor (if required) and indicator solutions. The analysis of low hardness samples should be accompanied by a blank analysis of analytical grade water (same volume as the sample) containing identical quantities of buffer, inhibitor (if necessary) and indicator.

Calculation:

$$\text{Hardness (EDTA) as mg/L } CaCO_3 = \frac{A * B * 1000}{\text{mL sample}}$$

where: A = mL titrant required
B = $CaCO_3$ equivalent to 1.00 mL EDTA titrant

Analytical Method: ASTM: D 1126-86 Standard Test Method for Hardness in Water
APHA
STORET No: 00900, 00902
EPA Method: 130

Precision: RSD = 2.9% at 610 mg/L
SD = 0.63 mg/L at 12.8 mg/L

Reporting: Report as mg/L $CaCO_3$
< 10 mg/L report to nearest whole number
≥ 10 mg/L report 2 significant figures

Nitrogen, ammonia dissolved

Definition: Dissolved ammonia is the reduced form of nitrogen in solution. Ammonia is a highly soluble, colorless, gaseous compound and can exist as NH_3 or NH_4^+ (ammonium ion) depending on solution temperature and pH. Ammonia and related oxidized nitrogen compounds are a major limiting nutrient in most aquatic systems an increase of which may result in eutrophication. Typically indicative of agricultural pollution or anaerobic degradation of nitrogen containing compounds.

Container: HDPE

Volume Required: 400 mL

Preservation: pH<2 with H_2SO_4, Refrigerate to 4°C

Holding Time: 28 days

Lab Procedure: Concentration of ammonia in water is typically determined using either the phenate method for low ammonia concentrations (0.1 - 0.5 mg/L NH_4 - N) or the Nessler Method for higher ammonia concentrations (0.2 - 5.0 mg/L NH_4 - N). The phenate method involves the catalyzed reduction of hypochlorite and phenol and comparison of the color to a standard curve. The Nessler Method also involves colorimetric analysis but consists of simple addition of "Nessler's reagent" to the sample .

Phenate Method:

1. Set spectrophotometer to 630 nm;
2. Pour 20 mL of sample into a 100 mL beaker, place on magnetic stirrer and initiate stirring;
3. Add 1 mL (approximately 2 drops) of $MnSO_4$ solution (dissolve 50 mg $MnSO_4$ in 100 mL analytical grade water);
4. Add 1 mL hypochlorous acid solution (see Standard Methods for solution preparation);
5. Add 1.2 mL phenate reagent immediately, drop by drop;

6. Wait 10 - 15 minutes for color change. Interference form alkalinity, acidity, color and turbidity may result in erroneous spectrophotometer determination. If necessary, the sample can be distilled prior to analysis to minimize interference ;

7. Place sample in spectrophotometer and record transmittance and compare to deionized water;

8. Compare with standard curve to determine mg/L ammonia.

Nessler Method:

1. Set spectrophotometer to 425 nm;

2. Pour 25 mL sample into a 50 mL Erlenmeyer flask;

3. Pour 25 mL analytical grade water into a separate 50 mL Erlenmeyer flask for use in spectrophotometer calibration;

4. Add 1 mL Nessler's reagent (see Standard Methods for preparation procedure) to both flasks, stopper and mix thoroughly by inverting the flasks several times. If water is of high hardness, interference may result in erroneous measurements. If necessary, add approximately 1 mL (one drop) of Rochelles salt reagent to both flasks prior to addition of Nessler's reagent to minimize interference;

5. Let sample stand for a minimum of 10 minutes for color change to occur (the sample should not be allowed to stand for greater than 25 minutes prior to reading);

6. Calibrate the spectrophotometer using the blank prepared as indicated above;

7. Place an aliquot of the sample into the spectrophotometer and record the result;

8. Compare percent transmittance to the standard curve and record mg/L ammonia nitrogen.

Analytical Method: ASTM: D 1426-89 Standard Test Methods for Ammonia Nitrogen in Water.
APHA: 4500 NH_3 C. Nessler
STORET No.: 00610
EPA Method: 350

Precision: Not available

Reporting: Report as mg/L NH_4-N

Nitrogen, nitrate (NO_3^-)

Definition: Nitrate is the oxidized form of aqueous nitrogen reported as mg/L NO_3 or mg/L NO_3 - N. Nitrogen is a major limiting nutrient in most aquatic systems an increase of which may result in eutrophication. Typically indicative of agricultural pollution.

Container: HDPE

Volume Required: 100 mL

Preservation: Refrigerate to 4°C

Holding Time: 48 hours

Lab Procedure: Two currently used procedures for the analysis of nitrate in water include colorimetric and the use of a cadmium reduction column. Commercially available colorimetric nitrate analysis equipment and reagents (e.g. HACH) can be used to determine nitrate concentration in water as follows:

1. Set spectrophotometer to 500 nm;
2. Pour 25 mL sample into a 50 mL Erlenmeyer flask;
3. Pour 25 mL analytical grade water into a separate 50 mL Erlenmeyer flask for use in spectrophotometer calibration;
4. Add nitrate reagent powder to sample and , stopper and shake vigorously for approximately 60 seconds;
5. Let sample stand for approximately 5 minutes until color change occurs (sample color change should occur within 15 minutes);
6. Zero the spectrophotometer following manufacturer's specifications (without sample). Calibrate the spectrophotometer by placing the solution prepared in Step 3 into the spectrophotometer and adjusting the scale to read 100% T ;
7. Place the sample into the spectrophotometer and record the result;

8. Compare the results to the standard curve provided with the instrument and record mg/L nitrate.

The cadmium reduction column method includes reduction of nitrate (using a column of cadmium filings) to nitrite (NO_2^-) which is measured. The procedure is outlined as follows:

1. Pour 100 mL sample into glass beaker and measure pH;
2. If necessary, adjust pH to between 8 - 9 using dilute HCl;
3. Add 2.0 mL concentrated NH_4Cl to the sample and mix thoroughly. Pour sample into cadmium reduction column;
4. Collect approximately 30 mL of the column effluent and discard;
5. Collect the remaining column effluent (50 mL is required for analysis);
6. Add 1.0 mL sulfanilamide solution to 50 mL of the column effluent, mix thoroughly and let stand for 3 - 5 minutes;
7. Add 1.0 mL 1-napthylethylenediamine solution to the sample, mix thoroughly and let stand for 10 minutes;
8. Compare sample absorbance to that of a blank and record the result;
9. Use standard curve to determine mg/L NO_3- N from absorbance values.

Analytical Method: ASTM: not available
APHA 4500 - NO_3^- : Nitrogen (Nitrate)
STORET No : 00620 (Brucine)
EPA Method: 300.0, 352.1

Precision: RSD = 14.4% at 0.5 mg/L and 15.4 at 5.0 mg/L (National Handbook)

Reporting: Report as mg/L NO_3-N

Nitrogen, Kjeldahl

Definition: The sum of the nitrogen contained in the free ammonia (NH_3) and other nitrogen compounds which are converted to ammonium sulfate [($NH_4)_2$ SO_4] under specific digestion conditions. Nitrogen is a major limiting nutrient in most aquatic systems an increase of which may result in eutrophication. Typically indicative of agricultural pollution.

Container: HDPE

Volume Required: 500 mL

Preservation: pH<2 with H_2SO_4, Refrigerate to 4°C

Holding Time: 28 days

Lab Procedure: The Kjeldahl nitrogen analysis determines the nitrogen in the trinegative state. If ammonia nitrogen is not removed as the initial procedure, the term Kjeldahl nitrogen is applied to the result. Should Kjeldahl nitrogen and ammonia nitrogen be determined individually, organic nitrogen is calculated as the difference (APHA, 1992).

The procedure requires an acid digest and should be left to a laboratory for analysis or requires a Kjeldahl digestor.

Analytical Method: ASTM: D3590-89 Standard Test Methods for Total Kjeldahl Nitrogen in Water
APHA: not available
STORET No.: not available
EPA Method: 351.2 (TKN)
Cadmium reduction column (AA)
Kjeldahl titration

Precision:

Colorimetric:	SD = 0.54 at 1.89 mg/L	
	SD = 1.85 at 5.81 mg/L	
Titrimetric:	SD = 0.20 at 0.20 mg/L	
	SD = 1.19 at 4.6 mg/L	

Reporting:	Colorimetric:	Report as mg/L Report 2 significant figures
	Titrimetric:	Report as mg/L $<$ 1.0 mg/L report to nearest 0.1 mg/L $\geq$ 1.0 mg/L report 2 significant figures.

Oil and Grease

Definition:	Any material or compound recovered as a substance soluble in trichlorotrifluoroethane. Includes biological lipids and mineral hydrocarbons. May cause surface films or shoreline deposits
Container:	Amber glass
Volume Required:	1000 mL
Preservation:	Refrigerate to 4°C, pH <2 H_2SO_4
Holding Time:	28 days
Lab Procedure:	Gravimetric determination following extraction with TTE. Partition-Gravimetric Method Partition-Infrared Method Soxhlet Extraction Method
Analytical Method:	ASTM: D4281-92 - Standard method for oil and grease (fluorocarbon extractable substances) by gravimetric determination D3921-85 - Standard test method for oil and grease and petroleum hydrocarbons in water APHA: 5520 - Oil and Grease STORET No.: not available EPA Method: 413
Precision:	not available
Reporting:	not available

Pesticides

Definition:	A chemical compound or substance designed to kill plant, animal or fungal pests. Includes herbicides, insecticides, fungicides, and rodenticides.
Container:	Amber glass
Volume Required:	250 mL
Preservation:	Refrigerate to 4°C until extraction
Holding Time:	7 days without extraction, 40 days with extraction
Lab Procedure:	Recommendations for analysis are provided by instrument manufacturer.
Analytical Method:	ASTM: not available APHA: 6630B Liquid-liquid extraction gas chromatography STORET No.: not available EPA Method: not available
Precision:	not available
Reporting:	not available

Phosphorus (P), orthophosphate

Definition: Quantity of orthophosphate in a water. Phosphorous is frequently a limiting nutrient in aquatic systems. A minor increase in phosphorous concentration can significantly affect water quality. The term orthophosphate is a chemistry based term that refers to the phosphate molecule only. Reactive phosphorous is a method based term that describes what is measured when testing for orthophosphate. Soluble reactive phosphorous (SRP) is identical to reactive phosphorous, but analysis is completed on a filtered sample. Sources of phosphorous include: sediments, fertilizer application (e.g. irrigation return flow), cleaning and laundry soaps and detergents.

Container: HDPE

Volume Required: 100 mL

Preservation: Refrigerate to 4°C

Holding Time: 48 hours

Lab Procedure: Ascorbic acid Method (Murphy-Riley) (APHA, 1992):

1. Measure a 50 mL sample into a 150 mL beaker;
2. Add 5 mL of Armstrong's reagent and 1.0 mL ascorbic acid and mix;
3. Allow at least 20 minutes for color development, but no more than 2 hours;
4. Adjust spectrophotometer to 0 absorbance with untreated sample;
5. Read sample absorbance at 885 nm and compare to standard curve.

Amino acid Method (Hach, 1989):

1. Measure a 25 mL sample into a 50 mL beaker;
2. Add 1.0 mL of molybdate reagent;

3. Add contents of one amino acid powder pillow;

4. Allow 10 minutes for color development, but not more than 15 minutes;

5. Adjust spectrophotometer to 0 absorbance with deionized water and reagents;

6. Read sample absorbance at 700 nm and compare to standard curve.

Analytical Method: ASTM D515-88 : Standard Test Method for Phosphorus in Water
APHA 4500 - P : Phosphorus
STORET No : 70507 (ortho-P)
00670 (total organic P)
EPA Method: 365.4 (total P)
Ascorbic acid method (Murphy-Riley)
Vanadomolybdate method

Precision: SD = 0.019 at 0.04 mg/L
SD = 0.014 at 0.04 mg/L
SD = 0.087 at 0.29 mg/L
SD = 0.066 at 0.30 mg/L

Reporting: Report as mg/L Phosphorous (P), orthophosphate dissolved
< 1.0 mg/L report to nearest 0.01 mg/L
≥ 1.0 mg/L report 2 significant figures

Phosphorus, total dissolved

Definition: The total phosphorous occurring in a water. Includes orthophosphate, condensed phosphates (acid-hydrolyzable) and organically bound phosphates. Reported as equivalent orthophosphate in mg/L PO_4^{3-}. Phosphorous is frequently a limiting nutrient in aquatic systems. Generally indicative of agricultural pollution.

Container: HDPE

Volume Required: 100 mL

Preservation: pH < 2 with H_2SO_4, Refrigerate to 4°C

Holding Time: 48 hours

Lab Procedure: to be determined

Analytical Method: ASTM D515-88 : Standard Test Method for Phosphorus in Water
APHA 4500 - P : Phosphorus
STORET No : 70507 (ortho-P)
00670 (total organic P)
EPA Method: 365.4 (total P)
Ascorbic acid method (Murphy-Riley)
Vanadomolybdate method

Note: The standard method includes sample digestion to oxidize organic matter and release orthophosphate. Similarly, acid hydrolysis converts dissolved and particulate condensed phosphates to dissolved orthophosphate.

Precision: not available

Reporting: Report as mg/L
< 1.0 mg/L report to nearest 0.01 mg/L
≥ 1.0 mg/L report 2 significant figures

Solids, total dissolved

Definition: Concentration of dissolved solids in a water. Operationally defined as the quantity of material not retained by a filter of pore size 0.45 μM average diameter. Typically reported in mg/L

Container: HDPE

Volume Required: 100 mL

Preservation: Refrigerate to 4°C

Holding Time: 24 hrs/48 hours

Lab Procedure: Total Dissolved Solids (TDS) can measured gravimetrically using the following procedure:

1. Weigh a clean, dry crucible. Procedure for drying is as follows:

   (a) Place a clean crucible in drying oven for 24 hours at 103 - 105 °C ;

   (b) Cool the crucible in desiccator prior to weighing;

2. Add filtrate from analysis of total suspended solids to the crucible (volume should be approximately 100 mL);

3. Place crucible and filtrate in to drying oven, dry for 24 hours at 103 - 105 °C ;

4. Following drying period, cool the crucible and it's contents in desiccator;

5. Weigh the crucible and it's contents and record the result. Repeat the drying procedure (Steps 3 and 4) until a constant weight is achieved. Differences in weight between successive drying cycles should not exceed 4% or 0.5 g (whichever is less);

6. Record the final weight of the crucible and it's contents and subtract the weight of the crucible from Step 1. Record the weight of the residue as solids, total dissolved (filterable residue)

upon drying at 103 - 105 °C in mg/L to the nearest whole number. For samples containing high TDS (>1000 mg/L) report three significant figures. Record the type of filter and filtration apparatus used in the procedure.

Calculation:

$$\text{mg/L TDS} = \frac{A * (1000)}{\text{mL of sample}}$$

where: A = measured weight of dissolved solids in mg.

Analytical Method: ASTM: D1888-78 Test Methods for Particulate and Dissolved Matter, Solids or Residue in Water; D4190-82 Standard Test Method for Elements in Water by Direct-Current Argon Plasma Atomic Emission Spectrometry.
APHA: 2540 C
STORET No : 70300, 70301
EPA Method: 160.1

Precision: not available

Reporting: Report as mg/L
< 1000 mg/L report to nearest whole number
≥1000 mg/L report 3 significant figures

Solids, total suspended

Definition: Concentration of settleable solids in a water. Operationally defined as the constituents present within a water of a diameter greater than 0.45μM. Typically reported in mg/L.

Container: HDPE

Volume Required: 100 mL

Preservation: Refrigerate to 4°C

Holding Time: 24 hrs/48 hours

Lab Procedure: Total Suspended Solids (TSS) can be measured gravimetrically using the following procedure:

1. Place filter (0.45 μm average pore diameter) on filtration apparatus and triple rinse with 20 mL aliquots of analytical grade water;

2. Place filter in weighing pan and dry for 24 hours at 103 - 105 °C;

3. Cool filter and weighing pan in desiccator;

4. Weigh filter and weighing pan prior to use and record result.

5. Place filter on filtration apparatus and pass 100 - 300 mL of sample through the filter. Sample volume required depends on TSS concentration (a sufficient residue for weighing is required);

6. Triple rinse the filter and apparatus with 10 mL aliquots of analytical grade water;

7. Following filtration, transfer the filter and residue to the weighing pan and dry for 24 hours at 103 - 105 °C;

8. Cool as described in Step 3;

9. Weigh the filter, residue and weighing pan and record the result. Repeat the drying procedure (Steps 3 and 4) until a constant

weight is achieved. Differences in weight between successive drying cycles should not exceed 4% or 0.5 g (whichever is less);

10. Record the final weight of the filter, residue and the weighing pan and subtract the weight of the filter and weighing pan from Step 3. Record the weight of the residue as solids, total suspended (non-filterable residue) upon drying at 103 - 105 °C in mg/L to the nearest whole number. Record the type of filter and filtration apparatus used in the procedure.

Calculation:

$$\text{mg/L TSS} = \frac{A * (1000)}{\text{mL of sample}}$$

where: A = measured weight of suspended solids in mg.

Analytical Method: ASTM: D 3977-80 Standard Practice for Determining Suspended-Sediment Concentration in water Samples.
APHA: 2540 D
STORET No : 80154
EPA Method: 160.2

Precision: ± 4 mg/L or 5%

Reporting: Report in mg/L
< 1000 mg/L report to nearest whole number (National Handbook)
≥ report 3 significant figures

Sulfate (SO_4^{2-}), dissolved

Definition: Concentration of the oxidized form of aqueous sulfur in a water. Sources include acid mine drainage (oxidization of sulfide minerals) and acid precipitation. The sulfate ion is reported to cause cathartic action in humans at a concentration above 250 mg/L. High sulfate concentration also contributes to poor water taste in the presence of sodium and magnesium.

Container: HDPE

Volume Required: 100 mL

Preservation: Refrigerate to 4°C

Holding Time: 28 days

Lab Procedure: Turbidimetric Method (Hach, 1992):

1. Measure a 25 mL sample into a 50 mL beaker;
2. Add the contents of one SulfaVer 4 Sulfate reagent powder pillow. Allow at least 5 minutes for turbidity to develop but not more than 10 minutes;
3. Adjust the spectrophotometer to 0 with an untreated sample;
4. Read the sample absorbance at 450 nm and compare to a standard curve.

Analytical Method: ASTM D516-90 : Standard Test Method for Sulfate Ion in Water
APHA 4500 - SO_4^2 : Sulfate
STORET No: 00945
EPA Method: 300.0, 375.2
Turbidimetric method (AA)

Precision: SD = 10 at 394 mg/L
SD = 1.1 at 21 mg/L

Reporting: Report as mg/L Sulfate ion (SO_4), dissolved
< 10 mg/L report to one decimal
≥ 10 mg/L report 2 significant figures

Trace Metals

Definition:	Generally defined as metallic elements analyzed using ICP. Includes Al, As, Sb, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, Se, Ag, The, Va, Zn.
Container:	HDPE
Volume Required:	200 mL
Preservation:	pH < 2 with HNO_3
Holding Time:	6 months
Lab Procedure:	submit to laboratory for analysis
Analytical Method:	ASTM: D1976-91 Standard Test Method for Elements in Water by Inductively-Coupled Argon Plasma Atomic Emission Spectrometry APHA: STORET No.: not applicable EPA Method: 200 series/200.7

Colorimetric Methods: Several methods have been developed for the colorimetric determination of metals. Those available from Hach Chemical (for use with DR/2000 visible spectrophotometer) include aluminum, arsenic, barium, boron, cadmium, chromium (total,III,VI), cobalt, copper, iron (total, II), lead, manganese, molybdenum, nickel, palladium, potassium, selenium, silica, silver, and zinc.

Precision:	not available
Reporting:	Report as mg/L or μg/L by constituent

Chapter 5

Quality Assurance and Quality Control

Introduction

Due to the variable nature of environmental conditions, measurements made under ideal field conditions can be expected to have random errors. Minimization of systematic error therefore becomes important since total error is defined as random error + systematic error. Systematic error can be minimized through a rigorous calibration and quality control program.

5.1. Chain of Custody

Chain of custody (COC) documentation is intended to provide information regarding the sampling equipment from the laboratory to the field sampling event and return to the laboratory. This paper trail is an integral part of the analytical result for each sample. The COC can be used to ensure the proper handling of samples and sampling equipment. All COC documentation should be completed and signed by personnel responsible for the field sampling event. Any discontinuity in the COC should be noted and the data collected under a suspect COC should be disregarded. An example COC documentation form is included in the Appendix.

5.2. Calibration of Field Instruments

The calibration of all field instruments is critical for the collection of reliable, repeatable data. Rigorous adherence to calibration schedules and identification of any discrepancies will ensure that data collected will be valid. Procedures for the calibration field instruments is included in Chapter 3.

5.3. Quality Assurance and Quality Control Procedures

5.3.1 Quality Assurance (QA) Samples

In addition to field sampling and measurement procedures described previously, sample analysis quality assurance is required to ensure the accuracy of the analytical results obtained. All samples have a designated preservation and holding time criteria (Table 3).

Sample analysis quality assurance includes the submission of blank and duplicate samples from the field to test the purity of chemical preservatives, to check the field and laboratory

equipment used in sample collection and preservation as a source of contamination, and to identify systematic or random errors that may occur from the time of sampling to the time of analysis. Duplicate samples will be collected and spiked samples will check the reproducibility and accuracy (errors or bias) of the analytical procedures.

Field Duplicates

Collect field duplicates as collocated samples, that is, one after another at the same point in the stream. After collecting the samples into separate containers, filter and analyze the field duplicates as two discrete samples. Collect a field duplicate once for every 10 locations sampled, with a minimum of 2 pairs of field duplicates per sampling round. Field duplicates are used to estimate the precision of the sampling process, including analytical precision.

Field Blanks

Collect a field blank by bringing deionized water (with conductivity < 2.0 μS/cm) to the field site and transferring the deionized water into containers normally used to collect the sample. From that point on, process the blank as if it were a regular sample; blank aliquots are to by (1) unfiltered for pH, ANC, and conductivity, (2) filtered for anions, (3) filtered and acidified for cations, and (4) unfiltered and acidified for total metals. Field blanks should be collected once for every 10 locations sampled, or a minimum of 2 per sampling round. Analysis of the blanks serves as a check on the presence of contamination from the sampling process.

Contamination should be assumed if analysis of a field blank yields values equal to or higher than expected (Table 4).

Bottle Blanks

Prior to a field sampling trip, one sample bottle for every ten of each type being used during the sampling trip should be selected at random, filled with ultrapure distilled water, preserved in the same manner as field samples, and set aside for submission with the field samples for chemical analysis for the parameters of interest as "bottle blanks". This should detect any widespread contamination caused by the bottle washing process.

Sampler Blanks

Periodic "sampler blanks" consisting of ultrapure distilled water poured into, or permitted to pass through the sampler should be prepared and analyzed in the laboratory for the parameter(s) of interest.

Filter Blanks

Prepare filter blanks by filtering deionized water (with conductivity < 2.0 μS/cm) into properly cleaned anion and cation containers. Preserve the filter blanks in the same manner as for regular samples. A set of filter blanks (one for anions and one for cations) should be collected once for every 10 samples. Filter blanks are archived until after the field blanks and regular samples have been analyzed, the data have been analyzed, and the data have been evaluated for suspected problems. The filter blanks need to be analyzed only if a contamination problem is indicated by the field blanks or the analysis of the lake data.

Table 4. Guidelines for determination of contamination from analysis of blank samples (U.S. EPA, 1991).

Variable	μeq/L	mg/L
ANC	10	--
pH	--	--
Conductivity	4 μS/cm	--
Ca	1.0	0.02
K	0.6	0.02
Mg	2.0	0.02
Na	0.8	0.02
Cl^-	1.0	0.02
NO_3^-	0.2	0.01
SO_4^{2-}	2.0	0.1
Metals	--	0.01 (μg/L)
SiO_2	--	0.1

5.3.2 Quality Control (QC) Samples

QC samples are used to check the calibration of analytical instruments. QC samples are analyzed a minimum of three times in each analytical batch.

Laboratory Duplicates

Laboratory duplicates are samples split into separate containers after filtration (if appropriate) but prior to analysis, and analyzed as separate samples within the same batch. There should be a laboratory duplicate for every 10 samples, with a minimum of 2 pairs per batch. Laboratory duplicates are used to estimate within-batch analytical precision.

Spiked Samples

The use of spiked samples is optional, but if they are used to estimate within-batch accuracy, a spiked sample should be prepared for each batch for each analyte being measured. Prepared a spiked sample by adding a known quantity of analyte to an aliquot of a sample, then analyzing the analyte in the spiked and unspiked aliquots. A percent recovery can them be calculated and used as an estimate of accuracy. The spike concentration should be at least 10 times the detection limit for the analyte, and should keep the measured value of the spiked sample within the linear range of the analytical instrument. The volume of the spike added should be negligible.

Replicate Samples (Temporal)

These are two or more samples taken at the same location sequentially at specified intervals over a specific period of time. They are taken to measure the uncertainty due to temporal variations of various parameters in the water body. The number and frequency of these samples are usually determined by a pilot study.

Replicate Samples (Spatial)

These are two or more samples taken simultaneously in a given predetermined cross section of the water body under study. They should be taken to measure the cross-sectional variations in the concentration of the parameters of interest in the system. The number and the exact location of these samples are usually determined by a pilot study.

Analytical Detection Limit

Measurement of the analytical detection limit on a regular basis is necessary for monitoring programs in order to provide regular assessment of instrument performance, as well as a

quantifiable concentration that will indicate when a measured value is above zero and is in fact detectable by the analytical instrument. The analytical detection limit can be defined as three times the standard deviation of a low-level check standard (Taylor, 1987). The concentration of the low-level check standard should be three to five times the required analytical detection limit. The low-level check standard should be used to monitor batch-to-batch detection limits. In addition, LTM cooperators should measure the actual instrument detection limit quarterly or semiannually by preparing a series of dilutions of the lowest calibration standard. The dilutions are analyzed from the lowest concentration to the highest, with the objective of determining which standard yields a detectable response.

5.3.3 Quality Control Charts

The most commonly used control charts are means charts for standards analyses and range charts for replicate analyses. The U.S. Environmental Protection Agency recommends using at least 15 to 20 sets of sample data from an in-control process to construct initial charts. Separate charts should be constructed for each instrument and analytical method employed.

A means control chart is constructed using the average or mean value and the standard deviation (SD) from a group (approx. 20) of standard solution measurements. Usually, ± 2 standard deviations are used to establish the upper and lower warning limits and ± 3 SDs are used to determine the upper and lower control limits. A means chart can be constructed from the calculated mean and SD from measured concentration or percent recovery values.

A range control chart is constructed by calculating a central line or mean range (R), a warning limit (WL) and a control limit (CL). A minimum of 20 range values should be used to construct the range control chart. Perfect agreement between duplicates results in no difference, so the baseline is zero. The standard deviation is converted to the range so values can be plotted.

The mean range is calculated as:

$$\overline{R} = D_2 \; S$$

The control limit as:

$$CL = \overline{R} \pm 3s\,(R) = D_4\overline{R}$$

and the warning limit as:

$$WL = \overline{R} \pm 2s(R) = \overline{R} \pm \frac{2}{3}(D_4\overline{R} - \overline{R})$$

where:

D_2 = factor to convert s to R
s = standard deviation of the range
D_4 = factor to convert the mean range to s of the range.

Number of observations	Central line (D_2)	Control Limit (D_4)
2	1.128	3.267
3	1.693	2.575
4	2.059	2.282
5	2.326	2.115
6	2.534	2.004

Once the control chart is established, plot the new data such that trends can be identified. If any range value is greater than the CL , repeat the measurements. If the repeated range value is within limits, continue with other analyses. If the repeated range value also is greater than the CL, stop analyses check all the variables in the procedure.

If two out of three consecutive range values are greater than the WL , repeat the measurements to obtain one more range value. If this range value is less than the WL, continue with other analyses. If this range value is also greater than the WL, stop analyses and check all the variables in the procedure.

If six consecutive range values are greater than or less than R, repeat measurements to obtain one more range value. If this value reverses the trend, continue with other analyses; if this value is the seventh consecutive point above or below R, stop analyses and check all variables in the procedure.

If four out of five consecutive range values are greater than 1 SD, repeat the measurements to obtain one more range value. If this value is less than 1 SD, continue with other analyses; if this value is also greater than 1 SD, stop analyses and check all variable is the procedure.

If four out of five consecutive range values are in decreasing or increasing order, repeat measurements to obtain one more range value. If this value changes this decreasing or increasing trend, continue with other analyses. If this value continues the decreasing or increasing trend, stop analyses and check all the variables in the procedure.

Once the procedure has been corrected for any of the problems listed above, the measurements than produced range values out of control should be analyzed again. As new data is collected and plotted on the range control chart, recalculate R, WL and CL using the 20 most recent range values. This will keep the control chart current.

More commonly the range can be expressed as a function of the relative standard deviation (coefficient of variation). Normalize the range by dividing by the average. Determine the mean range for the pairs analyzed by:

$$\overline{R} = \frac{(\Sigma Ri)}{n}$$

and the variance as:

$$s_R^2 = \frac{(\Sigma Ri^2 - n\overline{R}^2)}{(n - 1)}$$

Then draw lines on the chart at $\overline{R} + 2s_R$ and $\overline{R} + 3s_R$ and for each duplicate analysis , calculate normalized range and enter on chart.

Analyzing Chart Data

Once a control chart is established, new data can be plotted to analyze trends. If successive plottings indicate a movement toward warning limits, all the variables in the procedure should be checked in an effort to reverse the trend before the process is out of control. If a measurement exceeds the control limit, another sample should be measured immediately. If this measurement is also out of control, analysis should be stopped and all the variables in the measurement should be checked. Once the procedure is corrected, the samples that measured out of control should be analyzed again.

5.4 Assessing Precision and Accuracy

An estimate of precision and accuracy must be made for each analytical batch of samples, so

that the quality of the data can be adequately described. If an analytical batch includes samples other than project samples, but similar to project samples, duplicates and spikes of the other samples can be used to estimate precision and accuracy for that batch.

Precision

Precision is the degree of mutual agreement characteristic of independent measurements resulting from repeated application of the process under specified conditions (Taylor, 1987). In this program, we estimate (1) analytical and (2) sampling and analysis precision:

> Analytical precision refers to the precision of the analysis performed by analytical laboratory instruments; it is estimated by laboratory duplicates or replicates. Sampling and analysis precision refers to the precision of the entire sampling process, from sample collection through analysis; it encompasses analytical precision. It is estimated by field duplicates or replicates.

Both analytical precision and sampling and analysis precision are estimates of intralaboratory precision. Laboratory and field duplicates can be measured within the same analytical batch to estimate within-batch precision, or in different analytical batches to estimate among-batch precision. Among-batch precision includes more sources of error than within-batch precision. QA objectives for precision are compared to within-batch analytical precision, although it is desirable for all estimates of precision (i.e., from among-batches and field duplicates) to meet these QA objectives.

Precision measures how well the test results can be reproduced. A series of measurements on the same sample for the same parameter are compared to the average measurement. Remember that it is possible to produce test results with high precision but low accuracy. The most commonly used estimates of precision are the standard deviation (SD) and the relative standard deviation (RSD). RSD is also known as the coefficient of variation (CV).

Calculating the standard deviation

many electronic calculators have statistical capability programmed in so that calculating a SD is as simple as entering the data and pressing the appropriate keys. The formula for the SD calculation is as follows:

$$SD = \sqrt{\frac{\Sigma Xi^2 - \frac{(\Sigma Xi)^2}{n}}{n - 1}}$$

where:

SD = standard deviation
$\sum X_i^2$ = sum of squares of the individual measurements

$\sum X_i$ = sum of the individual measurements
n = number of the individual measurements

If samples have different orders of magnitude of concentrations, the standard deviations cannot be compared Thus calculating a relative standard deviation will allow comparison. The relative standard deviation (coefficient of variation) is:

$$RSD = \frac{SD}{\bar{x}}$$

where:
SD = standard deviation
$\bar{x}$ = sample mean

The smaller the value the higher the precision of the measurement.

Analytical Precision

Analytical precision is determined by analyzing an individual sample in replicate. There are two ways we can measure analytical precision: 1) with laboratory duplicates, which are samples split in the laboratory. A minimum of two pairs of laboratory duplicates per batch should be analyzed for each variable measured. These kinds of duplicates can, in some cases, be blind to the analyst and 2) with QC check samples, which are prepared from a source independent of the calibration standards. QC samples are analyzed after the instrument has been calibrated and before samples are analyzed, and then once after every 10 samples. At a minimum, the QC samples will be analyzed three times in each batch: at the beginning, in the middle, and at the end of the batch. QC samples are used by the analyst to keep the analytical instrument in control; if a QC sample is out of the acceptable range, the problem must be corrected before more samples are analyzed

Sampling and Analysis Precision

Sampling and analysis precision can be estimated from the analysis of the duplicate samples collected in the field. One field duplicate is collected for every 10 samples, with a minimum

of at least 2 pairs of field duplicates per batch. The %RSD should be calculated for each pair of duplicates.

Accuracy and Bias

Accuracy is the degree of agreement of a measured value with the true or expected value of the quantity of concern (Taylor, 1987). Accuracy is expressed as the percent difference from the reference value, or as percent recovery if spiked samples have been used. Accuracy can be estimated by measuring: (1) certified reference material or QC check samples, (2) performance evaluation samples, and/or (3) percent recovery on spiked samples. Certified reference materials, QC check samples, and spiked samples will give the analyst an immediate estimate of accuracy, whereas performance evaluation samples will provide an assessment of accuracy and basis for comparison with other laboratories. Either certified reference materials, QC check samples, or spiked samples should be used with each batch, to estimate accuracy.

Bias is a systematic error inherent in a method or caused by some artifact or idiosyncrasy of the measurement system (Taylor, 1987).

Certified Reference Material

Certified reference material or a QC check sample should be measured in each batch of samples; then the percent difference should be calculated.

$$\% \text{ difference} = \frac{\text{true value - measured value}}{\text{true value x 100}}$$

The % difference should be within the QA objectives for accuracy. If not, corrective action should be taken before samples are analyzed, such as correcting the instrument calibration, or the instrument settings.

Reference materials can be obtained from the National Institute of Standards and Technology (NIST), formerly the National Bureau of Standards, or from commercial firms that produce "U.S. EPA Certified" chemical reference materials in cooperation with the EPA. The American Association for Laboratory Accreditation (A2LA) also has a certification program for chemical reference materials that is acceptable to the EPA. Only the terms "U.S. EPA Certified" or "A2LA Certified" indicate certification that has been approved by the EPA. QC check samples can also be prepared from other sources, as long as the source and preparation are different from those used to prepared calibration standards.

Percent Recovery

Spike an aliquot of a sample with a known amount of analyte, analyze the spiked and unspiked sample, then calculate the percent recovery. A blank should also be spiked at the same time.

$$\% \text{ Recovery} = [(S - X) / A] 100$$

where: S = value of sample plus spike
X = value of unspiked sample
A = value of spike added

5.5 Data Validation and Reporting

We have developed the following general protocol for chemical analysis:

1. Determine the probable analysis range for each tested specie, then fabricate standards confirming to these ranges (range and standards listed under specific ion information). This provides a primary, low range, and high range standard. Also, fabricate a minimum of five different concentrations, grouped around the specified ranges, for instrument quality assurance (QA) tests.

2. Verify sample pH and conductivity in the lab.

3. Perform hardness and alkalinity titrations on anion samples, to verify range of instrumentally determined specie concentrations.

4. Analyze anion (non-acidified) sample for macronutrients (ICP) and anions (IC) using primary standards. If the concentration determined is below the designated range of the standard used, spike the sample (50% sample + 50% primary standard) and reanalyze. If the concentration determined is above the designated range of the standard used, dilute the sample accordingly and reanalyze. Include a minimum of 50% QA samples (both duplicate samples and known concentrations). If the values for the QA samples with known concentrations fall outside the acceptable error range (see specific specie information), the instrument must be restandardized and the run repeated.

5. Analyze dissolved metals sample for macronutrients and metals on the ICP or AA using primary standards. If the concentration of a specific specie is below the designated range of the standard used, restandardize the instrument with the low range standard and reanalyze. If the concentration determined is still below the range of the low standard, spike the sample (50% sample + 50% low standard) and reanalyze. If the concentrate determined is above the range of the high standard, restandardize the instrument with the high range standard and reanalyze. If the concentration determined

is still above the high range standard, dilute the sample accordingly and reanalyze. Include a minimum of 50% QA samples (both duplicate samples and known concentrations).

6. Use the results from the dissolved metal sample to group the total metal samples into probable specie concentration ranges. Analyze these samples the same way the dissolved metal samples were analyzed. Include a minimum of 50% QA samples (both duplicate samples and known concentrations).

7. Calculate actual dissolved and total sample metals concentrations by multiplying analyzed concentrations by a correction factor. Calculate the correction factor by determining the ratio of Ca and Mg in the anion (non-acidified) sample and the acidified sample in question. Also, any spikes or dilutions should be factored in here.

Once each variable in a sample has been determined, several procedures are used to provide a check on the analyses. These validation checks are completed as soon as possible after analyses are finished, so problems can be detected and samples can be reanalyzed, if necessary, before holding times are exceeded. Validation checks include: (1) cation-anion charge evaluation, (2) specific conductance evaluation, and (3) comparison with previous years' data.

Cation-Anion Charge Evaluation

Theoretically, the sum of anion equivalents equals the sum of cation equivalents in a sample. In practice, this rarely occurs, due to ions that are present but not measured. For each sample, the sums of the measured anion and cation equivalents and the ion ratio are calculated as follows:

$$\Sigma \text{ anions} = [Cl^-] + [F^-] + [NO_3^-] + [SO_4^{2-}] + [HCO_3^-] + [CO_3^{2-}]$$

$$\Sigma \text{ cations} = [Na^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}] + [NH_4^+] + [H^+] + [Al^{3+}] + [\text{heavy metals}]$$

$$\text{Ion ratio} = \frac{\Sigma \text{ cations}}{\Sigma \text{ anions}}$$

$$\text{Sum of ions} = \Sigma \text{ anions} + \Sigma \text{ cations}$$

Note: Omission of F^-, CO_3^{2-}, and NH_4^+ will not significantly affect results. ANC plus H^+ (calculated from pH) may be used for HCO_3^-, based on the following equation:

$$ANC = HCO_3^- + 2CO_3^{2-} + OH^- - H^+$$

when pH < 7.0, CO_3^{2-} and OH^- are negligible, therefore the equation becomes:

$$ANC = HCO_3^- - H^+; \text{ or } HCO_3^- = ANC + H^+$$

A percent ion difference can also be calculated instead of an ion ration to evaluate cation and anion charges:

$$\% \text{ difference} = \frac{\Sigma \text{ anions} - \Sigma \text{ cations}}{\Sigma \text{ anions} + \Sigma \text{ cations}}$$

All concentrations are expressed as microequivalents/liter (μeq/L) (Table 5). The acceptable difference between the cations and anions depends on the anion sum (APHA, 1989):

0-3.0 ($\pm$ 0.2 meq/L)

3-10 ($\pm$ 2%)

20-800 ($\pm$ 2-5%)

Specific Conductance Evaluation

An estimate of the specific conductance of a sample can be calculated by summing the equivalent conductance values for each measured ion at infinite dilution. The calculated conductance is determined by multiplying the concentration of each ion (in μeq/L) by the appropriate factor (F) (Table 6). The calculated conductance for the entire sample is obtained from the relationship:

$$\text{Calculated conductance} = \frac{\Sigma\ (\text{F x Concentration in } \mu\text{eq/L})}{1000}$$

The percent difference between measured conductance and calculated conductance is given by:

$$\%\ \text{conductance difference} = \frac{\text{Calculated - Measured}}{\text{Measured x 100}}$$

Or, the ratio of calculated to measured conductance can be determined by:

$$\text{Conductance ratio} = \frac{\text{Calculated conductance}}{\text{Measured conductance}}$$

The range of acceptable percent conductance differences or conductance ratios, that are used to decide if a sample should be reanalyzed, are as follows:

Measured Conductance (μS/cm)	Acceptable Conductance Ratio
<5	0.7 - 1.30
≥ 5 < 30	0.85 - 1.15
≥ 30	ND

Comparison with Previous Years' Data

All newly acquired data should be plotted and compared to historical data from the same lakes or streams within the holding time requirements, if possible, to further assist the detection of any analytical contamination, or reporting problems.

Table 3. Factors for converting mg/L to μeq/L (APHA, 1993):

Ion	(μeq/L per mg/L)
Ca^{2+}	49.9
Cl^-	28.2
CO_3^{2-}	33.3
K^+	25.6
Mg^{2+}	82.3
Na^+	43.5
NH_4^+ (as nitrogen)	71.4
NO_3^- (as nitrogen)	71.4
SO_4^{2-} (as sulfate)	20.8
ANC (as $CaCO_3$)	20.0

Table 4. Conductance factors (F) of Ions (APHA, 1993):

Ion	Conductance Factor	Ion	Conductance Factor
Ca^{2+}	59.47	NO_3^-	71.42
Mg^{2+}	53.0	Cl^-	76.31
Na^+	50.08	SO_4^{2-}	80.0
K^+	73.48	HCO_3^-	44.5
H^+	349.65	OH^-	198.0
NH_4^+	73.50		

5.6. Quality Assurance Reports

Data quality must be indicated whenever data are reported. Data quality is most easily indicated by estimates of precision and accuracy and by the results of blank analyses. Each analytical batch should have an estimate of precision and accuracy. Raw data used in estimates of precision and accuracy and in results of blank analyses should also be reported. Summaries of estimates of precision and accuracy for a sampling period can be used when reports on the data are prepared. Precision data can be presented by listing the range of precision values obtained in %RSD by variable for each year or sampling period, noting the number of duplicates, and the number of duplicates that exceeded the QA objectives. Accuracy data can be presented by listing the range of accuracy values in % difference by variable for each year or sampling period, noting the number and type of samples used to determine accuracy, and noting the number of samples that did not meet the QA objectives. Similarly, summaries of blank analyses can be included by listing the range of blank values by variable for each sampling period, the number and concentration of blanks that exceeded the concentration values listed, and the total number of blank analyses. If the total number of duplicates or blanks is 10 or less, report results from all duplicates or blanks, instead of writing a summary. Field blanks are intended to identify contamination being introduced through field procedures.

Chapter 6

Electronic Data Acquisition

Introduction

The use of electronic instruments to collect water quality is increasing. Often the level of precision of the data recorder, or the software used to download input exceeds the precision or the field method itself. Ensuring that electronically acquired data are of known quality requires adapting quality assurance techniques for data loggers and the measurement techniques. Three specific areas have been identified for quality assurance protocols: 1) sensor validation in the field; 2) time control for data loggers; and 3) precision and accuracy of sensors over time (Whitfield and Wade, 1993).

6.1. Field Verification

Sensor calibrations change over time. Water quality sensors are not as stable as meteorological sensors and thus require more frequent servicing. Field verification and calibration of water quality sensors should be based on independent sensors. Water quality sensors may include temperature, pH, specific conductivity, dissolved oxygen, oxidation-reduction potential (ORP), and stage (depth). In field analyses may be used to validate field sensors. Lab analyses may be used for the dissolved oxygen and ORP measurements if holding times and temperatures are considered. Field verification should be done every time the data logger is visited or services. If a departure is observed between the field sensor and the independent sensor, the departure is noted in the field log book. The purpose of the water quality monitoring program will determine the acceptable departure, i.e., is the pH $\pm$ 5 percent acceptable? If any of the departures between the field and independent sensor exceeds the acceptable limit, the departures should be noted and the data downloaded. Field instruments are recalibrated and the recording period initiated.

6.2. Time Check

The data logger will have an internal clock. The logger time is usually recorded as part of the sensor query and is often used as a record header. The internal clock time should be checked with each site visit, and again if the recorder time is significantly different than real time, the logger should be serviced. The time departure should be recorded in the field log book. The question of significance with respect to time departure depends on the purpose of the sampling program. As a general rule, if the time departure is greater than the scan frequency interval, the logger should be serviced and the clock reset. The scan frequency interval will determine if clocks can be set by the wrist watch tie of the field technician or if a time clock ratio (station

WWV, Fort Collins, Colorado) should be used. The scan frequency interval will also be a function of the data logger memory. See the logger instructions for suggested user information and details.

6.3. Precision and Accuracy

Electronic sensors will drift over time and perhaps more importantly, like sensors may be respond similarly (or linearly) over time. This may affect precision (reproducibility) and accuracy. Like sensors should have similar readings over the operating range and the ideal fit would have a 1:1 slope. Regression analysis (analysis of covariance) can be used to determine if there are significant differences between sensors. If there are significant differences, programmable loggers can be used, programmed for sensor agreement, otherwise the errant sensor should be replaced.

Table 5. Multiprobe Parameter Specifications (Hydrolab, 1994)

Parameter	Range	Accuracy	Sensor	Resolution	Calibration
Temperature	-5 to 50°C	± 0.15°C	Thermistor	0.01°C	none required
Specific Conductance	0 to 100 μS/cm	± 1% of range	6 electrode cell	4 digits	KCl or seawater stds
pH	0 to 14 units	± 0.2 units	glass pH, reference electrode	0.01 units	pH 7 buffer; one slope buffer
Dissolved Oxygen	0 to 20 mg/L	± 0.2 mg/L	polarographic	0.01 mg/L	saturated air, Winkler or saturated water
Redox	-999 to 999 mV	± 20 mV	Pt electrode	1 mV	Quinhydrone or transfers
Depth - 100m	0 to 100 m	± 0.45 m	transducer	0.1 m	set zero in air
Depth - 200m	0 - 200 m	± 0.90 m	transducer	0.1 m	set zero in air
Level	0 - 10 m	± 0.09 m	transducer	0.01 m	set zero in air
Salinity	0 - 70 ppt	± 0.2 ppt	calculated from specific conductance	0.1 ppt	calibrate from specific conductance
Turbidity	0 to 100 NTU and 100 to 1000 NTU	± 5% of range	ISO 7027 nephelometric with 880nm infrared and transmissive correction	0.1 to 1 NTU	dilutions of Formazin or AEPA-1 polymer beads

APPENDICES

Sampling Summary

PARAMETER	CONTAINER	VOLUME	PRESERVATIVE	HOLDING TIME
Temperature (field)	Glass/Poly	1000 mL	N/A	N/A
pH (field)	Poly	25 mL	N/A	N/A
Conductivity (field)	Poly	100 mL	N/A	N/A
Dissolved Oxygen (field)	Glass	300 mL	N/A	N/A
Alkalinity (field)			N/A	N/A
Turbidity (field)			N/A	N/A
Acid Neutralizing Capacity				
Alkalinity	Glass/Poly	100 mL	Refrigerate 4°C	14 days
Chloride, total dissolved	Poly	50 mL	Refrigerate 4°C	28 days
Chlorophyll				
Clarity/Turbidity	Glass/Poly	100 mL	Refrigerate 4°C	48 hours
Fecal Coliforms	Poly	100 mL	0.008% $Na_2S_2O_3$, 4°C	6 hours
Hardness	Poly	100 mL	pH<2 HNO_3 or H_2SO_4, 4°C	6 months
Nitrate, dissolved	Poly	100 mL	Refrigerate 4°C	48 hours
Nitrogen, total Kjeldahl	Poly	500 mL	pH<2 H_2SO_4, 4°C	28 days
Nitrogen, total dissolved	Poly	500 mL	pH<2 H_2SO_4, 4°C	28 days
Phosphate, dissolved	Poly	50 mL	Filter, pH<2 H_2SO_4, 4°C	24 hours
Phosphorous, orthophosphate	Poly	50 mL	Filter, 4°C	48 hours
Silica, dissolved	Poly	50 mL	Refrigerate 4°C	28 days
Solids, total dissolved	Poly	100 mL	Refrigerate 4°C	7 days
Solids, total suspended	Poly	100 mL	Refrigerate 4°C	7 days
Sulfate, dissolved	Poly	50 mL	Refrigerate 4°C	28 days
Trace Metals, dissolved	Poly	200 mL	pH<2 HNO_3, 4°C	6 months

CHAIN OF CUSTODY RECORD

SURVEY	SAMPLERS (SIGNATURE):

Station I.D.	Station Location	Date	Time	Sample Type			Seq. No.	Number of Containers	Analysis required
				Comp	Grab	Other			

Relinquished by (signature) *Date* *Seal*

Received by (signature) *Date* *Seal*

Relinquished by (signature) *Date* *Seal*

Received by (signature) *Date* *Seal*

Relinquished by (signature) *Date* *Seal*

Received by (signature) *Date* *Seal*

Relinquished by (signature) *Date* *Seal*

Received by (signature) *Date* *Seal*

GLOSSARY

Absorption	The incorporation of a substance into the body of another.
Accuracy	Refers to the agreement between the measured value and the accepted or "true" value. It is expressed
Acid Extractable Metal	The concentration of a metal in solution after treatment of and unfiltered sample with dilute mineral acid, cold or hot.
Acidity	The quantitative capacity of aqueous media to react with hydroxyl ions.
Acid Mine Drainage	Low pH drainage water from certain mines. The low pH is usually caused by the oxidation of sulfides to sulfuric acid. Mine drainage can also contain high concentration of metal ions.
Adsorption	The surface retention of solid, liquid or gas molecules, atoms or ions by a solid or liquid.
Algal Mat	A moribund surface algal population.
Algicide	A chemical used to kill algae. Algicides are often applied to water to control nuisance algal blooms.
Aliquot	A representative sample of a larger quantity.
Alkalinity	A measure of a water's capacity to neutralize an acid. It indicates the presence of carbonates, bicarbonates and hydroxides, and, less significantly, borates, silicates, phosphates and organic substances. It is expressed in milligrams of $CaCO_3$ per liter.
Ambient Temperature	The temperature of the surrounding medium, such as ambient air, which comes into contact with the apparatus.
Analytical Grade	A chemical with a level of purity high enough to permit its use in precise analytical determinations.
Aquatic Life	Those organisms found living or growing in, on or near water.
Bedload	Material moving on or near the stream bed by rolling, sliding, and sometimes making brief excursions into the flow a few diameters above the bed.
Bedload Discharge	The quantity of bedload passing a transect in a unit of time.
Bedload Sampler	A device for sampling the bedload.
Bed Material	The sediment mixture of which the bed of the water body is composed. In alluvial streams bed-material particles are likely to be moved at any moment.
Bed-Material Sampler	A device for sampling bed material.
Benthos	Bottom-dwelling organisms.
Biochemical Oxygen Demand (BOD)	A measure of the quantity of oxygen used in the biochemical oxidation of organic matter in a specified time, at a specified temperature, and under

specified conditions. The standard measurement is made for 3 days at 20°C. In general, a high BOD indicates the presence of a large amount of organic material. It is normal to find a BOD of 2 to 3 mg/L in river waters receiving natural drainage.

Biodegradability — The characteristic of a substance that can be broken down by microorganisms.

Biodegradation — The process of destruction or mineralization of either natural or synthetic materials by the microorganisms of soils, waters or wastewater treatment systems.

Biomass — The weight, wet or dry, of all living matter in a specified area or volume of environment, for example, a square meter of stream bottom.

Birge-Ekman Dredge — A sampler designed for the collection of the top 2-3 cm of bottom sediment. This apparatus is suitable for soft clays, muds, silts and silty sands.

Blank — A sample of distilled or deionized water.

Blanks — Prepared samples used to measure various cross-contamination sources.

Bloom — A clearly visible concentration growth or aggregation of plankton (plant and animal) in a water body.

Bottom Sediment — Those sediments which make up the bed of a body of running or still water.

Centroid of Flow — Midpoint of a channel of uniform flow.

Chemocline — A zone of rapid change, with depth, in the concentration of dissolved substances in a lake. The boundary between the circulating and non-circulating layers of a lake.

Coliform Bacteria — A group of bacteria predominantly inhabiting the intestines of man or animals, but also occasionally found elsewhere. Fecal coliform bacteria are those organisms associated with the intestine of warm-blooded animals, and they are used commonly as an indicator of the presence of fecal material and the presence of organisms potentially capable of causing disease in humans.

Colony — A group of individual animals or plants living together and dependent on one another to a varying degree. In some colonies the individuals are structurally connected and function as a single unit, as in many algae. In other colonies the individuals are not structurally connected but often, notably in insect colonies, show a high degree of social organization. Also, a growth of a particular type of bacterium on a culture medium.

Community — In ecology, a collection of populations of animals and plants that occur naturally together in a common environment, such as the organisms inhabiting a woodland. The individuals and populations within the community interact with one another and with the abiotic (non-living surroundings, with the community and abiotic surroundings together constituting an ecosystem. Communities vary considerably in size and one large community may contain a number of smaller ones.

Composite Sample — A sample obtained by mixing several discrete samples, or representative portions thereof, into one bottle (see flow proportional and sequential composite samples.)

Contamination	A foreign or unwanted material which renders a sample unit for meaningful analyses.
Cosmic-Ray-Produced Nuclides	Short-lived radioisotopes such as tritium, beryllium-7 and carbon-14 formed by the continuous "rain" of electrons and nuclei of atoms from space interacting with certain atmospheric and terrestrial elements.
Cross-Section	A plane perpendicular to the axis of flow.
Deionized Water	Water that has passed through a column to removed charged, usually inorganic particles.
Depth-Integrated Sample	A sample which represents the water-suspended sediment mixture throughout the water column so that the contribution to the sample from each point is proportional to the stream velocity at that point.
Detection Limit	The smallest concentration of a substance which can be reported as present with a specified degree of precision and accuracy by a specific analytical method.
Deterioration	A decline in the quality of a sample over a period of time due to improper preservation techniques.
Detritus	Finely divided non-living settleable material suspended in the water: organic detritus, from the decomposition of the broken down remains of organisms; inorganic detritus is settleable mineral materials.
Discharge	The flow rate of a fluid at a given instant expressed as volume per unit of time (see stream discharge).
Dissolved Concentration	The concentration of a constituent of an unacidified water sample that will pass through a 0.45-μm membrane filter. The filtration should be done immediately after sample collection.
Dissolved Load	The part of the stream load that is carried in solution, such as chemical ions yielded by weathering and erosion of the land mass.
Dissolved Oxygen (DO)	Is the amount of oxygen dissolved in a given volume of water.
Drainage Basin	The area tributary to or draining to a lake or stream (see also watershed).
Duplicate samples	A collocated sample, usually collected at some prescribed distance from a field sample. Provides short-range spatial variability.
Ecology	The study of the relationships of organisms to their environment.
Ecosystem	A functional system formed by the organisms of a natural community and their environment
Epilimnion	The uppermost layer of water in a lake, characterized by an essentially uniform temperature that is generally warmer than elsewhere in the lake and by a relatively uniform mixing caused by wind and wave action. Also the light (less dense) oxygen-rich layer of water than overlies the metalimnion in a thermally stratified lake.

Eutrophication	The process of over-fertilization of a body of water by nutrients that produce more organic matter than the self-purification processes can overcome.
Extractable Metal	See acid extractable metal.
Filterable Constituent	See dissolved constituent.
Filtrate	The fluid that has passed through a filter.
Filtration	The process of passing a liquid through a filter to remove suspended matter.
Floc	Small masses formed in a fluid through coagulation, agglomeration or biochemical reaction of fine suspended particles.
Flocculent or Flocculating Agent	A substance which, when added to water, forms a floc, thus expediting the settling of suspended matter; for example, alum, ferrous sulphate or lime.
Flow Proportional Composite Sample	Is obtained by (1) continuous pumping at a rate proportional to the flow; (2) mixing equal volumes of water collected at time intervals which are inversely proportional to the volume of flow; (3) mixing volumes of water proportional to the flow collected during or at regular time intervals. This sample will indicate a "flow" average water quality condition over the period of time compositing.
Fluvial Characteristics	Of or pertaining to a river or rivers; existing, growing or living in or about a stream or river; produced by the action of a stream or river.
Gauging Station	A selected location on a stream channel where discharge and other related parameters are measured continuously or periodically.
Geochemistry	A science that deals with the chemical composition of and chemical changes in the crust of the earth.
Geohydrology	The science involving underground water, often referred to as hydrogeology.
Glass Distilled Water	Water that has been freed from dissolved or suspended matter by distillation in a glass system.
Grab Sample	A sample taken at a selected location, depth and time.
Groundwater	All subsurface water.
Hardness, Total	The sum of calcium and magnesium concentrations, both expressed as $CaCO_3$, in milligrams per liter. Other ions such as iron, manganese and aluminum contribute to total hardness, although they are usually present in much smaller concentrations and thus do not normally make a significant contribution to the total hardness. The hardness relates to a water's capability to precipitate soap or to produce lather from soap. The harder the water, the more difficult it is to lather soap. Hardness is normally expressed in milligrams $CaCO_3$ per liter. Waters of various hardness are classified as follows:

Hardness of 1 to 60 mg/L as $CaCO_3$ - soft water

Hardness of 61 to 120 mg/L as $CaCO_3$ - medium - hard water
Hardness of 121 to 180 mg/L as $CaCO_3$ - hard water
Hardness > 180 mg/L as $CaCO_3$ - very hard water.

Heavy metals	Metallic elements with gravities greater than 5, such as cadmium, copper, lead and zinc.
Herbicide	Substances or a mixture of substances used to destroy specific vegetation.
Homogeneous	Uniform in composition.
Hypolimnion	The lowermost layer of water in a lake, characterized by an essentially uniform temperature (except during a turnover) that is generally colder than elsewhere in the lake, and often by relatively stagnant or oxygen-poor water. Also the dense layer of water below the metalimnion in a thermally stratified lake.
In Situ Measurements	Measurements made directly in the water body.
Kemmerer Sampler	A messenger-operated vertical point sampler for water suspended sediment.
Limnology	The study of the biological, chemical, geographical, and physical features of fresh water.
Macro Organisms	Plant, animal or fungal organisms visible to the eye.
Macrophytes	Large plants.
Measuring Point	The above ground point from which measurements will be referenced.
Messenger	A weight that slides down the drop-line to trigger the sampling device.
Metalimnion	See thermocline.
Membrane Filter	A specially prepared filter of cellulose ester with a controlled pore diameter.
Microphyte	A microscopic plant; a dwarfed plant due to unfavorable environmental conditions.
Molarity	The concentration of a solution expressed as the number of gram-molecular weights of a substance dissolved in 1 L of solution.
Multiple Sampler	An instrument permitting the collection of several water- suspended sediment samples of equal or different volumes at each site, simultaneously.
Non-Point Waste Source	A general, unconfined waste discharge.
Normality	The concentration of a solution expressed as the number of gram-equivalent weights of a substance dissolved in 1 L of solution. Normality is abbreviated by N.
Nutrient	A substance, element or compound necessary for the growth and development of plants and animals.

Oligotrophic Waters	Waters with a deficiency of nutrients and plentiful amounts of dissolved oxygen. They support little organic production.
Organic-Free Water	Water free from organic substances.
Particle Size	The dimension, such as average diameter or volume, of the particles in a sediment or rock, or of the grains of a particular mineral that make up a sediment or rock, based on the premise that the particles are spheres or that the measurements made can be expressed as diameters of equivalent spheres. It is commonly measured by sieving, by calculating settling velocities or by determining areas of microscopic images.
Periphyton	The association of aquatic organisms attached or clinging to stems and leaves of rooted plants or other surfaces projecting above the bottom.
Pesticide	A chemical agent that destroys pests.
pH	The negative $\log_{10}$ of the hydrogen ion activity in solution. Water with pH values between 0 and 7 is acidic, with pH value of 7 is neutral, and with pH values between 7 and 14 is alkaline.
Photosynthesis	The process by which simple sugars are manufactured from carbon dioxide and water in plant cells. It also requires the presence of chlorophyll and light.
Phytoplankton	Plant microorganisms, such as certain algae, living unattached in the water.
Plankton	Organisms of relatively small size, mostly microscopic, which either have relatively small powers of locomotion or drift in the water subject to the action of waves and currents.
Point Sample	See grab sample.
Point Wastes Source	Any discernible, confined and discrete conveyance such as any pipe, ditch, channel, tunnel or conduit from which pollutants are discharged.
Pollutant	Any introduced substance that limits a resource use for a specific purpose.
Pollution	The condition caused by the presence of substances of such character and in such quantities that the quality of the environment is impaired (see water pollution).
Population	A generic term denoting any finite or infinite collection of individual things, objects or events in the broadest concept. In ecology, a group of individuals of the same type, particularly of the same species, within a community. Populations have certain characteristics not shown by individual organisms or the community as a whole. Characteristics of a population include density (size in relation to unit space), birth and death rates (natality and mortality, respectively), age distribution, sex ratio, dispersion (distribution of the individuals within the area) and growth rate.
Precision	Denotes the agreement between the numerical values of two or more measurements on the same homogeneous sample made under the same conditions. The term is used to describe the reproducibility of the measurement or method. It can be expressed by the standard deviation.

Preservative	A substance added to the sample in order to maintain given component(s) in a particular state, e.g. dissolved metals in solution.
Pumping Sampler	A sampler with which the water-sediment mixture is withdrawn through a pipe or hose, the intake of which is placed at the desired sampling point.
Quality Control Samples	Also called quality assessment samples. Defined as those samples that allow statements to be made concerning the quality of the measurement system.
Radioactive Contaminant	A radioactive material which is present in places where it may harm life or property.
Radioactivity	The property possessed by some elements, e.g. uranium, or spontaneously emitting alpha, beta and gamma rays by the disintegration of their nuclei.
Radionuclide	An isotope of an element (nuclide) that exhibits radioactivity.
Range	The difference between the lowest and highest values in a set of data.
Reference Points	The graduation marks on a tape or drop-line used for determining depth.
Replicate Sample (spatial)	Two or more samples taken simultaneously in a given cross section of the water body under study. They are used for measuring the cross-sectional variations in the water quality parameters.
Replicate Sample (Temporal)	Two or more samples taken at the same place sequentially at specified intervals over a specific period of time. They are used to determine the uncertainty in various water quality parameters due to temporal variations.
Representative Sample	A sample of a universe or population whose composition is expected to exhibit their average properties.
Reservoir	An impounded body of water or controlled lake where water is collected and stored.
Residue	Material that remains after gases, liquids and some solids have been removed usually by heating up the sample at a specified temperature for a specified period of time.
Rinsate samples	A sample usually consisting of DDI water that was passed over (last rinse) the sampling device. To measure residual contamination after device is decontaminated.
Sampling Iron	An iron frame designed to hold sampling bottles of different sizes.
Sampling Vertical	A vertical line from the water surface to the bottom along which one or more samples are collected to determine various properties of the water body, such as the concentration of suspended sediment, nutrients and metals.
Secchi Disk	A circular metal plate, 20-30 cm in diameter, painted in black and white quadrants. It is used to determine the transparency of a water body.

Sediment	Solid fragmental material that originates from weathering of rocks and is transported or deposited by air, water or ice, or that accumulates by other processes, such as chemical precipitation from solution or secretion by organisms. The term is usually applied to material held in suspension in water or recently deposited from suspension and to all kinds of deposits, essentially of unconsolidated materials.
Sediment Discharge	Usually the mass or sometimes the volume of sediment passing a stream transect in a unit of time. The term may be qualified, for example, as suspended-sediment discharge, bedload discharge or total-sediment discharge.
Sediment Load	The amount of sediment passing a cross section of a river, stream, etc., in a specified period of time (see also bedload and suspended sediment load).
Sediment Sample	A quantity of water-sediment mixture or deposited sediment collected to characterize its properties.
Sediment Transport	See sediment discharge.
Sediment Yield	The total sediment outflow from a drainage basin in a specified period of time. It includes bedload as well as suspended load, and usually it is expressed in terms of mass, or volume per unit of time.
Semivolatiles	A group of organic compounds consisting of base/neutrals, acids, and the pesticides that are identified in and analyzed by Method 625 in 40 CFR Part 136.
Sequential Composite	A sample obtained either by continuous, constant pumping of water or by mixing equal volumes of water collected at regular time intervals. This sample will indicate an average water quality condition over the period of time of compositing.
Shipek Sampler	An instrument designed to collect relatively undisturbed samples of bottom surface sediments (also Mini-Shipek).
Species	A unit used in the classification of plants and animals. Includes closely related, morphologically similar individuals that interbreed with each other to produce fertile offspring. Members of different species do not normally interbreed; if they do, the progeny are sterile. In binomial nomenclature each species has two names. The first is the name of the genus and the second is the specific epithet (trivial name). For example, in the species Homosapiens, Homo is the generic name and sapiens is the specific epithet.
Species Population	A group of similar organisms residing in a defined space at a certain time.
Specific Conductance	A numerical expression of a water's ability to conduct an electrical current. It is measured in microsiemens per centimeter (μS/cm) at a standard temperature, usually 25°C. At a given temperature the conductivity of water depends on the concentration of ions in solution.
Split sample	A sample that is prepared for analysis and then split. It is used to measure homogeneity of prepared sample.

Standard Deviation	A measure of the dispersion or spread of data points around the mean value of the data set obtained by repetitive testing of a homogeneous sample under specified conditions.
Standing Crop	The biota present in an environment at a selected point in time.
Sterilization	The process of destroying all forms of microbial life on and in an object.
Stream Discharge	The quantity of water passing a stream transect in a unit of time.
Supernate or Supernatant	The liquid, e.g. water, above the surface of settled sediment.
Surface Water	Natural water bodies, such as rivers, streams, brooks and lakes as well as artificial water courses, such as irrigation industrial and navigational canals in direct contact with the atmosphere.
Suspended Load	The part of the sediment load that is in suspension.
Suspended Sediment	Those constituents of an unacidified water sample that are retained by a 0.45 μm membrane filter. It can impart a cloudy appearance to the sample.
Suspended Solids	See suspended sediments.
Teflon	A man-made plastic material inert to all chemical, reagents except molten alkali metals. It is used for laboratory and field equipment.
Thermocline	The layer in a thermally stratified lake, between the epilimnion and hypolimnion, in which the temperature decreases most rapidly with depth. The horizontal layer of water characterized by a rapid decrease of temperature and increase of density with depth; sometimes arbitrarily defined as the layer in which the rate of temperature decrease with depth is equal to at least 1°C per meter. Also known as metalimnion.
Time Composite Sample	See sequential composite sample.
Total Concentration	The concentration of a given constituent determined in an unfiltered sample after vigorous digestion; the sum of the concentrations in both filterable and unfilterable (suspended) fractions.
Total Dissolved Solids (TDS)	The concentration of dissolved substances in a water, usually expressed in mg/L.
Trace Element	A chemical element found naturally or required by living organisms in extremely small quantities (micronutrient).
Transect	A cross section of a water body.

Turbidity	A measure of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through the water sample. Turbidity in water is caused by suspended matter, such as clay, silt, finely divided organic and inorganic matter, soluble colored organic compounds, plankton and other microscopic organisms. The clarity of a natural body of water is a major determinant of the condition and productivity of that system.
Van Dorn Sampler	A messenger-operated water-suspended sediment point sampler used to collect samples at a specified depth. The long axis of the cylinder can be lowered either horizontally or vertically.
Volatile	Solids or liquids that are relatively unstable at standard temperature and pressure and undergo spontaneous phase change to a gaseous state.
Volatile Constituents	Components of a sample which are readily lost by evaporation. They include dissolved gases as well as substances with low boiling points.
Watershed	All lands enclosed by a continuous hydrologic-surface drainage divide and lying upslope from a specified point on a stream (see also drainage basin).
Water Pollution	The addition of harmful or objectionable materials to water in sufficient quantities to affect its usefulness adversely.
Water Quality Criteria	Scientific information, e.g. concentration-effect data, used to recommend water quality objectives.
Water Quality Objective	A concentration or a narrative statement describing the water body, which, when met, will protect the uses of the water.
Water Quality Standard	The concentration of a constituent or a narrative statement describing the water body established under statutory authority, e.g. legally enforceable.
Zooplankton	Microscopic animals living unattached in aquatic ecosystems. They include small crustacea, such as Daphnia and Cyclops, and single-celled animals, such as protozoa.

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