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WATER QUALITY MONITORING
PROGRAMS

DEVELOPED BY
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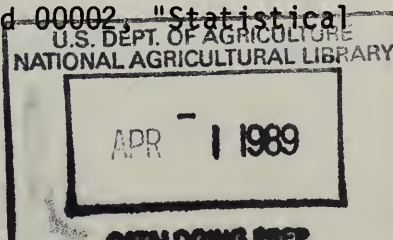
PREFACE

Recent legislation, such as Public Law 92-500 (the Federal Water Pollution Control Act Amendments of 1972), RPA and NFMA, and public opinion have forced water quality considerations to surface in many land and resource decision processes. This has generated a need to provide decision-makers with information about existing water quality and the impacts of land management practices on water quality. In general, this information is obtained through water quality monitoring.

Water quality monitoring, which is defined in the Forest Service Manual as "the systematic evaluation of achievement of water quality management goals, objectives, or targets," is usually the responsibility of the forest hydrologist. The purpose of this Technical Paper is to help forest hydrologists develop technically sound water quality monitoring programs. The material presented here is the result of an extensive literature review and personal experience.

It is intended that this paper be used as a technical guide, not a "cook book." Every water quality monitoring program will be different. As a result, each program will require that the hydrologist understand the hydrologic system at hand as well as the interaction between land-use activities and water quality. In my opinion, there is no substitute for careful planning by the professional forest hydrologist when developing a water quality monitoring plan of operation for a National Forest.

This paper was designed to be used in conjunction with Watershed Systems Development Group (WSDG) Technical Paper 00001, "Statistical Methods Commonly Used in Water Quality Data Analysis"; and WSDG Application Documents 00001, "Statistical Analysis Using the Statistical Analysis System (SAS) at the EPA National Computer Center"; and 00002, "Statistical



Analysis Using the Statistical Package for the Social Sciences (SPSS) at the USDA Fort Collins Computer Center."

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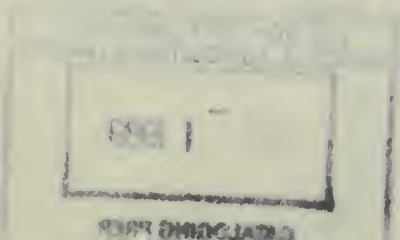


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WATER QUALITY MONITORING PROGRAMS

1.0 Introduction

Designing a water quality monitoring program that will provide useful information is an intellectual activity. It requires a great deal of thought and careful planning. Thinking about the measurements you are going to make and why you are going to make them leads to problem solving.

Just as a blood sample gives a physician insight into the functions of the human body, a water sample can tell a hydrologist a great deal about the complex system of a watershed. The quality of the water resource is directly related to natural factors, such as climate, geology, soils and terrestrial and aquatic vegetation; and man's land-use activities, such as timber harvesting, road building, grazing, recreation and mining.

Consequently, to obtain useful information from water quality monitoring, the sampling network for collection of data must be properly located in both time and space and the constituents which are relevant to the management objectives must be sampled. In addition, if the monitoring is to be cost effective, the hydrologist needs to evaluate, at the outset of the program, what can be accomplished with the resources that are available.

The purpose of this paper is to (1) summarize the various types of water quality monitoring commonly carried out on National Forest System lands and (2) provide a series of guidelines to aid you with problem definition, establishing study objectives, locating past work, data analysis, locating sampling stations, selecting water quality constituents, determining sampling frequency, and collecting and handling samples.

One final comment before we begin our discussion on developing water quality monitoring programs. It is strongly recommended that you document your program in the form of a water quality monitoring plan of operation (see FSM 2542). A written monitoring plan serves several purposes. First, it forces you to clearly define your problem and study objectives as well as develop a logical approach to collecting data which will provide information. Second, it provides your supervisor and other interested parties with a statement of the problem you plan to address, how you will do it, the type of data that will be obtained, how the data will be analyzed, the expected knowledge to be gained, the financial commitment required, and when reports are to be done. Finally, if you leave the Forest before the project is completed, it provides the next hydrologist with the proper framework to continue the study. In general, the structure of a water quality monitoring plan varies from Region to Region. However, the major components of most plans are the topics discussed in this paper.

2.0 Types of Monitoring

In general, the types of water quality monitoring performed on National Forest System lands can be divided into four categories: cause-and-effect, compliance, baseline, and inventory. A brief summary of each follows.

Cause-and-effect (project) monitoring is performed to quantify the impacts of specific land management activities on water quality. The information obtained from this type of study is often used to evaluate the effectiveness of "Best Management Practices," calibrate existing models which were developed at different locations or under different conditions, and develop and verify models designed specifically for the Forest.

Cause-and-effect monitoring is generally implemented on a project level. The surveys are designed to deal with questions about what happened and why. The monitoring is generally short-term, lasting three years or less. Whenever possible, paired sampling is employed with samples being collected before, during and after the treatment.

Compliance monitoring on National Forest System lands is performed primarily to protect public health. It includes the monitoring of drinking water and water used for primary contact recreation. The water quality is generally compared with existing State water quality standards and when these standards are not met, corrective action should be taken as soon as possible.

Baseline monitoring is performed to provide land managers with reliable information on water quality trends. The data are generally used to determine if water quality maintenance and improvement criteria required by law and/or policy are being met and for long-term trend assessment. If the data indicate that water quality degradation is occurring as a result of activities on the National Forest, corrective action may be evaluated and appropriate action initiated. Water quality stations associated with this type of monitoring program are usually located at strategic points within the Forest and sampled on a routine basis for many years.

Inventory monitoring is carried out to provide land managers with reliable information of existing water quality conditions. The data are generally used to provide information for the land management planning process and to establish water quality goals. Usually the inventory data are obtained from existing stations established for cause-and-effect, compliance and baseline monitoring. However, if additional stations are

required, they are often located at strategic points within the Forest and sampled intensively for a short period of time.

One of the keys to an effective water quality program is to integrate the various types of monitoring so that they are complementary. Some of each type of monitoring will generally be carried out on all Forests. Enough of each type should be accomplished to characterize the quality of the water resource, to assess the impacts of management activities on water quality and to determine if water quality standards, goals and objectives are being met.

Priorities for monitoring should be established because it is not feasible to monitor the water quality of all management activities or all water bodies within the Forest. Variation of priorities between Forests will exist depending on the existing data base, management issues and concerns, and water quality management objectives.

3.0 Defining Problem Areas and Setting Study Objectives

The first step in developing an effective water quality monitoring plan is to define problem areas. Each problem definition must evolve from the needs identified by the line officer for information which will aid in making management decisions (Boynton, 1972). It is very important that the needs of the line officer be clearly identified since water quality monitoring can only be justified if it is done to address specific needs of management for information. Furthermore, commitment by line officers to monitoring programs is achieved through their involvement in problem identification and setting specific study objectives.

The role of the hydrologist in the problem definition phase is to take the lead in suggesting specific problem areas which are technically

feasible and satisfy the managers needs. The hydrologist has the technical expertise and the familiarity with land use and water quality relationships to make this linkage. Involvement of other functional specialists with an interest in water quality, such as fishery biologists, is often appropriate at this stage to coordinate common data needs. Interdisciplinary involvement can avoid duplication of effort and address a multitude of management needs at one time (Potyondy, 1980).

Problem definitions should be as specific as possible. A problem definition, such as "What is the effect of land use on the quality of water draining the Routt National Forest?" is too broad to be of much use. In this case, the problem definition could be greatly improved if (1) the land management activity of interest was identified (timber harvesting, mining, recreation, etc.); (2) the water resource was specified (stream, lake and/or ground water); and (3) the type of water quality was stated (physical, chemical, biological and/or radiological). An improved problem definition might read "What is the effect of clearcutting on the sediment regime of Trout Creek?" The problem definition is now very clear and direct. Often times problem definitions will not be this specific. More often they are as follows:

1. A reliable method to predict the effect of clearcutting on the sediment yield for the various stream types found in the Forest is needed.
2. A simple, reliable approach to classify lakes by water quality within the Forest is needed.

These problem statements, broad as they may appear, are consistent with the water quality information needed in the land management planning process and still provide the hydrologist with sufficient guidance to formulate study objectives.

Once the problem areas have been defined, the next step is to establish study objectives. This process should also be a mixed effort between the hydrologist and the line officer. The hydrologist's role, because of his technical knowledge of the watershed system and land use/water quality interactions, is to suggest specific monitoring objectives while the line officer's role is to act as a sounding board, continually asking why and making sure the objectives speak only to his needs and that the plan fits within the available resources (Boynton, 1972). When the objectives are agreed upon by the hydrologist and line officer, they should be documented in written form.

Objectives should be specific statements of measurable results to be achieved within a stated time period. In addition, they should be specific enough so that the hydrologist can convert them into statistical hypotheses which can be tested with the data obtained from the water quality monitoring program (more about this in Section 5.0). Some illustrations of problem definitions and related study objectives are given in Example 1.

Defining the problem and setting the study objectives phase of the study may seem like a lot of work which will require a substantial amount of your time. It is and it does. However, it is time very well spent. The point is, if you have spent time defining your objectives and making sure that they are compatible with management's needs, there is a very good chance that your study will be successful and provide meaningful information to the land manager.

Example 1
Establishing study objectives from problem definitions.

Case A.

Problem Definition:

Does the water at Public Beach A pose a health hazard to primary contact recreationists?

Study Objective:

To determine if the water at Public Beach A meets the State standards for swimming during the summer of 1980.

In this case, the strategy is to monitor the water quality at Swimming Beach A over the summer and compare it with the State standards for primary contact recreation.

Case B.

Problem Definition:

Is acid precipitation adversely affecting the productivity of Agnes Lake?

Study Objectives:

1. To determine the pH of the precipitation on a seasonal basis at Agnes Lake over the next five years.
2. To determine the seasonal trend of pH, alkalinity and conductivity in Agnes Lake over the next five years.
3. To determine the biological significance of any change in pH, alkalinity and conductivity in Agnes Lake that occurs over the next five years.

In this case, the strategy is to quantify the seasonal input of acid (hydrogen ions) to the lake from precipitation, to develop the trend of the lake's response over the next five years, and determine if this response is biologically significant.

4.0 Reviewing Past Work

After the objectives have been established, the next step is to determine what has already been done. Several common sources of data of interest to the wildland hydrologist are listed below:

1. Forest, District, and Regional Office resource reports.
2. U.S. Forest Service research, U.S. Geological Survey, U.S. Environmental Protection Agency, Bureau of Land Management, Water and Power Resources Administration, Corps of Engineers, National Oceanic and Atmospheric Administration, and Soil Conservation Service.
3. State Geological Survey, State Department of Health, State Department of Engineering, and State Water Pollution Control Agency.
4. State universities, especially the departments specializing in watershed management, hydrology, geology, chemistry, aquatic biology, limnology, and microbiology.
5. River basin commissions.
6. STORET.

In addition to the sources mentioned above, several of the Regions now have agreements with Forest Service research libraries or other libraries which provide computerized literature searches. The major indexes presently available or soon to be available are summarized in Table 1.

Most of the time, you can expect that little if any data will be available from your watershed of interest, or if they are, they often will be the wrong kinds of data. You can sometimes circumvent this problem by reviewing information available from tributary streams or adjacent drainages. However, you must be cautious when transferring data from one place to another.

Whenever data are available from your watershed of interest, they probably will have been collected for another purpose and will not solve your specific problem. Nevertheless, such data can provide you with

Table 1. Indexes for computerized search of water resources literature (modified from Busby, 1980).

INDEX	SUBJECT AREA
AGRICOLA	Covers worldwide journal and monographic literature in agriculture and related subject fields, including forestry, natural resources, chemistry and water resources. Prepared by the U.S. National Agriculture Library.
AQUALINE	Provides access to information on every aspect of water, waste water, and the aquatic environment. Worldwide sources cited are 400 periodicals, research reports, legislation, conference proceedings and preprints, books, monographs, pamphlets, dissertations, translations, standards and specifications, and miscellaneous publications from water-related institutions worldwide. Prepared by the Water Research Centre.
BIOSIS PREVIEWS	Includes contents of Biological Abstracts and Bio-Research Index, covering the entire life sciences. Citations are taken from approximately 8,000 serial publications, as well as books. Prepared by Biological Sciences Information Service.
CDI	Comprehensive Dissertation Index, containing all dissertations accepted for academic doctoral degrees granted by United States education institutions and some non-U.S. universities. Prepared by University Microfilms International.
COMPENDIX	Covers civil, environmental and geological engineering; mining, metals, petroleum and fuel engineering; mechanical, automotive, nuclear and aerospace engineering; chemical, agricultural and food engineering; and industrial engineering, management, mathematics, physics and instruments. Prepared by Engineering Index, Inc.
GeoRef	Geological Reference file, covering geosciences literature from 3,000 journals, plus conferences and major symposia and monographs in such areas as environmental geology, geochemistry, and fluvial geomorphology. Prepared by the American Geological Institute.
NTIS	This is a broad and cross-disciplinary file containing citations and abstracts of government-sponsored research and development reports and other government analysis prepared by Federal agencies on their contractors and grantees. Prepared by National Technical Information Service of the U.S. Department of Commerce.

INDEX	SUBJECT AREA
POLLUTION	Covers non-U.S., as well as domestic reports, journals, contracts, patents and symposia in the areas of pollution control and research. Prepared by Pollution Abstracts, Data Courier, Inc.
WATERLIT	Covers the water resources and water-related literature of the world. WATERLIT topics include, but are not limited to, water supply, reservoirs of all types, water utilization, water standards, limnology, health aspects of water, water law and water ecology. It is produced by the South African Water Information Centre.
WRD	Water Resources Abstracts is a computerized version of Selected Water Resources Abstracts, a semimonthly journal published by the Office of Water Research and Technology. It covers literature of water related aspects of the life, physical and social sciences as well as related engineering and legal aspects of the characteristics, conservation, control, use, or management of water.

information about the interactions between land use, hydrology and water quality and be very useful in the design of your sampling program.

5.0 Thinking About Data Analysis

This is the stage of your study design when you should begin thinking about how the data will be analyzed. You should start by converting your objective statements into null (H_0) and alternative (H_a) hypotheses. For example, consider the objective presented in Case A, Example 1. The study objective is a very specific water quality concern which can be readily converted into a set of null and alternative hypotheses. The hypotheses to be tested could be stated as follows:

H_0 : The water at Public Beach A does not exceed the State water quality standards for swimming during any portion of the summer of 1980.

H_a : The water at Public Beach A exceeds the State water quality standards for swimming at some time during the summer of 1980.

At this point, we are ready to select a statistical model which will allow an efficient test of the null hypothesis against the alternative hypothesis. The statistical methods that you select, along with the knowledge you have gained about the system through reviewing past work, will influence where you sample, such as above or below a treatment or at the mouths of paired watersheds offering impact and controlled data comparisons; and when and how often you sample, such as once a season without replication or diurnally with replication. If you do not feel comfortable designing your statistical analysis, you should review in detail WSDG Technical Paper 00001 ("Statistical Methods Commonly Used in Water Quality Data Analysis", Ponce, 1980) and/or seek the aid of a statistician.

There are a few principles that you should keep in mind when you begin thinking about your data analyses. These have been summarized from Green (1979).

1. Carry out some preliminary sampling to provide a basis for evaluation of sampling design and statistical analysis options. Those who skip this step because they do not have enough time or money usually end up losing both time and money.
2. To test whether a condition (treatment) has an effect, collect samples both where the condition (treatment) is present and where it is absent but all else is the same. Remember, an effect can only be demonstrated by comparison with a control.
3. If possible, take replicate samples within each combination of time, space, and any other controlled variable. Differences among can only be demonstrated by comparison to differences within. For example, if you are comparing NO_3 yield from a clearcut area with a forested area, only if you take replicate samples can you separate sampling error from differences due to the treatment.
4. If the system to be sampled has a large-scale environmental pattern, break up the system into relatively homogeneous subsystems and allocate samples to each by some predetermined weighting criteria. For example, if you are measuring TDS in the northern Rockies, you could reduce the overall variance substantially if you broke your sampling periods into three strata; baseflow, snowmelt, and stormflow; and weigh each by discharge.

It is very important that you consider the statistical analysis at this stage of the study design. As Averett (1979) states "problems almost always arise when statistical methods become an afterthought of study design and are used as a salvage operation. This 'afterthought' application of statistical methodology leads to the deadliest data analysis trap of all--the mathematical manipulation of non-related, non-correlated data, into a probability function."

One final comment before we proceed; it is important that you keep the role of statistical methods in proper perspective. Their primary use is to reduce data and to help us make "yes" or "no" statements about the

relation of samples collected from different populations. While there is much merit in designing water quality sampling studies around a statistical framework, it must be emphasized that the statistical testing of data is not interpretation of data (Averett, 1979). It is the responsibility of the hydrologist to interpret the results of the statistical analysis and provide the line officer with information which can be used in the decision making process.

6.0 Where, What and When

At this stage of your study design, you are ready to select your sampling stations (where), choose the water quality constituents to be sampled at each station (what), and determine the sampling frequency of each constituent at each sampling station (when). This phase of the study design requires a sound understanding of the hydrologic system and how the water quality relates to the beneficial uses of the water resource. If the study objectives have been clearly stated and you have spent time thinking about the interaction between land use, hydrology, and water quality in your system, the determination of where, what, and when should be fairly straightforward.

Throughout this section you should keep two points in mind. First, where, what, and when you sample should be directly related to the needs and objectives of the study. Remember, the line officer holds you responsible for the water quality data collected and it is your job to see to it that unnecessary data are not obtained. Second, station location, parameter selection, and sampling frequency are all very important. You cannot short cut one without affecting the others (Averett, 1976).

6.1 Guidelines for Locating Sampling Stations

There are two factors which strongly influence the location of sampling stations: (1) the type of monitoring and (2) the type of water body. Guidelines for locating sampling stations are discussed for each of these factors separately.

6.1.1 Station Location as Influenced by the Type of Monitoring

As you recall, water quality monitoring on National Forest System lands can generally be classified as (1) cause-and-effect, (2) compliance, (3) baseline, and (4) inventory. Locating the sampling stations for cause-and-effect monitoring is generally the easiest to carry out. The strategy in this case is to isolate the treatment effects by (1) sampling above and below the treatment and/or (2) sampling before and after the treatment. Consider the example presented in Figure 1. There we have a treatment which covers only a portion of a small stream. Stations A and B have been placed immediately above and below the treatment, respectively, to isolate it. Station A represents the control. Station B, in theory, is assumed to be similar to Station A in all respects except that it includes the effect of the treatment. Whenever the "above and below" approach is used, you must be certain the above station is a satisfactory control.

The type of sampling design shown in Figure 1 readily lends itself to two types of statistical testing: (1) comparison of the means of Stations A and B and (2) comparison of the regression of Stations A and B. If the variance of the water quality parameter of interest is not strongly influenced by fluctuations in the stream flow, a simple comparison of the means can be made to test for treatment effect. The hypotheses to be tested are as follows:

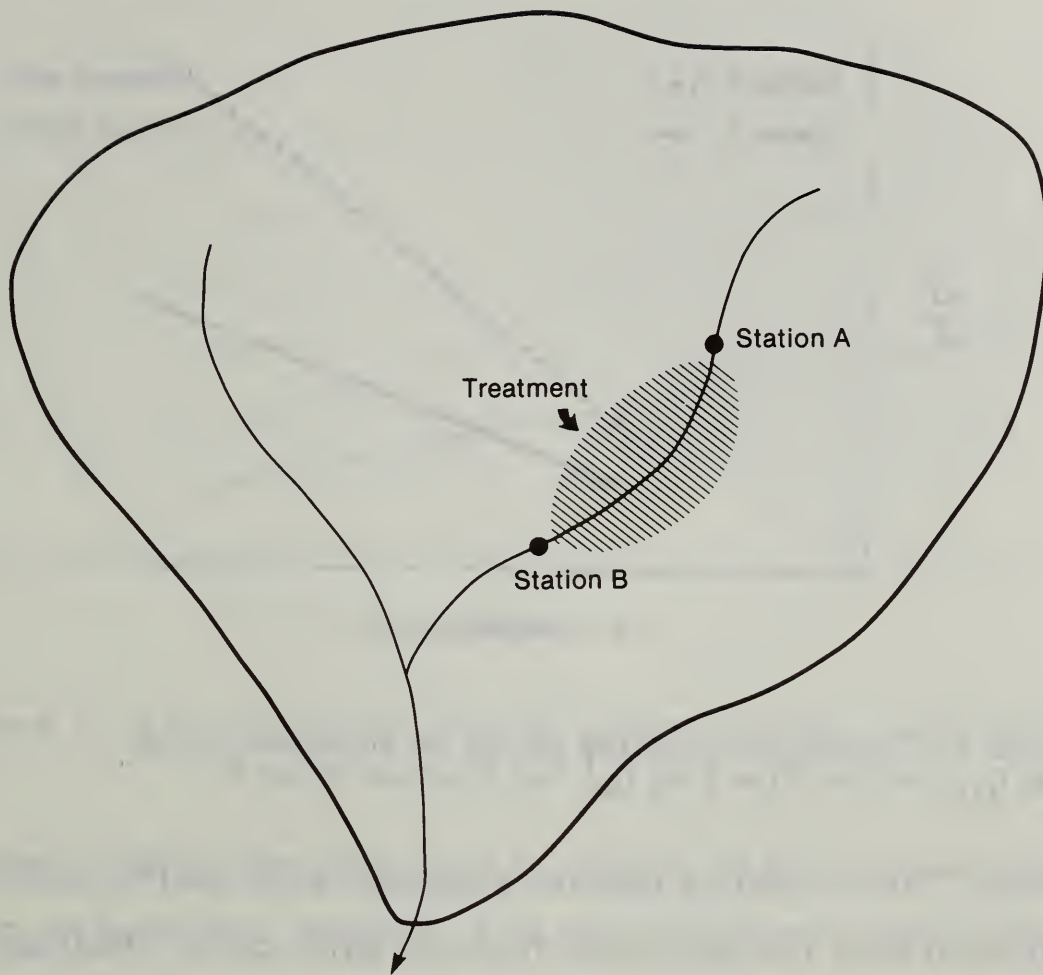


Figure 1. Example of station location for cause and effect monitoring study where the treatment can be readily isolated.

$$H_0: \mu_A = \mu_B$$

$$H_a: \mu_A \neq \mu_B$$

where μ_A and μ_B denote the mean at Stations A and B, respectively. The statistical method generally employed to make this comparison is the paired t-test. However, if the variance is strongly influenced by discharge, it is very likely that the treatment effects will be masked. If you develop a regression of the water quality constituent versus discharge (commonly referred to as a rating curve) you can remove or explain much of the variance due to flow and make a stronger test of the treatment effect.

A suspended solids rating curve is illustrated in Figure 2. Note, a log X transformation has been applied to the data to obtain a linear

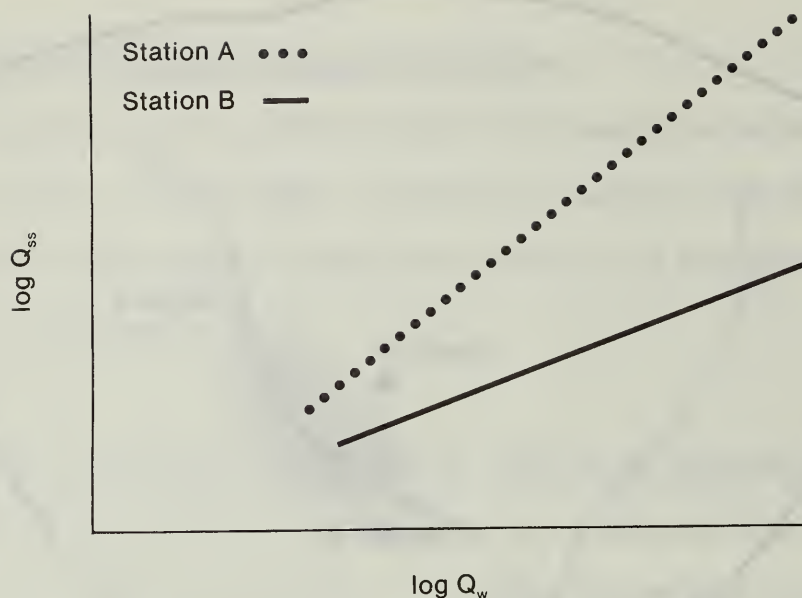


Figure 2. Hypothetical rating curves of suspended solids ($\log Q_{SS}$) versus flow ($\log Q_w$) for Stations A and B.

regression. This is usually required since most water quality constituents are best related to flow by a power function, which can be linearized with a $\log X$ transformation. To test for the treatment effect, we would compare the slopes of the regression lines and their intercepts. The hypotheses to be tested are as follows:

$$\begin{array}{ll}
 H_0: \text{ slope A} = \text{ slope B} & H_0: \text{ intercept A} = \text{ intercept B} \\
 H_a: \text{ slope A} \neq \text{ slope B} & H_a: \text{ intercept A} \neq \text{ intercept B}
 \end{array}$$

Covariance analysis would be the statistical method employed to make these comparisons.

If the above and below stations were established prior to the treatment and a paired sample data base developed both before and after the treatment, the opportunity exists to develop a paired-station plot. Such a plot for suspended solids concentrations at Stations A and B, both before and after treatment, is illustrated in Figure 3. In general, these regressions have strong correlation coefficients because many of the

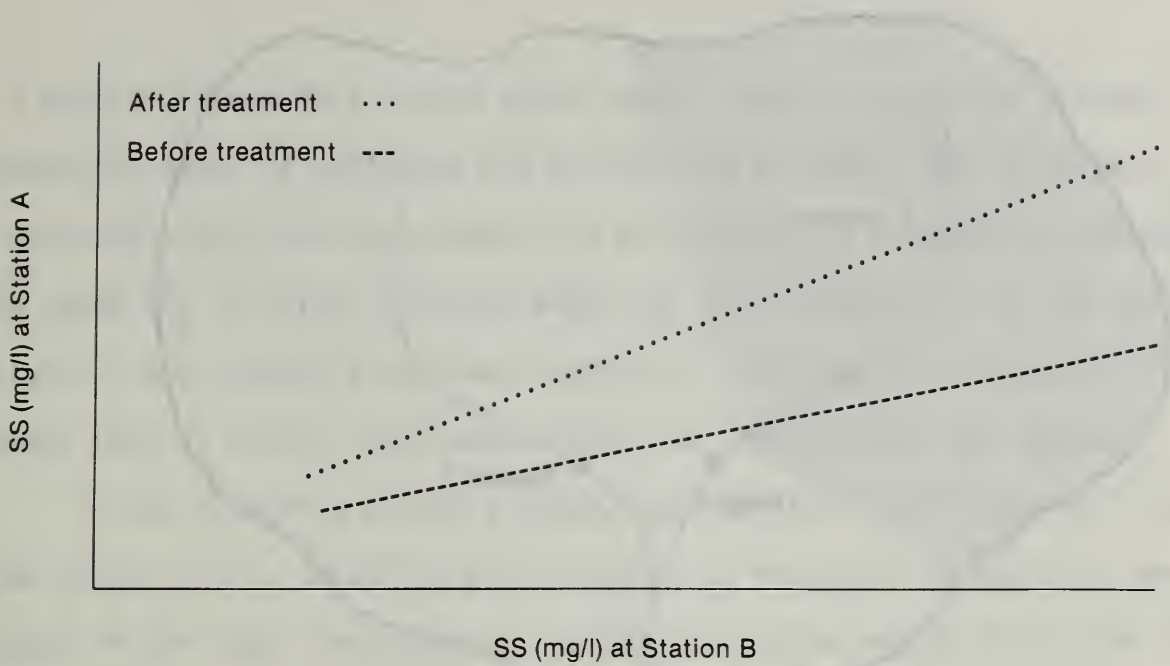


Figure 3. A paired-station plot for suspended solids concentration.

background variables that contribute to variance in the data, such as climatic and hydrologic variables, have been normalized at both stations. Consequently, this method enables us to make a better assessment of the treatment effects than any of the methods previously described. The actual statistical comparison is the same as that explained for the regression curves.

In some cases, we cannot isolate a treatment by placing stations above and below. Such an instance is illustrated in Figure 4. Here the treatment, which could be a vegetative conversion on a grazing allotment, covers an entire tributary system. There are two approaches to locating sampling stations in this case. The first is to simply position a station immediately below the treatment (such as Station A, Figure 4), and another one (such as Station B, Figure 4) on a watershed which is similar to the treated watershed in all respects (that is climate, geology, soils, vegetation, land use, etc.) except it is not influenced by the treatment.

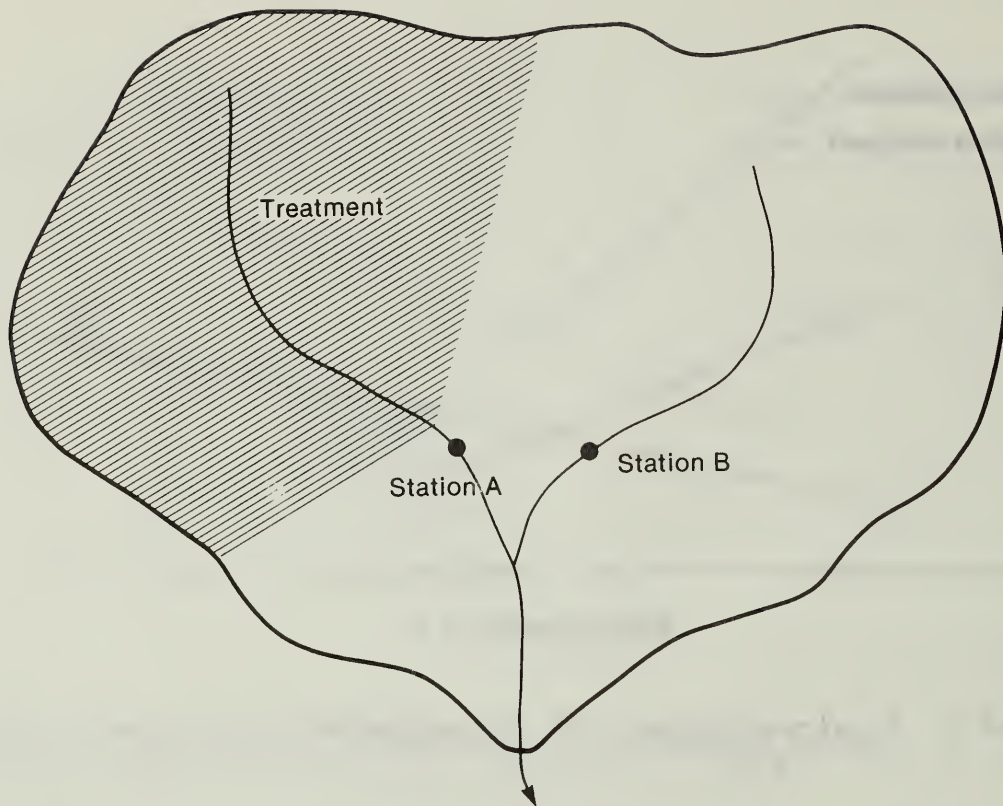


Figure 4. Sample station location for the paired watershed approach.

With either approach, a valid assessment of the treatment effect would require sampling both before and after the treatment. If only one station is established, the statistical comparison will be made using the before and after means or regression lines. If two stations are established, the comparisons can be made using the before and after means or paired-station regressions. The paired station approach is recommended over the single station approach because it allows you to account for year-to-year variation in climate and hydrology.

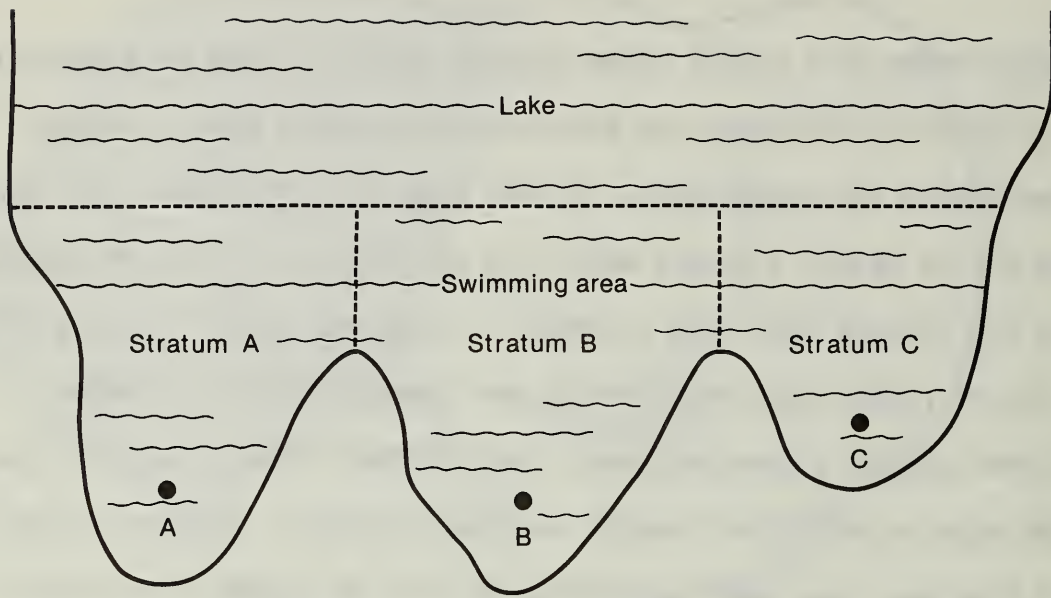
Compliance monitoring is generally performed to protect public health and to assure that waters draining from National Forest System lands meet State water quality standards. In general, station location involves the positioning of a single sampling station or a pair of stations. Consider the situation where the drinking water in a campground needs to be tested.

In general, there is a single water source, such as a well or stream, from which the water is collected and distributed through lines to various locations within the campground. In this type of a situation, care should be taken not to select a single water tap and designate it as the sampling station, but instead each time a sample is required, select any one of the water taps at random (not haphazardly) and then collect the sample.

In the case of a swimming beach, such as that illustrated in Figure 5, you might have to establish several sampling stations. Because of the shape of the lake, one sampling station may not be enough to provide a representative sample. Consequently, the area of concern may have to be divided into homogeneous strata, each of which is sampled separately. This type of sampling design enables you to make a direct comparison with the standard or compare the sample mean with the standard.

Sometimes compliance monitoring requires the surveillance of point sources. Consider, for example, a sewage lagoon which treats the waste from a campground and whose effluent drains into a perennial stream (Figure 6). There are two approaches to locating sampling stations in this situation. If the State standards require the effluent to be of a fixed quality or better, the station should be positioned to sample the effluent directly, such as in Case I, Figure 6. If the State standards require that the effluent not increase the stream's composite load by a certain difference, such as temperature by 2°C, stations would have to be positioned above and below the outfall (Case II, Figure 6).

Baseline monitoring is designed to provide information on water quality trends. In general, stations are positioned strategically throughout a Forest or District (such as at the mouths of major streams or confluences of major tributaries) to obtain trend information for a **wide**



● = Sampling station

Figure 5. A plane view of a sampling station location at a swimming beach along a lake.

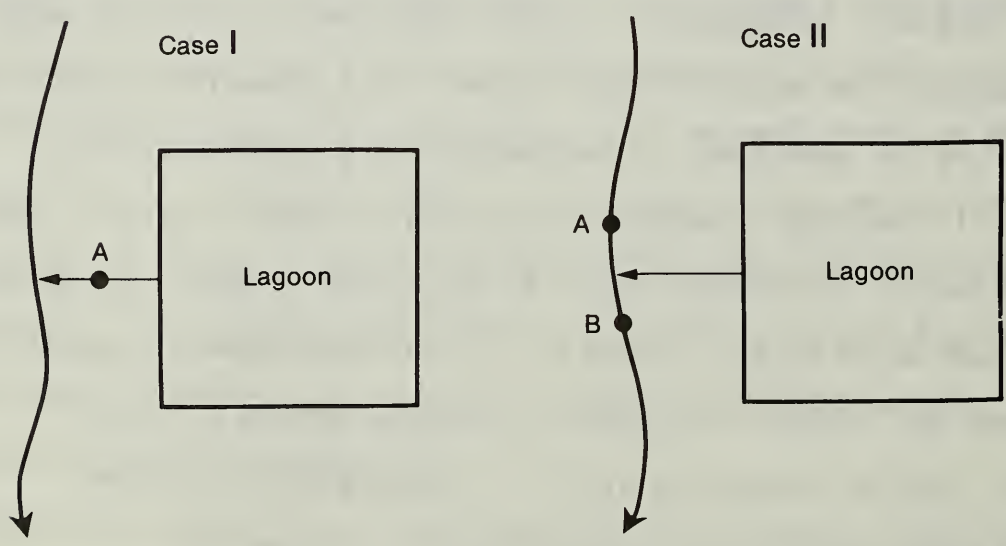


Figure 6. Sampling station location for two cases, I and II, in which a point source effluent is draining into a stream.

range of conditions, such as climate, topography, geology, soils, vegetation and land use.

Inventory monitoring is designed to characterize the water quality of a Forest on a broad scale. Sampling stations are usually located on major streams at or near the Forest boundary or at other strategic locations within the Forest. These stations are often positioned so that they integrate several different land uses. As a result, the quality of water at these stations often times represents the cumulative impacts resulting from multi-resource management activities on the Forest.

6.1.2 Station Location as Influenced by the Water Type

In general, there are three types of water bodies of concern to the forest hydrologist: (1) streams, (2) lakes and reservoirs, and (3) groundwater. The establishment of sampling stations along or in any of these water bodies is directly related to the characteristics that control the movement of water and distribution of water quality parameters in that water body.

There are several factors that you should consider when you are locating sampling stations in streams: (1) tributaries, (2) mixing characteristics, (3) suitability for discharge measurements, (4) accessibility, and (5) suitability for biological monitoring. Tributaries should always be considered in locating sampling stations because of the effect they can have on the receiving water. The question, however, is whether or not a specific tributary should be included in the monitoring program. In general, tributaries involved in cause-and-effect and compliance monitoring studies should be monitored. If they are not included, it is very difficult to isolate constituents of concern and

minimize variability. An example of station location for a cause-and-effect study in which a tributary is involved is presented in Figure 7. By placing sampling stations above and below the clearcuts (treatment of concern) on both the mainstem and tributary allows us to assess the effect of logging on stream quality and to exclude the effects of the pasture and the mountain home development.

The problem lies with baseline, inventory, and mixed monitoring studies where large areas are involved. It is not practical to include every tributary in our monitoring network, yet, how do we decide which ones to include? Ideally, the best way to make this assessment is to carry out a preliminary reconnaissance and sample all the tributaries at least once.

However, most of the time this is not possible because of constraints in manpower, time, and money. The hydrologist, therefore, must consider each tributary separately and develop a list of potential tributaries to sample. Averett (1976) suggests you consider the following guidelines when performing this task.

1. Be thoroughly familiar with the physical characteristics of the system you are studying. Consider such things as drainage area, geology, soils, vegetative type and land use. A large variation of any of these factors in a tributary from the conditions of the mainstem calls for the tributary to be included in the sampling network.
2. Consider the dissolved solids concentration or the electrical conductivity of the tributary. If during low flow periods electrical conductivity or dissolved solids are higher or lower when compared to the mainstem flow, then you have strong reason to consider monitoring the tributary.
3. Look for sediment plumes and sand and gravel bars near the mouth of tributaries. The presence of these features is an indicator of erosion upstream and is reason to consider monitoring the tributary.
4. If a tributary provides a proportionately large volume of flow to the mainstem, you should consider establishing a monitoring station at its mouth. An upstream tributary may be small compared to the downstream mainstem. However, in its upstream

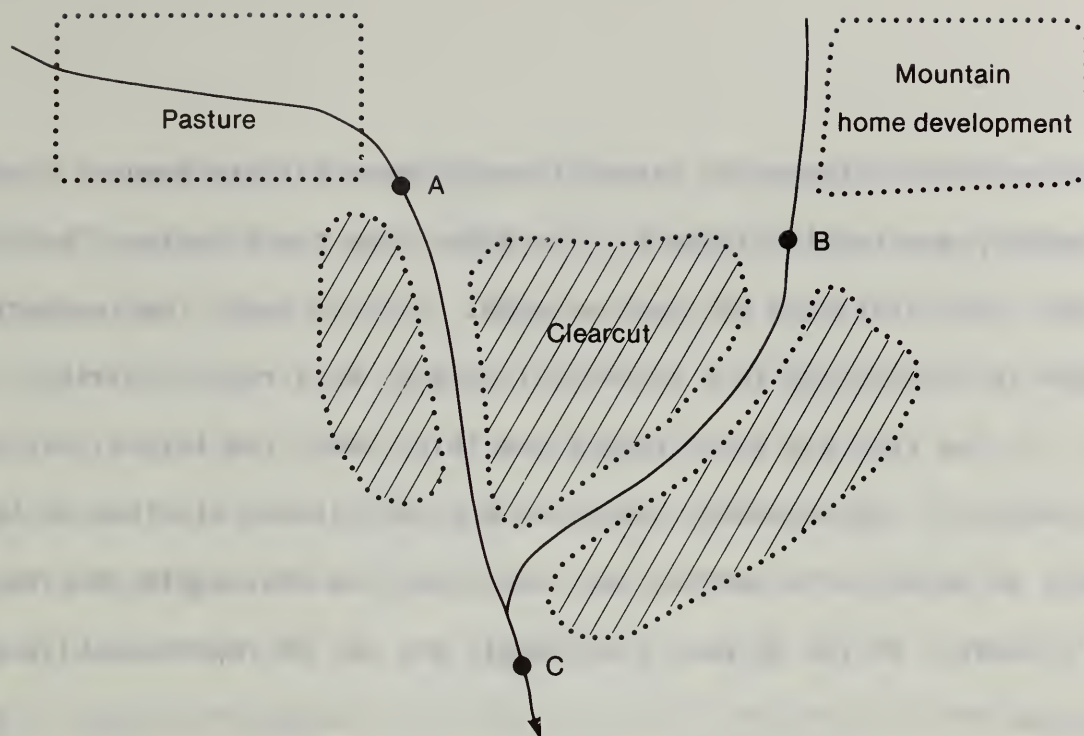


Figure 7. Example of sampling station location for a cause-and-effect monitoring study in which a tributary is involved. Stations A and C lie on the mainstem while Station B is on the tributary.

location, the tributary may contribute substantially to the mainstem both in quantity and quality. In other words, you should not select tributaries for sampling based upon volume of flow alone, but rather based on their volume relative to the mainstem at the confluence.

5. If a tributary is of sufficient volume and different water quality to influence the mainstem, it may be useful to establish some stations on the tributary other than at its mouth.

How well-mixed a water quality constituent is in a stream is dependent upon the physical and chemical nature of the constituent as well as the physical characteristics of the stream. The physical characteristics of the stream which affect mixing include temperature, depth, velocity, turbulence, slope, changes in direction, and roughness of the bottom.

In general, if the sampling point of interest is some distance downstream from a tributary or other point source, such as a sewage outfall or irrigation return flow, the water quality is usually fairly well mixed across the cross section. Most sampling problems involve mixing below tributaries and other point sources. Vertical mixing (from surface to bottom) is usually quite rapid due to the turbulence of mountain streams. Lateral mixing (from one side to the other), on the other hand, may not be

complete until the stream has passed through several sharp bends. Consider the example presented in Figure 8. The water from the tributary "hugs" the bank until the first bend has been entered. In this bend, the tendency of the water is to continue in a straight line and, as a result, mixing begins. By the time the water enters the third bend, the lateral mixing is nearly complete. Consequently, when you are positioning stations below a tributary or other point source, make sure that you thoroughly consider the mixing effects. If you do not, your sample may not be representative of the system.

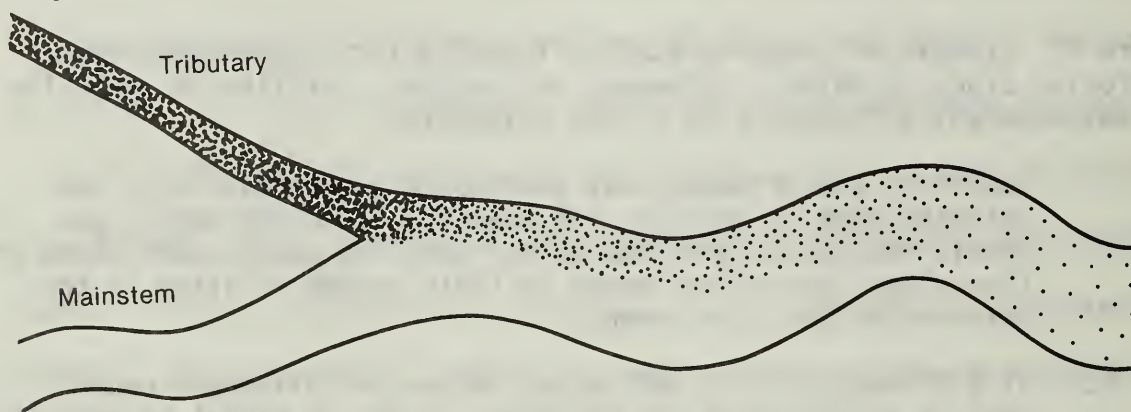


Figure 8. An illustration of lateral mixing.

When establishing sampling stations in the field, it is important that you consider the suitability of each station for discharge measurements. Many water quality studies on streams have been of little use because discharge measurements were not made and most water quality constituents are flow dependent. Without discharge measurements, you cannot perform a mass balance or determine mass yield, both of which are important water quality data analysis techniques.

Another concern when locating stations is accessibility. If a sampling station is located a substantial distance from a road, make sure time and manpower costs of sampling are considered. In many cases, bridge

locations are selected for sampling stations. They provide ready access to the entire cross section, even during high flows. Bridges are, however, not without their disadvantages. Their purpose is to move traffic and, as such, may not be positioned properly for water quality monitoring purposes. Bridges may influence the water flow and quality at a site.

If biological sampling is to be involved in the study, you should consider the physical substrate (boulders, rubble, sand, and mud), velocity of flow, exposure to the sun and the width and depth of the stream. In general, aquatic biological sampling in streams involves systematic resampling of (1) a transverse or longitudinal transect or (2) a grid or quadrant system. Transect sampling consists of collecting samples either along a section of stream length or in a line across the stream (Figure 9). Samples may be collected at uniform intervals along the transect line or at random. If the transect line is along the stream length and includes pools and riffles, each habitat is usually considered separately and sampled equally. A sampling grid or quadrant consists of an imaginary or physical rectangular arrangement of lines, covering all or part of a given habitat (Figure 9). A grid or quadrant sampling scheme should, as with the transect scheme, give equal consideration to the various habitat types.

When locating sampling stations in a lake or reservoir, you need to consider the (1) thermal stratification, (2) circulation of the water, and (3) morphology of the basin. Each of these factors strongly influences the spatial distribution of the water quality parameters throughout the lake or reservoir.

In temperate regions, lakes and reservoirs deep enough to stratify will typically develop a temperature profile similar to that in Figure 10. This profile consists of three zones, the epilimnion, the metalimnion, and



Figure 9. Examples of transect and grid sampling schemes. A illustrates longitudinal and transverse transects while B illustrates a grid of nine sampling sites (after Averett, 1977).

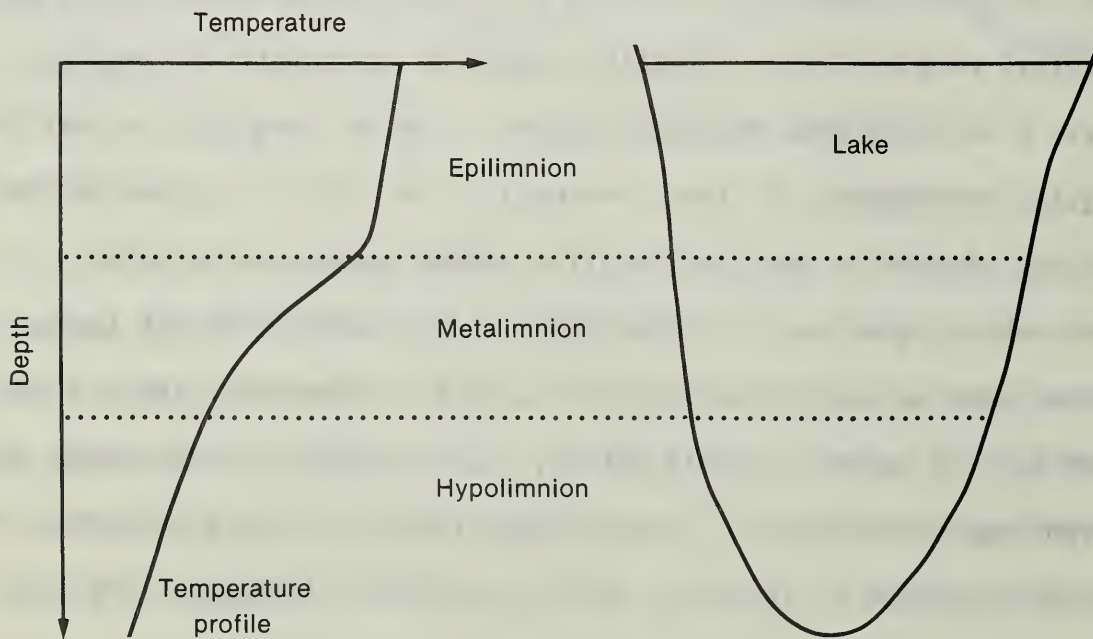


Figure 10. The three zones of a temperature profile in a stratified lake.

the hypolimnion, each defined by the rate of change in temperature with depth. In general, the epilimnion is a fairly wide zone consisting of warm water which has a moderate temperature gradient. The metalimnion is commonly a narrow zone characterized by a very rapid temperature change in depth. The hypolimnion spans from the base of the metalimnion to the bottom of the lake or reservoir and has a slight to moderate temperature gradient. Density differences of the water, which are related to the temperature, effectively isolate the hypolimnion from the zones above except for particle exchange due to gravity or movement of fish. If bacterial respiration is excessive in the hypolimnion, which is usually the case when the water body is in a eutrophic or enriched state, the dissolved oxygen can be depleted and anaerobic conditions may develop. If this condition occurs the dissolution of phosphorus, iron, manganese and other trace metals from the sediments can be expected.

The epilimnion and metalimnion are warmer than the hypolimnion and are the zones of phytoplankton production. As a result, the water quality in these zones may be substantially different than that of the hypolimnion.

The point to remember here is that the thermal zones in a lake or reservoir can have water quality quite different from one another. When a surface site is selected you must consider the thermal zones below it and make certain that the samples you obtain are representative of the system you think you are sampling. In many studies, you will find it necessary to establish several sampling stations along a depth profile (Figure 11). Temperature, dissolved oxygen, specific conductance, and pH are very useful measurements to make when deciding where to locate sampling stations along a depth profile.

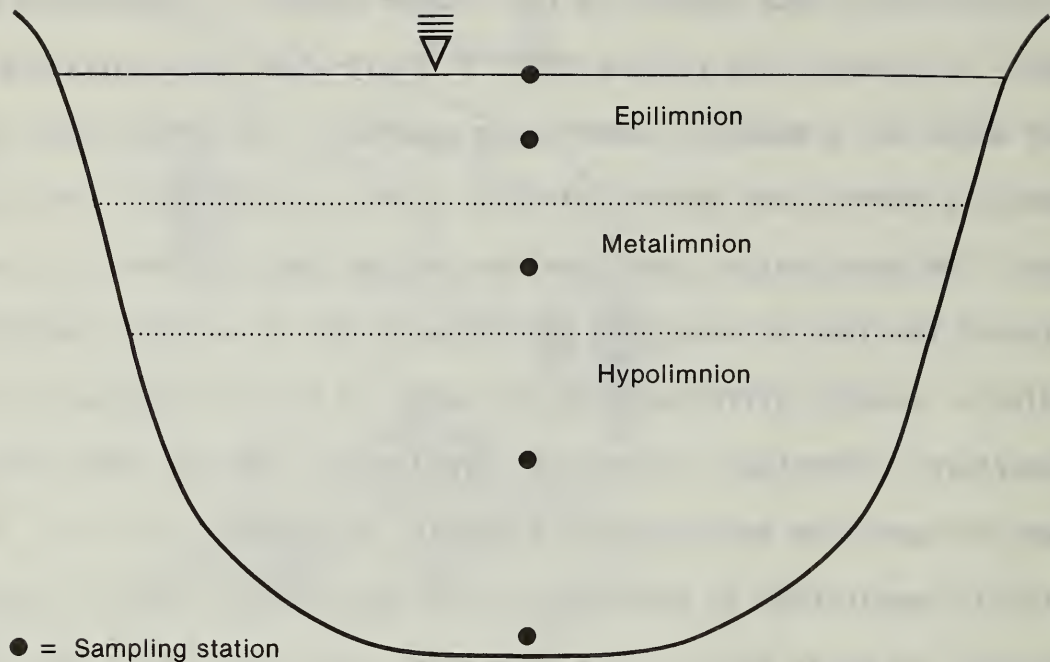


Figure 11. Illustration of sample locations along the depth profile in a stratified lake.

Circulation of the water is another factor that you need to consider when locating stations in lakes and reservoirs. During the spring and fall, the water mass overturns, due to a density change derived from the seasonal cooling or warming, and the water obtains a uniform temperature throughout the entire depth profile (Figure 12). At this time, the water quality is generally uniform throughout the depth of the lake and a single sample collected at 0.5 to 1.0 meters depth may be representative of the water column.

Wind will generally cause the water in the epilimnion to circulate and facilitates the mixing of water quality constituents throughout this zone (Figure 13). In the case of a circular lake where wind mixing has occurred, a sample collected at the lake's outlet would probably be as representative of the water quality of the epilimnion as a sample collected at the center of this zone.

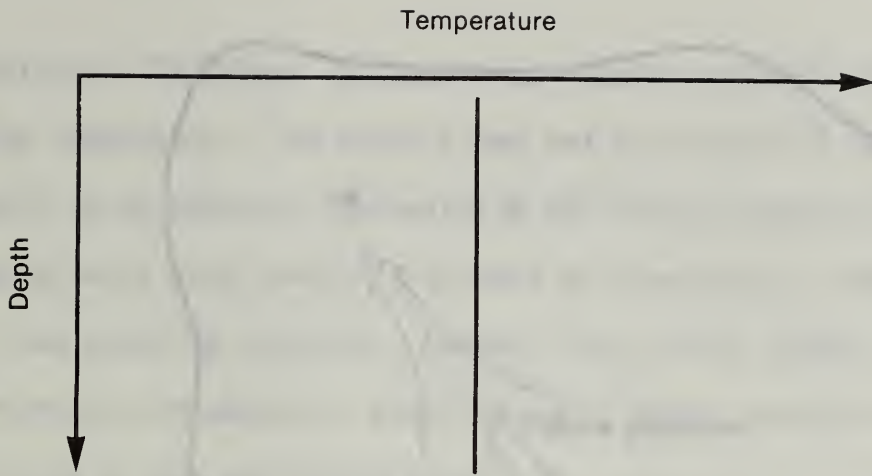


Figure 12. Temperature profile in a lake or reservoir during the period of overturn, either in the spring or fall.

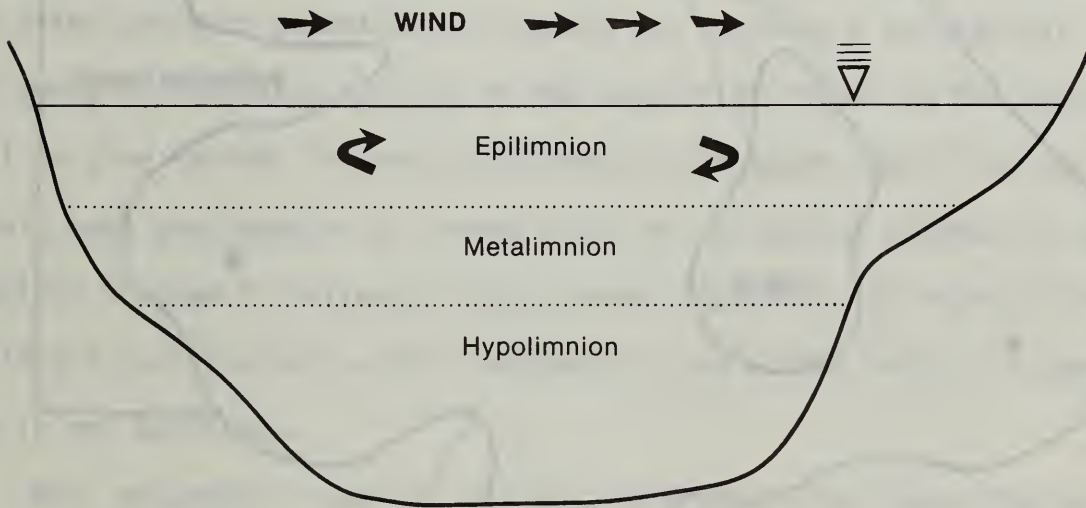


Figure 13. An illustration of the effect of wind on the mixing of water in the epilimnion.

If the morphology of a lake or reservoir is irregular, the mixing patterns of the epilimnion by the wind may vary substantially. As a result, several sampling stations may be required to characterize the water quality of the lake. For example, consider the lake illustrated in Figure 14. Here we have several land uses located around a lake which is irregularly shaped. The area around the recreational home development is shaped like an hour glass and should probably have each "bulb" sampled

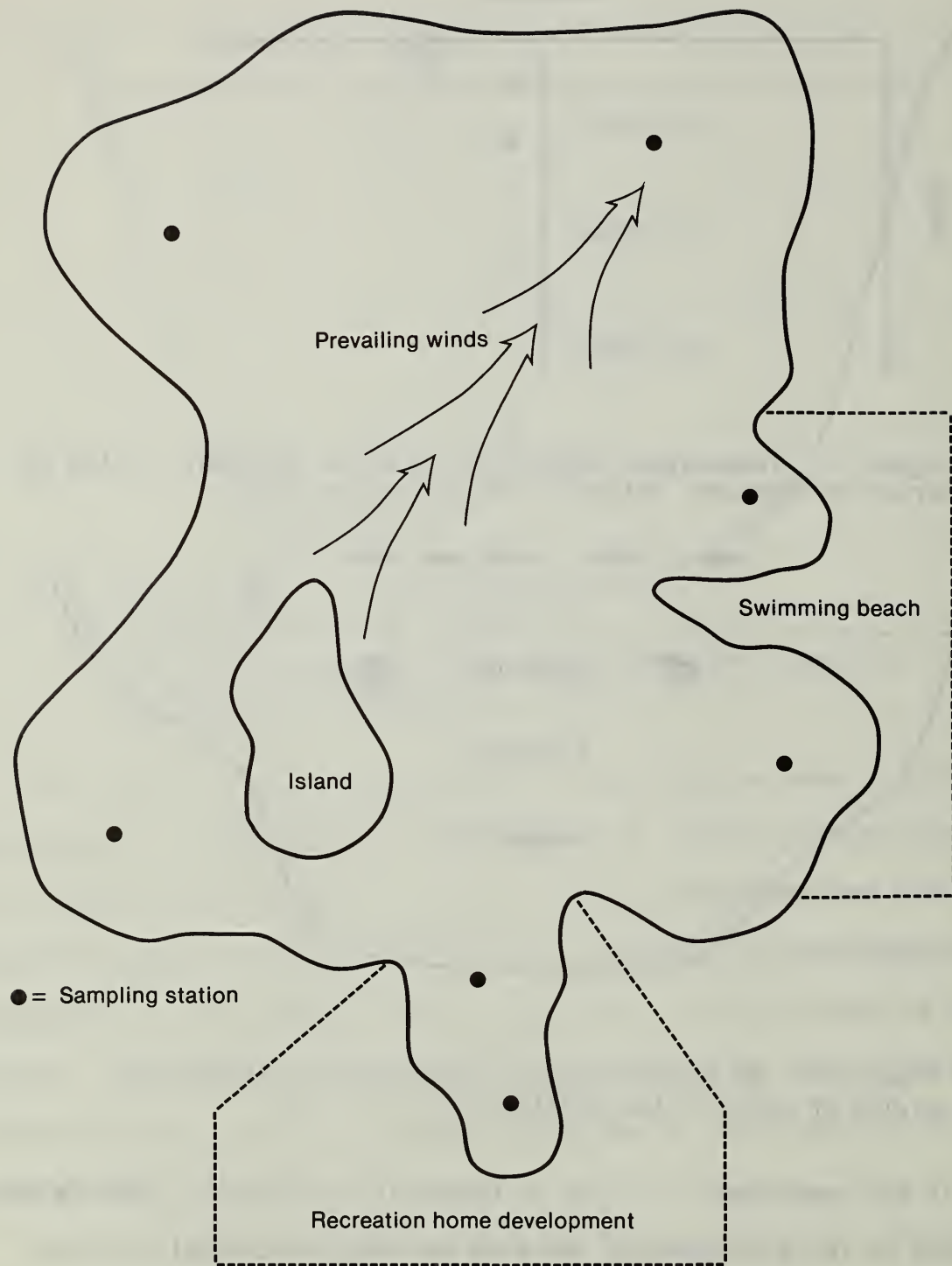


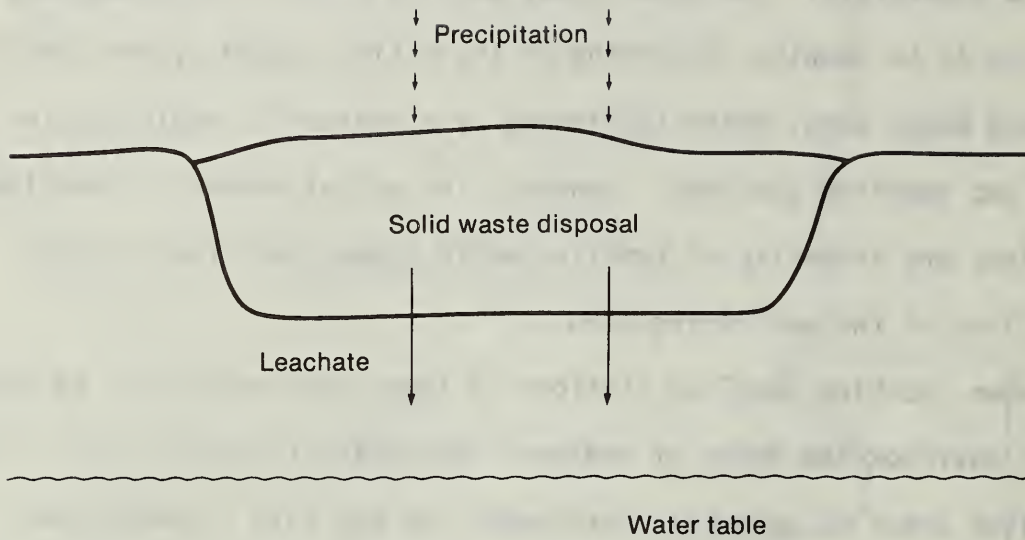
Figure 14. A hypothetical example of where to locate sampling stations to monitor surface water quality on a multiple use lake.

separately. The island isolates a cove which would require that it be sampled separately. The other coves and the center of the lake may or may not have to be sampled, depending on the mixing caused by the wind. The swimming beach area, which is divided by a peninsula, would require at least two sampling stations. However, the actual number of sampling locations and intensity of sampling would depend upon the original objectives of the monitoring plan.

When locating sampling stations in lakes and reservoirs, be careful not to overlook the areas of sediment deposition (Averett, 1976). These are often areas of potential enrichment and may have a substantial influence on the water quality of the lake or reservoir in the future as well as give insight to past conditions of the water body. You may need to obtain some grab samples or dredge hauls of the bottom sediment in your sampling program to delineate these areas. You also may wish to further delineate your stations with a bathymetric map of the lake or reservoir if one is not available.

Most groundwater quality problems confronting the forest hydrologist involve the contamination of unconfined or water table aquifers from point sources, such as solid waste disposals or leach fields below sewage treatment facilities. When locating your sampling stations for this type of problem, you need to consider the soils and geology of the area, flow direction of the ground water and accessibility. Consider the example illustrated in Figure 15 where we have a solid waste disposal site. Precipitation leaches through the disposal, picks up metals and other contaminants and transports them to the water table. The soil and geology of the area influence the rate at which leachate moves toward the water table. Depending on the nature of the contaminant, the soil and geology

CROSS-SECTION VIEW



PLANE VIEW

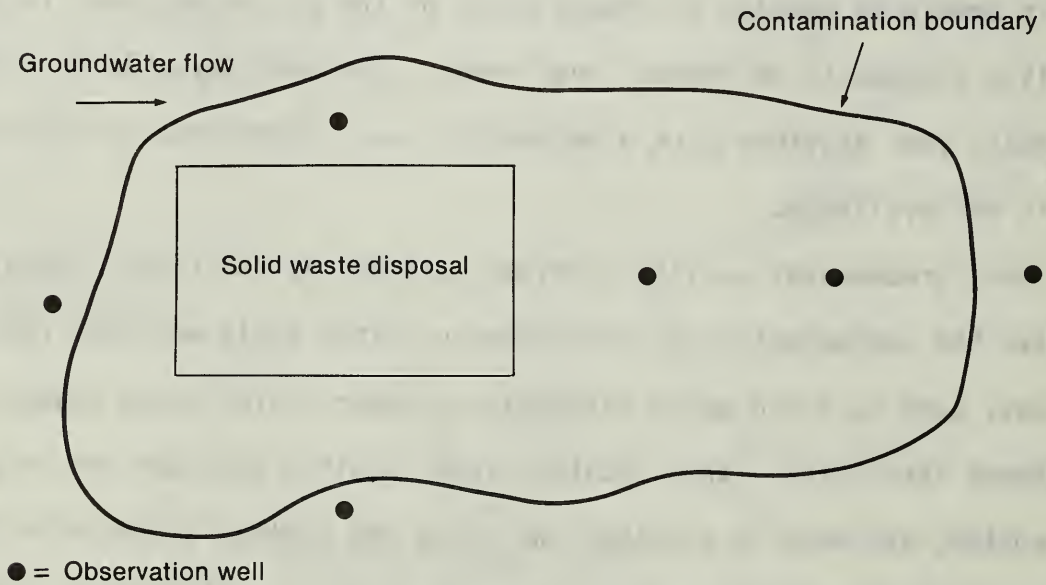


Figure 15. Location of sampling stations around a solid waste disposal site.

may act as a filter and reduce the concentration of the contaminant reaching the water table. If a clay lens is present, a perched water table may develop. The movement of the ground water strongly influences where the observation wells are placed. In many cases, wells are simply located above and below the source to quantify the effect of the treatment. In other cases, the concern might lie with the rate and extent of contamination which would require a more extensive monitoring program (Figure 15). Sometimes, we are not even sure which way the ground water flows and must position our observation wells in a radial pattern around the source (Figure 16).

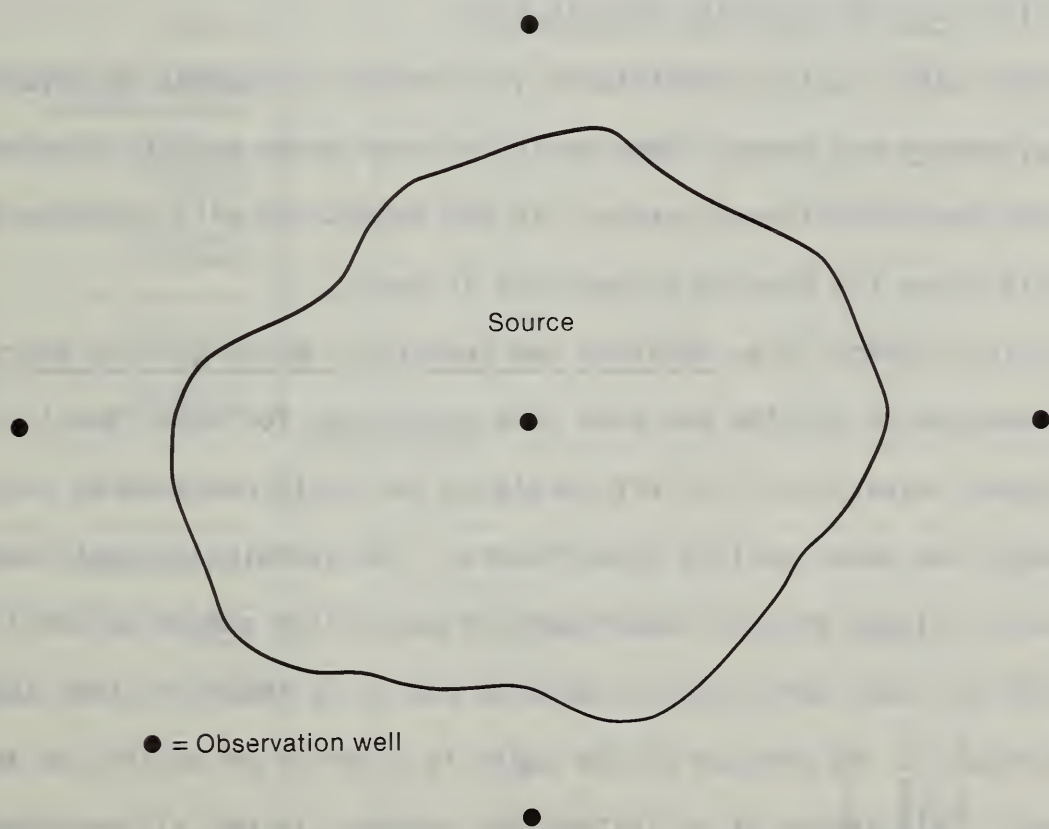


Figure 16. Radial design of observation wells around a point source.

If the groundwater problem involves a confined aquifer, it is important that you obtain knowledge of the aquifer in question. At a minimum this should include the areal extent of the aquifer, its width and its transmissibility. Walton (1970) and Freeze and Cherry (1979) present several excellent illustrative examples of groundwater monitoring.

In general, access is limited to existing wells and as a result, we can only obtain sketchy information about the system. The cost of drilling new wells is usually prohibitive. However, if the opportunity arises to establish a well for monitoring purposes, you should consult a geologist about placement.

6.2 Selecting Water Quality Constituents

Every water quality constituent you monitor represents an investment in time, energy and money. When designing your water quality program be sure that each constituent carries its own weight and will contribute data that help solve the problem or question at hand.

Table 2, which is an Activity and Concerns - Water Quality Matrix, has been developed to provide you with some guidelines for water quality constituent selection. The left margin of the table consists of pertinent hydrologic and water quality constituents. The hydrologic constituents have been included because measurement of water flow and/or volume is essential for most water quality studies and it is important that they are not overlooked. At the top of the table is a series of activities and concerns. This series of activities and concerns is not all encompassing, but does include the major ones of interest to the forest hydrologist. Each activity and concern, in turn, has been subdivided by water type: stream (S), lake or reservoir (L), and ground water (G). For each

Table 2. Activities and Concerns - Water Quality Matrix

ACTIVITIES AND CONCERNS

HYDRO-LOGIC CONSTITUENTS	ROAD CONSTRUCTION		ROAD MAINTENANCE		PRESCRIBED BURNS AND WILDFIRE		FERTILIZATION		INSECTICIDE APPLICATION		HERBICIDE APPLICATION		DEVELOPED CAMPGROUNDS AND PICNIC AREAS ^{b/}		SKI AREAS		SECOND HOME DEVELOPMENTS		SEWAGE DISPOSAL		REFUSE DISPOSAL		COAL AND METAL MINING		URANIUM MINING		GRAZING		IMPROVEMENT CONSTRUCTION		SWIMMING AREAS		ACID PRECIPITATION		RECONNAISSANCE SURVEYS		DRINKING WATER SUPPLIES			
	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC	S/LC		
STREAMFLOW	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		
LAKE WATER LEVEL	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
GROUND WATER LEVEL	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	
SUSPENDED SOLIDS (SS)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
BEDLOAD (BL)	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
SEDIMENT CORE	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	
TURBIDITY (TURB)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
TEMPERATURE (TEMP)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
HYDROGEN ION (PH)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
ELECTRICAL CONDUCTIVITY (EC)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
TOTAL DISSOLVED SOLIDS	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	
CALCIUM (Ca)																																								
MAGNESIUM (Mg)																																								
SODIUM (Na)																																								
POTASSIUM (K)																																								
BICARBONATE (HCO ₃)																																								
SULFATE (SO ₄)																																								
CARBONATE (CO ₃)																																								
CHLORIDE (Cl)																																								
BORON (B)																																								
IRON (Fe)																																								
SELECTED METALS																																								
ALKALINITY																																								
AMMONIA (NH ₃ + NH ₄)	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
NITRATE (NO ₃)	3	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
TOTAL NITROGEN (TN)	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
TOTAL DISSOLVED NITROGEN (TDN)	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
ORTHOPHOSPHATE (PO ₄)	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
TOTAL PHOSPHORUS (TP)	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
TOTAL DISSOLVED PHOSPHORUS (TDP)	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
TOTAL ORGANIC CARBON (TOC)	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	
DISSOLVED OXYGEN (DO)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
BIOCHEMICAL OXYGEN DEMAND (BOD)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
HERBICIDES	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
INSECTICIDES																																								
PETROLEUM HYDROCARBONS	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	
RADIONUCLIDES																																								
TOTAL COLIFORM (TC)																																								
FECAL COLIFORM (FC)																																								
FECAL STREPTOCOCCI (FS)																																								
MACROINVERTEBRATES	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	
ALGAE	2																																							

Notes: a/"S" denotes streams, "L" denotes lakes and reservoirs, and "C" denotes groundwater.
 b/ Does not include sewage treatment.
 c/ Primary sampling code.
 d/ Tertiary sampling code.
 e/ Secondary sampling code.

combination of activity or concern, water quality type, and constituent, there is one of four priority codes: 1, 2, 3 or blank. A primary code, 1, suggests that it is very important that the constituent be monitored. Sampling these constituents will provide information which is necessary to meet study objectives. A secondary code, 2, suggests that it is important that a constituent be monitored, however, if funds are restricted, these constituents should be considered a lower priority than those coded by a 1. These constituents usually supply supporting information which address the study objectives. A tertiary code, 3, means that this constituent probably will contribute little direct information to the study objectives, but may be useful for other purposes. A blank suggests there is no need to monitor the constituent.

Please keep in mind that these priority codes are presented only as guidelines. The specific needs and objectives of your study objectives of your study may require more emphasis be placed on certain constituents and less on others.

For individuals interested in a review of the various water quality constituents, their significance to beneficial uses and land use-water quality interactions, the following literature is suggested: Brown (1972), U.S. EPA (1977, 1976a, 1976b, 1973 and 1971), U.S. Forest Service (in press), Greeson, et al (1977), Guy (1970), Hem (1970), Krygier and Hall (1971), McKee and Wolf (1963), McNeely, Neimans and Dwyer (1979), and Thatcher, Janzer and Edwards (1977).

6.3 Guidelines for Determining Sampling Frequency

The frequency of sample collection should be designed to provide the data necessary to (1) calculate an estimate of a specific population

parameter, such as the mean, and/or (2) develop a regression relationship. In either case, we want our parameter and regression estimators to fall within some pre-established bound of reliability. As a result, sampling frequency should be directly related to the variance of the water quality constituent of concern. In other words, the more variable a constituent is in time and space, the more frequently it must be sampled to achieve a given level of reliability.

In this subsection, guidelines for determining sampling frequency for several different sampling methods are presented. It should be noted that emphasis has been placed on application of the methods opposed to the intricacies of the underlying statistical theory. For a more detailed discussion of each method, including the underlying theory, two references are suggested: Mendenhall, Ott, and Schaeffer (1971) and Cochran (1963). Much of what follows in this subsection has been taken from Freese (1962), with minor modifications.

6.3.1 Systematic Sampling

Systematic sampling is easily carried out and under some circumstances is a useful method. It consists of randomly selecting the first time of sampling and then selecting the remaining samples at some pre-determined interval, such as weekly, biweekly or monthly. While this simple method can be easily used in most water quality studies, it has serious limitations in that the data may be biased. If the data are biased, the statistical analysis may lead to erroneous inferences about the water body being examined.

6.3.2 Simple Random Sampling

The fundamental principle in simple random sampling is that, in choosing a sample of "n" observations, every possible combination of "n" observations should have an equal chance of being selected. For example, if you plan on collecting 25 daily samples over a period of one year, you must choose the 25 days of sample collection in a random manner.

The question of interest here is, How do we determine "n"? More often than not, "n" has been arbitrarily selected by a sampler basing the decision of what "looks right." Fortunately, a simple, objective procedure exists for determining "n" when using the simple random sampling method. The procedure is based on the level of risk the sampler is willing to take when estimating the mean. The level of risk, in turn, is directly related to the beneficial use of water. Obviously, if you are dealing with a drinking water supply you would be more concerned with the accuracy of your estimate than if you were dealing with a stock watering tank.

In planning a water quality survey, we might state that unless the 1-in-20 chance ($\alpha = 0.05$) occurs, we would like our sample estimate of the mean to be within some specified error range of the population mean such as $\pm E$ mg/l. Since the small sample confidence limits are computed as

$$\bar{X} = \pm t_{\alpha} s_{\bar{x}} \quad (1)$$

where \bar{X} is the mean, t denotes the Student's t value for a specified α and $s_{\bar{x}}$ is the standard error of the mean, this is equivalent to stating that we want

$$E = t_{\alpha} s_{\bar{x}} \quad (2)$$

For a simple random sample the standard error of the mean can be determined by

$$s_{\bar{x}} = \sqrt{\frac{s^2}{n} \left(1 - \frac{n}{N}\right)} \quad (3)$$

where s^2 is the sample variance, "n" the number of units sampled and N is the total number of units in the population. Substituting equation (3)

into equation (2) and solving for "n" yields equation (4).

$$n = \frac{1}{\frac{E^2}{t^2 s_x^2} + \frac{1}{N}} \quad (4)$$

To determine "n", we must have some estimate of the population variance, s^2 . Sometimes the information is available from previous surveys. In the absence of this information, a small preliminary survey might be made in order to obtain an estimate of the variance. When, as often happens, neither of these solutions is feasible, a very crude estimate can be made using equation (5) where R is the estimated range from the smallest to the

$$s^2 = \left(\frac{R}{4}\right)^2 \quad (5)$$

largest concentration (mass) likely to be encountered in sampling. This approximation procedure should be used only when no other estimate of the variance is available and the observations are approximately normally distributed.

Having specified a value of E and obtained an estimate of the variance, the last piece of information required is the value of t. Here we hit a circular problem. To use t we must know the number of degrees of freedom. However, the number of degrees of freedom is "n-1" and "n" is not known and cannot be determined without knowing t.

An iterative approach can be used to solve this problem. The procedure is to guess at a value of "n," use the guessed value to get the degrees of freedom for t and then substitute the appropriate t value into the sample-size formula (equation 4) and solve for a first approximation of n. Selecting a new "n" somewhere between the guessed value and the first approximation, but closer to the latter, we compute a second approximation. The procedure is repeated until successive values of "n" are nearly the same; usually three trials will suffice.

If the sampling fraction is likely to be small ($\frac{n}{N} < 0.05$) the term $1 - \frac{n}{N}$ of the standard error formula (3) can be ignored and the sample size formula (4) simplifies to

$$n = \frac{t_{\alpha}^2 s^2}{E^2} \quad (6)$$

Examples 2a and 2b illustrate the estimation of sample size for the simple random sampling method.

Example 2a
Estimating Sample Size for the Simple Random Sampling Method

Problem:

Blue Spruce Reservoir, which is underlain by gypsum bearing rock formations, drains into Camp Creek. There is some concern by downstream users that the sulfate concentrations are excessively high. The Forest Supervisor would like an estimate, within 15 mg/l, of the mean annual SO_4 concentration passing the stream gage immediately below the outlet spillway with a fairly high degree of reliability ($\alpha = 0.05$). There is little fluctuation in the discharge from the dam, therefore, simple random sampling can be applied. Assume the SO_4 concentration varies between 20 and 100 mg/l during the year. Estimate the necessary sample size, n.

Solution:

If the sample size is less than 18, then we may use the simplified formula since $18/365 = 0.049 < 0.05$.

$$n = \frac{t_{\alpha}^2 s^2}{E^2}$$

We know from the problem that $E = 15$ mg/l, $\alpha = 0.05$ and $R = 80$ mg/l. The variance can be estimated as follows.

$$s^2 = \left(\frac{R}{4}\right)^2 = \left(\frac{80}{4}\right)^2 = 400$$

To determine t we can use as a first approximation $n = 18$ which yields 17 d.f. and $t_{.05}(17) = 2.110$ (See Appendix Table A, Values of t). The first estimate on n can now be calculated.

$$n = \frac{t_{\alpha}^2 s^2}{E^2}$$

$$n = \frac{(2.110)^2 (400)}{15^2}$$

$$n = 7.91$$

The correct solution is somewhere between 7.91 and 18, but much closer to 7.91. For our second trial we select $n = 8$. The value of t now becomes 2.365.

$$n = \frac{(2.365)^2 400}{(15)^2}$$

$$n = 9.94$$

We now know the correct solution lies between 8 and 9.94. Repeated trials will give values between 9.1 and 9.94. Since the sample size, n , must be an integral value and, because 9 is too small, a sample of $n = 10$ observations would be required for the desired precision.

Example 2b
Estimating Sample Size for Simple Random Sampling

Problem:

A preliminary sample (10 observations) of electrical conductivity in the epilimnion of Elk Lake yielded the following statistics.

$$\bar{X} = 187 \quad s = 35$$

What sample size would be required to estimate the mean EC in the epilimnion of Elk Lake within plus or minus 10 percent, with a 1-in-20 chance of being wrong in the conclusion that you have done so. Assume simple random sampling is to be employed and $\frac{\sigma}{\bar{X}}$ is less than 0.05.

Solution:

The confidence limits on the mean are given by

$$\bar{X} \pm t_{\alpha} \frac{s}{\sqrt{n}}$$

Therefore:

$$187 \pm t_{0.05} \frac{35}{\sqrt{n}}$$

The 95 percent confidence limits of plus or minus 10 percent of the mean gives

$$18.7 = t_{0.05} \frac{35}{\sqrt{n}}$$

Solving for "n" yields

$$n = \frac{t_{0.05}^2 (35)^2}{(18.7)^2}$$

For our first trial we select $n = 25$ which gives us 24 d.f.; therefore $t_{0.05}(24) = 2.064$.

$$n = \frac{(2.064)^2 (35)^2}{(18.7)^2}$$

$$n = 14.9$$

We know the correct solution lies between 14.9 and 25, but closer to 14.9. For our second trial n is set at 16.

$$n = \frac{(2.131)^2 (35)^2}{(18.7)^2}$$

$$n = 15.9$$

From repeated trials we find little difference in the calculated n, therefore we select 16 as the sample size.

In some cases you may want to determine your sample size based on a pre-established estimate of the magnitude of change (difference) in the concentration or mass of a water quality constituent between paired stations. As with other procedures used to estimate sample size when simple random sampling is employed, this method is also based on a good estimate of the sample variance. The method outlined below is discussed in detail by Snedecor and Cochran (1967) and has been summarized by Potyondy (1977).

The procedure requires you to select a value, d , which represents the size of difference between the paired stations that is regarded as important. If the difference is as large as d , we would like the monitoring program to have a high probability (probabilities of 0.80 and 0.90 are common) of showing a statistically significant difference between the paired stations. In statistical jargon, the calculation allows the selection of the confidence level of the test ($1 - \alpha$) as well as the power of the test ($1 - \beta$) and combines these two elements in determination of the sample size.

The following example taken from Potyondy (1977) is used to illustrate the mechanics of this procedure. Consider the following sample statistics from a set of turbidity data collected on the East Fork Smiths Fork Barometer Watershed in Utah and Wyoming: $\bar{X} = 4.5$ JTU; $s = 2.83$. (It should be noted that an underlying assumption of this procedure is that the data are normally distributed.) The standard deviation, s , can be expressed as a percent of the mean, referred to as the coefficient of variation, CV. Therefore:

$$CV = (s/\bar{X})100 = (2.83/4.5)100 = 63\% \quad (7)$$

The standard deviation of the difference, s_d , is estimated as:

$$s_d = 2\sqrt{CV} = 2\sqrt{63} = 89\% \quad (8)$$

Suppose we wish to detect a difference of 5 JTU's between the paired stations of interest. Expressed as a percent of the mean, the difference to be detected, d , is determined as follows:

$$d = (5.0/4.5)100 = 111\% \quad (9)$$

Assume that we want to be 90 percent certain of showing a statistically significant difference between means in a two-tailed t-test at the $\alpha = 0.05$ level of significance.

The following formulas apply:

$$n_i = (s_d^2/d^2) M_{(1-\beta, \alpha)} \quad (10)$$

where $M(0.90, 0.05)$ is a multiplier from Table 3 which is equal to 10.5.

Substituting and solving for n_i yields:

$$n_i = (89^2/111^2)(10.5) = 6.75$$

which is rounded up to the next highest integer

$$n_i = 7$$

Degrees of freedom, ν , are determined as follows:

$$\nu = 2n_i - 2 = (2)(7) - 2 = 12 \quad (11)$$

The required sample size, n , can now be determined.

$$\text{Sample size} = n = (\nu + 3) n_i / (\nu + 1) = (15)(7) / (13) = 8.08 \quad (12)$$

The sample size to use is rounded to 8.

Table 3. Multiplier (M) of (s_d^2/d^2) to be used in paired comparative sample size calculations (after Potyondy, 1977).

$(1 - \beta)$	Two-tailed Tests α level			One-tailed Tests α level		
	0.01	0.05	0.10	0.01	0.05	0.10
0.80	11.7	7.9	6.2	10.0	6.2	4.5
0.90	14.9	10.5	8.6	13.0	8.6	6.6
.95	17.8	13.0	10.8	15.8	10.8	8.6

Although simple random sampling has its place in water quality monitoring, it is limited because the watershed system under investigation is too variable with regard to its component parts. Fortunately the component parts of most watershed systems vary within a definite and repeated pattern and their variability can be reduced and better understood using stratified random sampling methods (Averett, 1976).

6.3.3 Stratified Random Sampling

Stratified random sampling is a commonly used sampling method in water quality studies. This method allows the hydrologist to take advantage of prior knowledge concerning the mechanisms and processes controlling the water quality in a watershed system. In stratified random sampling, the units of the population are grouped together on the basis of similarity of some characteristic, such as flow regime (that is baseflow, stormflow, snowmelt runoff, etc.) or temperature in a lake, such as the epilimnion and the hypolimnion. Each group or stratum is then sampled and the stratum estimates are combined to give a population estimate.

Stratified random sampling offers two primary advantages over simple random sampling. First, it provides separate estimates of the mean and variance of each stratum. Second, for a given sampling intensity, it generally gives more precise estimates of the population parameters than would a simple random sample of the same size. For this latter advantage, however, it is necessary that the strata be established so that the variability among sample values within the strata is less than the variability in the population as a whole.

Some drawbacks of stratified random sampling are that: (1) each unit in the population must be assigned to one and only one stratum; (2) the

size of each stratum must be known; and (3) a simple random sample must be taken in each stratum. The most common barrier to the use of stratified random sampling is lack of knowledge of the strata sizes.

To illustrate the computational procedures required to determine the mean and its confidence limits from a stratified random sample consider the electrical conductivity data tabulated in Table 4. The flow regime was divided into three periods (strata): (1) winter baseflow (November 1/ April 15); (2) snowmelt runoff (April 16/July 15); and (3) summer runoff (July 16/October 30). Grab samples were collected ten times during winter baseflow, 25 times during snowmelt runoff and 15 times during summer runoff. Only one sample was collected per day and each sample day was selected at random.

Table 4. Electrical conductivity data ($\mu\text{mhos/cm}$) collected from a Rocky Mountain stream.

<u>Stratum</u>	<u>Observations</u>				
I. Winter Baseflow	110	112			
	100	119			
Total = 1087	105	113			
$\bar{X} = 108.7$	115	106			
$s = 6.25$	107	100			
II. Snowmelt Runoff	89	73	51	41	57
	72	54	43	47	69
Total = 1505	43	50	49	51	77
$\bar{X} = 60.2$	51	62	68	63	81
$s = 14.6$	68	74	39	48	85
III. Summer Runoff	156	172	191		
	145	164	210		
Total = 2476	129	178	139		
$\bar{X} = 165.1$	187	154	145		
$s = 21.78$	159	167	180		

The mean EC of the stratified sample is computed by the general equation

$$\bar{X}_{TS} = \frac{\sum_{h=1}^L N_h \bar{X}_h}{N} \quad (13)$$

Where \bar{X}_{TS} is the mean of the stratified sample, L the number of strata, N_h is the total size (number of possible observations) of stratum h, and N is the total number of observations in all strata. Using the data presented in Table 2, the mean can be calculated as follows:

$$L = 3$$

$$N_I = 166$$

$$\bar{X}_I = 108.7$$

$$N_{II} = 91$$

$$\bar{X}_{II} = 60.2$$

$$N_{III} = 108$$

$$\bar{X}_{III} = 165.1$$

$$N = 365$$

$$\bar{EC}_{TS} = \frac{166(108.7) + 91(60.2) + 108(165.1)}{365}$$

$$\bar{EC}_{TS} = 113 \mu\text{mhos/cm}$$

The mean \bar{EC} computed here is basically a time weighted average which is the average daily EC of the water passing the point of measurement.

The standard error of the mean of a stratified random sample is calculated by the general equation

$$s_{\bar{X}_T} = \sqrt{\frac{1}{N^2} \sum_{h=1}^L \left[\frac{N_h^2 s_h^2}{n_h} \left(1 - \frac{n_h}{N_h} \right) \right]} \quad (14)$$

where n_h is the number of observations in stratum h, s_h^2 is the variance of sample from stratum h and the other terms are as previously

defined. If the sampling fraction within a particular stratum (n_h/N_h) is small (that is less than 0.05), the term $(1-n_h/N_h)$ can be omitted for that particular stratum when calculating the standard error of the mean. For the electrical conductivity example the standard error can be calculated as follows:

$$s_{\bar{x}_T} = \sqrt{\frac{1}{(365)^2} \left[\frac{(166)^2 (6.25)^2}{10} \left(1 - \frac{10}{166}\right) + \frac{(91)^2 (14.6)^2}{25} \left(1 - \frac{25}{91}\right) + \frac{(108)^2 (21.78)^2}{15} \left(1 - \frac{15}{108}\right) \right]}$$

$$s_{\bar{x}_T} = 1.88$$

A rough estimate of the 95% confidence interval about the mean can be obtained using equation (15).

$$\bar{X}_{ST} \pm 2(s_{\bar{x}_T}). \quad (15)$$

For our electrical conductivity example, the confidence interval would range from 109 to 117 $\mu\text{mhos/cm}$.

Before an estimate of the total sample size can be made, the hydrologist must select the method of sample allocation. Basically, there are two methods of sample allocation: proportional and optimal. In the proportional allocation procedure, the proportion of the sample that is selected in the h^{th} stratum is made equal to the proportion of all units in the population which fall in that stratum. If a stratum contains half of the units in the population, half of the samples would be collected in that stratum. In equation form, if the total number of sample units is to be "n," then for proportional allocation the number to be observed in stratum "h" is

$$n_h = \left(\frac{N_h}{N}\right) n \quad (16)$$

In optimum allocation the observations are allocated to the strata so as to give the smallest standard error possible with a total of "n"

observations. For a sample size "n," the optimum allocation is

$$n_h = \left(\frac{N_h s_h}{\sum_{h=1}^L N_h s_h} \right) n \quad (17)$$

The best way to allocate a sample among the various strata depends on the study objectives and our information about the population. The optimum allocation is preferable if the objective is to get the most precise estimate of the population mean for a given cost. If we want separate estimates for each stratum and the overall estimate is of secondary importance, we may want to sample heavily in the strata having high-value information. Then we would ignore both optimum and proportional allocation and place our observations so as to give the degree of precision desired for the particular strata.

The procedure for estimating the total size of sample (n) needed in stratified random sample can now be addressed. Basically three pieces of information are required:

- (1) a reasonably good estimate of the variance (s_h^2) or standard deviation (s_h) among individuals within each stratum.
- (2) the method of sample allocation.
- (3) a statement of the desired size of the standard error of mean, symbolized by D.

Some preliminary sampling is generally required to determine the desired size of the standard error of the mean. The estimate of D in the sample size equations is generally taken to be some portion, such as two-thirds or one-half, of the standard error calculated from the preliminary sample.

Given this hard-to-obtain information, the stratified random sample size can be estimated by the following equations.

For proportional allocation:

$$n = \frac{t_{\alpha}^2 N \sum_{h=1}^L N_h s_h^2}{N^2 D^2 + t_{\alpha}^2 \sum_{h=1}^L N_h s_h^2} \quad (18)$$

For optimum allocation:

$$n = \frac{t_{\alpha}^2 \left(\sum_{h=1}^L N_h s_h \right)^2}{N^2 D^2 + t_{\alpha}^2 \sum_{h=1}^L N_h s_h^2} \quad (19)$$

The value "2" is commonly used as an estimate of the Student's t value. When sampling fractions (n_h/N_h) are likely to be very small for all strata, the second term of the denominators of the above equations may be omitted leaving only $N^2 D^2$.

If the optimum allocation formula indicates a sample (n_h) greater than the total number of units (N_h) in a particular stratum, n_h is usually made equal to N_h . The previously estimated sample size (n) should then be dropped, and the total sample size and allocation for the remaining strata recomputed omitting the N_h and s_h values for the offending stratum, but leaving N and D unchanged.

Example 3 illustrates how to estimate the sample size for a stratified random sample.

 Example 3
 Estimating Sample Size for a Stratified Random Sample

Problem:

The mean daily electrical conductivity is to be determined at the mouth of Cabin Creek which is located in the northern Colorado Rockies. Estimate the sample size that would be required and distribute the samples over a one year period.

Solution:

The flow regime can be divided into three periods (strata): winter baseflow (November 1/April 15); snowmelt runoff (April 16/July 15); and summer runoff (July 1/ October 30). Data collected on a nearby stream provided information about the variance.

Stratum (h)	N_h	s_h
1 (WB)	166	8
2 (SM)	91	24
3 (SRO)	108	41

An estimate of the standard error of the mean, $s_{\bar{x}}$, was made from past data.

$$s_{\bar{x}} = 5.05$$

The desired D is set equal to one-half of $s_{\bar{x}}$. Therefore, $D = 2.53$. In addition, the optimal allocation method is selected to allocate the samples.

The sample size, n, can now be determined using the optimal allocation method.

$$n = \frac{\left[(2)^2 \left(\sum_{h=1}^L N_h s_h \right)^2 \right] / N^2 D^2}{1 + \left[(2)^2 \sum_{h=1}^L N_h s_h^2 \right] / N^2 D^2} = \frac{296}{2.15} = 138$$

The determined n is the sample size necessary to estimate the sample mean with a standard error of 2.53. However, because of budgetary constraints, it may not be possible to sample the stream 138 times. If that is the case, then we would have to lower the reliability constraint on the estimate of the mean. If we set $D = s_{\bar{x}}$ the required sample size becomes

$$n \approx 58.$$

In this hypothetical problem assume that $n = 58$ is accepted. The next step is to allocate the sample by strata. This is achieved as follows [from equation (19)].

Strata 1.

(winter)
$$n_1 = \frac{(166)(8)(58)}{7940} \approx 10$$

Strata 2.

(snowmelt runoff)
$$n_2 = \frac{(91)(24)(58)}{7940} \approx 16$$

Strata 3.

(summer)
$$n_3 = \frac{(108)(41)(58)}{7940} \approx 33$$

At this point you should look at the allocation and ask yourself if it looks right. In this case, most of the samples are allocated to the summer runoff period. This is the period of greatest variation in the water quality and, hence, the period that should be sampled most intensely. On the other hand, the water quality is fairly stable during baseflow and requires the least amount of sampling. Snowmelt varies twice as much as baseflow but occurs over a period equal to two-thirds of the period for baseflow. As a result, the sampling of snowmelt looks about right. It is decided that the allocation is acceptable.

7.0 Guidelines for Collecting and Handling of Water Quality Samples

Obtaining representative samples and then maintaining the integrity of the constituents is an integral part of any wildland water quality program. If the samples are not collected and handled properly the data will be of little value no matter how well the sampling program was designed.

Although analytical techniques have been standardized to a very high degree (American Public Health Association (APHA) 1976), at this time, there are no established standards for USDA-Forest Service hydrologists to follow when collecting and handling water quality samples even though the National Handbook of Recommended Methods of Water Data Acquisition (USGS, 1977) exists. As a result, collection methods may differ between hydrologists. When analyzing data, it is generally taken for granted that the data are representative of the water body from which the sample was obtained. However, this assumption can result in erroneous inferences about the quality of water body being studied, especially if several different individuals were involved in the collection of the samples. Before you compare data collected by different individuals, satisfy yourself that the samples were collected and handled properly and that the data are truly representative of the water body from which they were collected. The methods of sample collection and handling as well as the analytical methods used to measure each constituent, should be clearly documented in the Water Quality Monitoring Plan of Operation.

The purpose of this subsection is to discuss the types of sampling and to present guidelines for collecting and handling water quality samples.

7.1 Types of Samples

7.1.1 Grab Samples

A grab sample is a sample collected at a particular time and place. Strictly speaking, a grab sample can represent only the composition of the water body at that time and place. However, when a water body is known to be fairly constant in composition over a considerable period of time or over substantial distances in all directions, then a grab sample may be said to represent a longer time period or a larger volume, or both, than the specific point at which it was collected (APHA, et al, 1976). When a water body is known to vary with time, grab samples collected at suitable intervals and analyzed separately can be of great value in documenting the extent, frequency and duration of these variations. Sampling intervals should be selected on the basis of the frequency with which changes are expected.

7.1.2 Composite Samples

In most cases, the term "composite sample" refers to a mixture of grab samples collected at the same sampling point at different times or to a sample formed by continuously collecting a portion of the flow. The formation of a composite sample serves as an alternative to the separate analysis of a large number of grab samples, followed by computation of the average. Composite sampling can represent a substantial saving in laboratory effort and funds; however, it should be noted that this savings in energy and money is sometimes obtained at the expense of data resolution.

Composite samples can only be used for constituents that do not change appreciably in character during the interval from collection to analysis.

Under no circumstances should microbiological samples be composited. If preservatives are used, add them to the sample bottle initially so that all portions of the composite are preserved as soon as collected.

7.2 Sample Collection

When samples are collected from a stream, the sampler must consider the variability of constituent concentration with streamflow, depth, water velocity, distance from the bank and distance from one bank to the other. It is very important that samples be collected during representative flows over the time period of interest. If storm flows occur, it is important that they are sampled. In some cases, such as suspended solids, the majority of mass transport will occur during storm flow and/or snowmelt runoff. In some cases, data resolution will require sample collection on both the rising-limb and falling-limb of the hydrograph.

If equipment is available, it is best to take an "integrated" stream sample from the water surface to the stream bottom at selected intervals across the channel in such a way that the sample is made composite according to flow. If only a grab sample can be collected, it is best to take it in the middle of the stream at the 0.6 depth. Brown and others (1970), Guy (1970) and Greeson and others (1977) discuss the various types of sampling equipment in detail.

Lakes and reservoirs are subject to considerable variations in water quality from normal causes, such as seasonal stratification, precipitation, runoff and wind. The choice of location, depth and frequency of sampling will depend on local conditions and the purpose of the investigation. A detailed discussion of sample collection methods in lakes and reservoirs

and equipment used to collect the samples is presented by Lind (1979), Schwoerbel (1970) and Welch (1948).

The chemical quality of ground water at a sampling point may vary in response to changes in rate of water movement, to pumpage, or to differences in rate and chemical composition of recharge from precipitation and from the surrounding area (Brown and others, 1970). Although concentrations of dissolved constituents in ground water from any one well may vary widely, sometimes several fold, in general the changes take place much slower than those commonly associated with surface water. Usually, it is safer to assume that the quality of the water from a well fluctuates rather than that it is uniform for long periods of time. Changes in ground water quality usually can be described satisfactorily by a monthly, seasonal or annual sampling schedule. For more information about sampling ground water, see Hem (1970), Walton (1970) and Freeze and Cherry (1979).

Samples should be collected from wells only after the well has been pumped sufficiently to insure that the sample represents the ground water that feeds the well. Before samples are collected from distribution systems, such as water lines in a campground, flush the lines sufficiently to insure that the sample is representative of the water supply and sterilize the water tap.

In all cases, sampling points should be fixed by detailed description, by maps, or with the aid of stakes, buoys or landmarks in such a manner as to permit their identification by other persons without reliance upon memory or personal guidance.

7.3 Sample Handling

A record should be made of every sample collected and every sample container should be identified, preferably by attaching an appropriately inscribed tag or label (APHA, et al, 1976). The record should contain sufficient information to provide positive identification of the sample at a later date as well as the name of the sample collector, the date, hour and exact location, the water temperature, how the sample was handled (that is refrigeration, acidification, degassing, etc.), and any other data which may be needed in the future for correlation, such as weather conditions, water level, stream flow, or the like.

After the sample has been collected, care must be exercised to protect the integrity of the sample to assure at the time of analysis that it is representative of the water body from which it was collected. In general, the shorter the time that elapses between collection of a sample and its analysis, the more reliable will be the analytical results. For certain constituents, such as pH, immediate analysis in the field is required to obtain dependable results because the sample composition may change before it arrives at the laboratory.

It is impossible to state exactly how much time may be allowed to elapse between collection of a sample and its analysis; this depends on the character of the sample, the particular analyses to be made and the conditions of storage. Changes caused by the growth of organisms are greatly retarded by keeping the sample in the dark and at a low temperature until analysis. Where the interval between sample collection and analysis is long enough to produce changes in either the concentration or the physical state of the constituent to be measured, follow the preservation

Table 5. Summary of special sampling or sample requirements (APHA and others, 1976; Stainton and others, 1977). a/

Determination	Container <u>b/</u>	Minimum Sample Size, ml.	Storage and/or Preservation
Acidity	P, G(B)	100	24 hr; refrigerate
Alkalinity	P, G(B)	200	24 hr; refrigerate
BOD	P, G	1,000	6 hr; refrigerate
Boron	P	100	-
Carbon, organic, total	G(brown)	100	Analyze as soon as possible, refrigerate or add HCl to pH \leq 2
Carbon dioxide	G	100	Analyze immediately
Dissolved Organic Carbon	G	100	Analyze as soon as possible, filter, refrigerate
COD	P, G	100	Analyze as soon as possible, add H ₂ S ₄ to pH $<$ 2
Chlorine dioxide	P, G	500	Analyze immediately
Chlorine, residual	P, G	500	Analyze immediately
Chlorophyll	P, G	500	30 days in dark; freeze
Color	G	500	-
Cyanide	P, G	500	24 hr; add NaOH to pH 12; refrigerate
Fluoride	P	300	-
Fluvial sediment <u>c/</u>	G, wide-mouth, calibrated	1,000	Add HCl to pH $<$ 2
Grease and oil	P, G	500	Analyze immediately
Iodine	P, G	-	For dissolved metals separate by filtration immediately; add 5 ml conc HNO ₃ /l
Metals	P, G	-	-
Nitrogen	P, G	500	Analyze as soon as possible; add 0.8 ml conc H ₂ S ₄ /l; refrigerate
Ammonia	P, G	100	Analyze as soon as possible; filter, add 0.8 ml conc H ₂ S ₄ /l; refrigerate
Nitrate	P, G	100	Analyze as soon as possible; filter, add 40 mg HgCl ₂ /l and refrigerate or freeze at -20°C
Nitrite	P, G	100	-

Determination	Container <u>b/</u>	Minimum Sample Size, ml.	Storage and/or Preservation
Total Dissolved Nitrogen	P, G	100	Analyze as soon as possible; add 40 mg HgCl ₂ /l and filter, refrigerate
Organic	P, G	500	Analyze as soon as possible; refrigerate or add 0.8 ml conc H ₂ SO ₄ /l
Microbiological	P, G	500	6 hr; refrigerate
Odor	G	500	Analyze as soon as possible; refrigerate
Oxygen, dissolved	G, BOD bottle	300	Analyze immediately
Pesticides (organic)	G(S)	-	-
pH	P, G(B)	-	-
Phenol	G	500	24 hr; add H ₃ PO ₄ to pH ≤ 4.0 and 1 g CuSO ₄ ·H ₂ O/l; refrigerate
Phosphorus (dissolved)	G(A)	100	Analyze as soon as possible; For dissolved phosphates separate by filtration immediately, freeze at < -10°C and/or add 40 mg HgCl ₂ /l
Orthophosphate (dissolved)	G(A)	100	Analyze as soon as possible; filter immediately, add 40 mg HgCl ₂ , refrigerate.
Total Dissolved Phosphorus	G(A)	100	Analyze as soon as possible, filter immediately, add 40 mg HgCl ₂ /l, refrigerate.
Residue (TDS)	P, G(B)	100	-
Salinity	G, wax seal	240	Analyze immediately or use wax seal
Silica	P	-	-
Sulfate	P, G	-	Refrigerate
Sulfide	P, G	100	Add 4 drops 2N zinc acetate/100 ml
Sulfite	P, G	-	Analyze immediately
Taste	G	500	Analyze as soon as possible; refrigerate

Table 5 continued

Determination	Container <u>b/</u>	Minimum Sample Size, ml.	Storage and/or Preservation
Temperature Turbidity	P, G	- -	Analyze immediately Analyze same day; store in dark for up to 24 hr

a/ See Standard Methods (APHA et al, 1976) and The Chemical Analysis of Fresh Water (Stainton et al, 1977) for additional details. Use glass or plastic containers, preferably refrigerate during storage and analyze as soon as possible. Samples for cation and anion analysis should be filtered in the field. For the design of a portable unit for filtering water samples at field sites, see Kennedy and others (1976).

b/ P = plastic (polyethylene or equivalent); G = glass; G(A) or P(A) = rinsed with 1+1 HNO₃; G(B) = glass, borosilicate; G(S) = glass, rinsed with organic solvents.

c/ Follow USGS methods (Guy and Norman, 1970).

practices outlined in Table 5. Record the time elapsed between sampling and analysis, and which preservative, if any, was added.

Stainton and others (1977) suggest several special precautions when sampling for nutrient elements. The usually low levels of these elements in upland water resources make contamination a significant problem. While the need for clean samples and sample containers is obvious, there are several other contamination sources which must be avoided. Small amounts of tobacco ash, dandruff and perspiration contributed by field personnel, or plant pollen and other atmospheric particulates all can introduce significant errors into nutrient element analysis. Field personnel must be made aware of these and other possible sources of contamination.

The foregoing discussion is by no means all inclusive. It is impossible to prescribe absolute rules for the prevention of all possible changes. Some advice will be found in the discussions of methods of determination of various constituents in Standard Methods (APHA and others, 1976) and The Chemical Analysis of Fresh Water (Stainton and others, 1977). However, to a large degree, the dependability of water quality data must rest on the experience and good judgement of the samples and analyst.

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APPENDIX

THE UNIVERSITY OF CHICAGO
DEPARTMENT OF CHEMISTRY

REPORT OF THE
COMMISSIONERS OF THE BOARD OF CHEMISTRY

FOR THE YEAR ENDING
MAY 31, 1911

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Table A-1. Values of t (Steel and Torrie, 1960).

df	Probability of a larger value of t , sign ignored								
	0.5	0.4	0.3	0.2	0.1	0.05	0.02	0.01	0.001
1	1.000	1.376	1.963	3.078	6.314	12.706	31.821	63.657	636.619
2	.816	1.061	1.386	1.886	2.920	4.303	6.965	9.925	31.598
3	.765	.978	1.250	1.638	2.353	3.182	4.541	5.841	12.941
4	.741	.941	1.190	1.533	2.132	2.776	3.747	4.604	8.610
5	.727	.920	1.156	1.476	2.015	2.571	3.365	4.032	6.859
6	.718	.906	1.134	1.440	1.943	2.447	3.143	3.707	5.959
7	.711	.896	1.119	1.415	1.895	2.365	2.998	3.499	5.405
8	.706	.889	1.108	1.397	1.860	2.306	2.896	3.355	5.041
9	.703	.883	1.100	1.383	1.833	2.262	2.821	3.250	4.781
10	.700	.879	1.093	1.372	1.812	2.228	2.764	3.169	4.587
11	.697	.876	1.088	1.363	1.796	2.201	2.718	3.106	4.437
12	.695	.873	1.083	1.356	1.782	2.179	2.681	3.055	4.318
13	.694	.870	1.079	1.350	1.771	2.160	2.650	3.012	4.221
14	.692	.868	1.076	1.345	1.761	2.145	2.624	2.977	4.140
15	.691	.866	1.074	1.341	1.753	2.131	2.602	2.947	4.073
16	.690	.865	1.071	1.337	1.746	2.120	2.583	2.921	4.015
17	.689	.863	1.069	1.333	1.740	2.110	2.567	2.898	3.965
18	.688	.862	1.067	1.330	1.734	2.101	2.552	2.878	3.922
19	.688	.861	1.066	1.328	1.729	2.093	2.539	2.861	3.883
20	.687	.860	1.064	1.325	1.725	2.086	2.528	2.845	3.850
21	.686	.859	1.063	1.323	1.721	2.080	2.518	2.831	3.819
22	.686	.858	1.061	1.321	1.717	2.074	2.508	2.819	3.792
23	.685	.858	1.060	1.319	1.714	2.069	2.500	2.807	3.767
24	.685	.857	1.059	1.318	1.711	2.064	2.492	2.797	3.745
25	.684	.856	1.058	1.316	1.708	2.060	2.485	2.787	3.725
26	.684	.856	1.058	1.315	1.706	2.056	2.479	2.779	3.707
27	.684	.855	1.057	1.314	1.703	2.052	2.473	2.771	3.690
28	.683	.855	1.056	1.313	1.701	2.048	2.467	2.763	3.674
29	.683	.854	1.055	1.311	1.699	2.045	2.462	2.756	3.659
30	.683	.854	1.055	1.310	1.697	2.042	2.457	2.750	3.646
40	.681	.851	1.050	1.303	1.684	2.021	2.423	2.704	3.551
60	.679	.848	1.046	1.296	1.671	2.000	2.390	2.660	3.460
120	.677	.845	1.041	1.289	1.658	1.980	2.358	2.617	3.373
∞	.674	.842	1.036	1.282	1.645	1.960	2.326	2.576	3.291
df	Probability of a larger value of t , sign considered								
	0.25	0.2	0.15	0.1	0.05	0.025	0.01	0.005	0.0005

The following table shows the results of the experiments conducted on the effect of temperature on the rate of reaction between hydrogen peroxide and potassium iodide. The reaction is catalyzed by the presence of a small amount of potassium iodide. The rate of reaction was measured by the volume of oxygen gas evolved in a given time.

Temperature (°C)	Volume of O ₂ (ml) in 10 min
10	10
20	20
30	40
40	80
50	160

It is seen from the above table that the rate of reaction increases with increase in temperature. This is due to the fact that at higher temperatures, the molecules of the reactants possess more kinetic energy and hence collide more frequently and with more force, resulting in a higher rate of reaction.

