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MARYLAND SYNOPTIC STREAM

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Prepared for
 STATE OF MARYLAND
 DEPARTMENT OF NATURAL RESOURCES
 POWER PLANT RESEARCH PROGRAM

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MARYLAND POWER PLANT RESEARCH PROGRAM



As Secretary of the Maryland Department of Natural Resources, I am convinced that public support of DNR's mission is essential if we are to restore the State's once bountiful natural resources, especially the Chesapeake Bay, to the level which earned the title "America in Miniature." The information in this publication is designed to increase your understanding of our program and of Maryland's natural resources.

Torrey C. Brown, M.D.



MARYLAND SYNOPTIC STREAM CHEMISTRY SURVEY DESIGN REPORT

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> Prepared for: State of Maryland Department of Natural Resources Power Plant Research Program

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FOREWORD

This report is submitted to Mr. Michael Bowman, Acid Deposition Administrator, Maryland Department of Natural Resources, Power Plant Research Program, under contract PR87-071-02 to International Science & Technology, Inc. The design and implementation plans for the Maryland Synoptic Stream Chemistry Survey are presented.

The design presented here resulted from a Stream Survey Design Workshop, held November 19 and 20, 1986. Participants in this workshop included scientific and technical advisors to International Science & Technology, Inc. (IS&T) and to the Maryland Power Plant Research Program (PPRP), in addition to representatives of both IS&T and PPRP. Scientific and technical advisors included: Dr. Paul Godfrey, University of Massachusetts; Mr. Jim Gracie, J.W. Gracie and Associates; Dr. George Hornberger, University of Virginia; Dr. Ronald Klauda, Johns Hopkins University; Dr. John Kraeuter, Baltimore Gas and Electric; Dr. Jim Lynch, Pennsylvania State University; Dr. Douglas Robson, Cornell University; Dr. Cullen Sherwood, James Madison University; and Dr. Kent Thornton, FTN Associates. Representatives of the State of Maryland were Mr. Michael Bowman, PPRP, and Mr. Paul Slunt, Department of Health and Mental Hygene. IS&T representatives in attendance included: Mr. Michael Bonoff, Mr. Douglas Britt, Dr. Gerald Filbin, Mr. Charles Knapp, Mr. Ky Ostergäard, Mr. Peter Saunders, and Dr. Alan Steiner.

ABSTRACT

A stratified random sampling design from a list frame of stream reaches delineated on 1:250,000 scale USGS topographic maps covering Maryland is presented. Elements of the design include: stratification based on physiography modified by soils and geology, a digitized stream reach data base, stream reaches as basic sampling units, criteria for excluding non-interest streams, one-time sample collection during spring high flows, and sample collection with the assistance of volunteers. Measurements of pH, ANC, DIC, DOC, conductivity and color will be made in samples from 600 streams in six sampling strata. Various aspects of implementation are presented, including: itinerary; the sampling obtaining access permission for sample collection; protocols for sample collection and handling; recruiting, training, and organizing volunteer samplers; and logistics of sample collection and analysis. Methods of exploratory multivariate data analyses that will be used are discussed.



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EXECUTIVE SUMMARY

The Maryland Synoptic Stream Chemistry Survey (MSSCS) is an extension of several studies that have shown that acidic or acid sensitive streams may be relatively common in the Appalachian Plateau and Coastal Plain physiographic provinces of Maryland. The objectives of the MSSCS project are to design and implement a synoptic chemistry survey of Maryland streams; estimate the number and extent of streams that are affected by, or are sensitive to acidification; and utilize survey and other data to design a long-term monitoring program to detect changes in stream water chemistry related to acid deposition. This report presents the sampling design of the MSSCS and elements of survey implementation and data analysis as they relate to the sampling design for the MSSCS.

The survey design is the product of a process constrained by logistic and human resource considerations. The objective of this process is to optimize the distribution of a fixed level of sampling effort to produce minimum variance estimates of the population of resources at risk. A list frame, stratified random sampling design, is developed for the population of stream reaches delineated on 1:250,000 scale USGS topographic maps. This population includes streams with significant biological resource potential. Because of the project's focus on streams that may have a high probability of being sensitive to acidification, stream reaches with drainage areas greater than 100 km², reaches with known sources of industrial pollutants and acid mine drainage, and reaches immediately downstream from large impoundments are excluded from the sampled population.

Six sampling strata, reflecting regional patterns in potential sensitivity of surface waters to acidification, are defined. These are: Appalachian Plateau - Western Valley and Ridge, Eastern Valley and Ridge, Blue Ridge, Piedmont, Northern Coastal Plain, and Southern Coastal Plain. The strata are based on the physiographic provinces of Maryland with modification of boundaries to provide for consideration of geology and soils in the stratification scheme. Six water chemistry parameters will be measured for all sampled streams. These are: pH, acid neutralizing capacity (ANC), dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), conductivity, and color. Strong mineral acidity titrations will be performed for samples with low pH (pH \leq 4.5) to assess the potential influence of acidic industrial or mine discharges. Quality assurance and quality control sampling will involve collection of field duplicates (10 percent of reaches sampled) to assess sampling system variability; laboratory duplicates (5 percent of field samples) to assess analytical precision; and laboratory audits (5 percent of field samples) to assess analytical accuracy.

One routine water chemistry sample will be collected from each of 600 stream reaches in the state. Samples will be collected by volunteers on weekends during the period March 7 through May 9. Sampling will be organized regionally, beginning in southeastern Maryland and proceeding north and west in concert with the phenological development of spring conditions.

Based on previous reviews of stream chemistry data, the MSSCS sampling design will result in a relative error of the estimates of the proportion of streams affected by or sensitive to acidification of less than \pm 15 percent. Estimates for those strata likely to contain relatively high proportions of acidic or acid sensitive reaches will have relative error of \pm 30 percent or less. Estimates for strata likely to contain relatively few acidic or acid sensitive reaches will have low relative precision, but are likely to be within 3-5 percent of the true value for the proportion of sensitive reaches.

Representatives of the Maryland Forest, Park, and Wildlife Service will assist in obtaining site access permission for sample collection prior to initiation of water sampling. A central feature of the survey is the use of volunteers in the collection of samples. These volunteers will be recruited from conservation organizations (such as Trout Unlimited) and the general public. Sampling will be coordinated from a regional field headquarters, where samplers will assemble to be trained in sample collection protocols, receive stream sampling assignments, and

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return with collected samples. The field headquarters facilities will be staffed at all times when samplers are in the field, for safety reasons and to provide communications.

Collected samples will be stored in coolers and transported to the laboratory immediately following completion of sampling. Analysis of pH and DIC will be initiated immediately, other analyses will be conducted during the two weeks following the collection date. Quality assurance and quality control procedures are integral components of all aspects of the survey. Quality control procedures will be utilized throughout the implementation of the survey to ensure the development of a high quality data base, and quality assurance evaluations will be employed to provide estimates of error frequency and analytical imprecision for each aspect of the survey.

Analysis of survey data will provide estimates of the proportions of reaches or number of reach kilometers in the population of interest that might be considered acidic or sensitive to acidification. The categories "acidic" and "acidification sensitive" will each be operationally defined at several levels of pH and ANC, respectively.

Exploratory classification analyses such as cluster analysis and discriminant analyses will be performed. These analyses will attempt to identify patterns of stream chemistry and related watershed characteristics that improve our understanding of the distribution of acidic or potentially acid sensitive streams in Maryland. These classification analyses also will be used to develop classification functions useful for selecting "typical" streams for long-term monitoring of trends in acidification in Maryland streams.

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CHAPTER I

INTRODUCTION

PROJECT BACKGROUND

In January of 1984, the Maryland Interagency Working Group on Acid Deposition (Bowman and Wierman, 1984), established the following conclusions:

- The average pH of rural rainfall in Maryland for the previous nine years was approximately 4.0.
- No adverse effects of this acidic deposition in Maryland had been documented, but such effects could not be ruled out.
- Headwater streams in Western Maryland and the Coastal Plain may be especially sensitive to acidic deposition.
- Existing water quality in 23 headwater tributaries of the Chesapeake Bay had pH values and aluminum concentrations that could be hazardous to anadromous fisheries.

Other studies, conducted for the Maryland Department of Natural Resources (DNR) (Bartoshesky, et al. 1986; Klauda and Palmer 1986) and International Science & Technology, Inc. (IS&T) (Saunders, et al. in preparation), have indicated that some first, second, and third order tributaries of the Chesapeake Bay respond to acidic atmospheric events with rapid and substantial declines in surface water pH. Additionally, Hendrey, et al. (1984) identified 126 streams in Maryland that were exhibiting significant trends in pH (107 of these were considered to be acidifying).

These results and information from other recent and on-going surveys conducted by private, state, and Federal research organizations suggest that acidification may pose a serious threat to aquatic biota, especially fisheries, in some small streams in poorly buffered regions of the state. For example, Coastal Plain streams are sensitive to acid deposition, because acidic precipitation is in contact with the sandy soils of the region for a relatively short time, which provides little opportunity for acid neutralization by ion exchange. The acidity of storm runoff increases solubility of aluminum (Bachman and Katz 1986), which is toxic to fish. The relatively short residence time of solubilized aluminum does not allow sufficient time for further mineral weathering to immobilize this aluminum (Bachman and Katz, 1986).

AND DESCRIPTION OF

Uncertainty regarding the present and future acidification status of stream resources in Maryland is a major concern of the State. Α comprehensive survey of all Maryland streams to determine water quality conditions is neither economically nor logistically feasible. However, a synoptic survey of a subpopulation of Maryland streams will provide results that can be extrapolated to assess the degree of acidification and potential vulnerability of the entire population of headwater streams in the state. Such a survey also can be used to identify classes, or categories, of streams that are particularly sensitive to acidic atmospheric deposition. This information, in turn, can be used to identify a subset of critical streams that can be observed for indications of acidification or recovery in a long-term monitoring program.

OBJECTIVES OF THE MARYLAND SYNOPTIC STREAM CHEMISTRY SURVEY

The following objectives have been established by the Maryland Department of Natural Resources, Power Plant Research Program (PPRP) for the Maryland Synoptic Stream Chemistry Survey:

- To design a synoptic stream chemistry survey for Maryland streams that will allow an estimate of resources presently affected by, or at risk from, acidic deposition
- To implement the survey design
- To analyze the data collected to produce statistically valid population estimates of resources at risk
- To design a long-term monitoring program to be implemented by the Office of Environmental Programs, that can detect changes in stream chemistry due to acidic deposition.

The major goal of the survey design is to develop a program that will allow the detection of statewide and regional acidification status (indicated by stream pH) and potential acidification sensitivity status (indicated by acid neutralizing capacity or ANC) of small, headwater stream systems.

OVERVIEW OF THE DESIGN REPORT

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This report presents the selected design for the Maryland Synoptic Stream Chemistry Survey (MSSCS) and describes the steps that will be taken to implement this design. The survey design, presented in Chapter II, is based on the results of a Stream Survey Design Workshop, held November 19 and 20, 1986, at the Mariott Hotel at Dulles Airport, VA. The Stream Survey Design Workshop was attended by personnel and technical advisors of the PPRP and IS&T. During the workshop, four major elements of the design were discussed:

- Definition of the population of interest
- Development of the basis for statewide stratification
- Selection of a population sampling method
- Development of a sampling design and determination of the distribution of sampling effort.

Alternative approaches to each of the four elements listed above were discussed in the Stream Survey Design Workshop; one approach to each design element was selected as the preferred alternative. The alternatives discussed at the workshop and the selected approach are presented in Chapter II. Additional topics that were not subject to extensive discussion at the Stream Survey Design Workshop, but that are nonetheless essential to the survey design (e.g., analytes to be measured, quality control and quality assurance procedures), also are described in Chapter II.

Chapter III describes the tasks that will be performed during implementation of the MSSCS. These tasks include the development of a list frame data base, selection of stream reaches for sampling,

preparation for field sampling, and conducting field and laboratory operations. An integral component of field operations in the MSSCS is the use of volunteers to collect samples. Procedures for recruiting, training, and organizing these volunteers are described in the discussion of field operations. Implementation of Quality Control and Quality Assurance procedures is also discussed in Chapter III.

Procedures that will be used to analyze the data are presented in Chapter IV. Additional analytical approaches will be identified and implemented as data are generated and the design of the long-term monitoring program is developed.



CHAPTER II

SURVEY DESIGN

BLEMENTS AND CONSTRAINTS OF THE SURVEY DESIGN

A number of inter-related design elements comprise the Maryland Synoptic Stream Chemistry Survey:

- The total number of streams to be sampled
- The number of times each stream is sampled
- The number of strata selected for sampling
- The number of streams sampled in each stratum
- The basis for sample collection location on each stream
- The number of analytes measured per sample
- The specific analytes to be measured
- The scope and detail of Quality Control and Quality Assurance (QA/QC) incorporated into the program
- The timing of sample collection activities with regard to daily, seasonal, and annual cycles
- The degree of training and reliability of the field samplers
- The desired precision for statewide and regional estimates of resources at risk from acidification.

A change in any one of the design elements may affect one or more other elements, particularly in a case where resources (financial, logistic, and human) are fixed. Within a fixed resource framework a number of "trade-offs" among design elements often are required before an optimal study design can be realized. Optimization requires clear definition of resource constraints and statement of study objectives.

A number of constraints pertain to the MSSCS. Foremost among these are the following:

 A limited number of water quality analytes can be measured (pH, ANC, DIC, DOC, conductivity, and color)

- A maximum of 600 routine samples can be collected
- Routine samples must be allocated to provide statewide and regionally valid population estimates
- Samples will be collected by volunteers
- Training and supervision of volunteers will be performed by scientific staff with experience in collection of water samples for acidification studies.

The primary objective of the survey design is to develop a survey approach that will produce minimum variance estimates of the number and extent (e.g., stream miles) of Maryland streams presently affected by, or sensitive to acidification. This objective is restricted by definition of a population of "streams of interest." Streams of interest include those that are small (e.g., first to third order), because of their high potential susceptibility to acidification, and that have biological resources of concern (i.e., fishery resources).

In addition to statewide estimates of stream resources at risk, a secondary objective of the survey design is to provide regional estimates of such resources. Regional estimates are potentially of great use to resource managers because the nature and susceptibility to acidic conditions of important biological resources varies from region-to-region throughout the state.

SAMPLING DESIGN FRAMEWORK

The design for the MSSCS relies upon the body of mathematical theory developed for randomly selected probability samples. A sampling frame that uses random selection has the advantage of allowing the sampler to predict from sample data the approximate error associated with estimates based on those data (Cochran 1977). Additionally, it is possible to use prior knowledge of the population being sampled to estimate sample sizes required to meet certain precision goals.



The sampling design framework for MSSCS incorporates consideration of two components: sampling frame and stratification. Knowledge of these components is a necessity for making the trade-offs among design elements discussed earlier.

Sampling Frame

Two methods of random sample selection were considered for MSSCS. ∋у The first, list frame sampling, has the property that the exact size of nd the population (N) is known, because it requires that all units in the or population be listed. Selections of units to be sampled are made at on random from the list and, once selected, a unit may not be re-selected. 1e The alternative sampling approach considered is a point frame. In a γh point frame sample a grid of uniformly spaced points is superimposed 31 (with a randomly located origin) on a map of the stream population. Random selection of grid points is followed by locating the nearest streams that lie downhill from selected grid points to provide the This procedure is useful where it is logistically impossible to sample. 35 develop a list frame, but because N is not known exactly and must be 20 estimated, estimates of population characteristics based on point frame ic samples are usually less precise than those resulting from list frame on samples. Because of this, the list is preferred as the sampling frame for the MSSCS.

Stratification

Simple random sampling is the most obvious method of selecting streams from the statewide list. Simple random sampling is a desirable sampling method when the parameter of interest (e.g., alkalinity) has a uniform geographic distribution and there is no reason to attempt to apportion the sampling effort among different geographic regions.

If the parameter of interest is not uniformly or randomly distributed, stratified sampling has several advantages over simple random sampling (Cochran 1977). For the MSSCS, several potential advantages of stratified random sampling exist:

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- Increased precision in the estimate of the number of affected streams statewide
- Assurance of adequate geographic coverage for all areas of the state
- Allowance of estimates for regional subdivisions of the population of Maryland streams of interest.

These objectives are realized when certain conditions are met. For example, an increase in the precision of statewide estimates will result only when the proportions of affected streams in different strata vary considerably. Regional estimates and geographic coverage are desirable only if those strata are chosen in relation to areas or domains of interest that are meaningful to state resource management agencies.

Review of information on differences in the frequency of occurrence of acid sensitive streams in different physiographic regions (Janicki and Greening 1986, Harman 1984) indicates that precision of estimates will be increased by stratification. Janicki and Greening (1986) also noted that the physiographic regions are somewhat related to regions likely to have different fishery management priorities.

Based on the above discussion, the preferred sampling design utilizes stratified random sampling from a list frame.

DEFINITION OF THE STREAM POPULATION OF INTEREST

Specification of the population of Maryland streams of interest incorporates consideration of the potential susceptibility of the streams to acidification and the potential for those streams to contain important biological resources. In general, very small streams are most likely to be affected by atmospheric inputs and precipitation. Important biological resources (e.g., fish populations), on the other hand, are rare in very small streams, particularly those streams that are dry or have extremely low flows during certain times of the year. The goal in defining the population of interest is to specify streams small enough to be potentially affected by acidification, but large enough to contain important biological resources.

Stream Reaches

Before continuing with discussion of the stream population of interest, it is necessary to define clearly what is meant by the term "stream". The naming of streams is somewhat arbitrary. A named stream on a map may flow for many kilometers and may have a large number of streams tributary to it. Tributaries contribute to the total flow of a stream. In addition, tributaries may drain basins of different geology, soils, vegetation, or land use and thus alter the stream chemically. This gives rise to the problem of determining where to collect a sample that is representative of the stream's chemistry. Thus, it is difficult to delineate the sampling unit if it is based only on a named stream.

In the National Stream Survey (NSS), conducted by the U.S. EPA, the sampling unit was defined as a stream reach. A reach was defined as the section of stream between two adjacent confluences or between the head of a stream and the first downstream confluence. Blue line streams on U.S. Geological Survey (USGS) 1:250,000 scale topographic maps were used by EPA to define confluences (and reaches); however, this approach can be applied to maps of any scale.

Stream reaches allow sampling units to be delineated precisely. Reaches also are relatively homogeneous units with respect to flow. For these reasons, the stream reach will be the sampling unit used in MSSCS.

Map Base

The map base used for stream selection defines the population from which samples are drawn. The objective in selecting a map base is to select one compatible with the population of interest. Four map products are available for defining the population of Maryland streams. These include:

• USGS 7.5-minute series topographic quadrangles (7.5-minute quads) at 1:24,000 scale

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- Maryland Geological Survey county maps at 1:62,500 scale (county maps)
- USGS 30 x 60 minute series topographic quadrangles at 1:100,000
 scale (1:100,000 maps)
- USGS 1 x 2 degree series topographic quadrangles at 1:250,000 scale (1:250,000 maps).

The 7.5-minute quads and the county maps are virtually identical in terms of the streams represented. The smaller scale maps (1:100,000 and 1:250,000 maps) appear to provide a good representation of streams, although fewer streams are represented on those products than on the 7.5-minute quads.

The choice of map base was reviewed at the Stream Survey Design Prior to the workshop, several reviewers expressed concern Workshop. that the 1:250,000 maps did not represent sufficiently small streams to evaluate adequately the biological resources at risk. The 7.5-minute quads were suggested as an alternative map base that represented more comprehensive coverage of biological resources at risk. Figure II-1 provides a comparison of the number of reaches identified from the area of a 7.5-minute quad on a 1:250,000 map with the number of reaches on the corresponding 7.5-minute quad. Approximately twice as many reach confluences are represented on the 7.5-minute quads as are represented on the 1:250,000 maps. Many of the "new" reaches found on the 7.5-minute quads are formed by the confluence of a very small headwater reach with a reach that was present on the 1:250,000 map. The result of such a confluence of two reaches is three reach segments, the "new" reach (present on the 7.5-minute quad but not in the 1:250,000 map) plus two segments of the original (1:250,000 map) reach. Thus, the increase in resolution provided by the 7.5-minute maps is not as great as it first appears. In addition, a large number of the "new" reaches are likely to be intermittent or ephemeral streams.

Use of 7.5-minute quads would require development of exclusionary criteria to remove streams with little or no biological resource potential from the sample. Finally, use of 7.5-minute quads also would

	1:250,000	:	7.5-minute	1:250,000) :	7.5-minute	1:250,000	1	7.5-minute	1:250,000	1	7.5-minute	1:250,000	:	7.5-minute
	CUMBERLA	ND	BITTINGER	BALTIMO	RE	FUNKSTOWN	BALTIMORE		BLUE RIDGE	BALTIMORE		BEL AIR	BALTIMOR	E	ROUND BAY
NUMBER OF Confluences	31	÷	51	17	:	56	21	:	41	28	:	40	33	ļ	96
NUMBER OF REACHES															
1ST ORDER	32	:	53	18	:	58	24	÷	42	30	:	43	32	:	96
2ND ORDER	16	ł	22	7	:	27	12	ŧ	23	12	:	23	10	:	43
3RD ORDER	7	÷	18	1	-	7	5	ļ	12	8	:	8	o	ł	5
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Figure II-1. Comparison of Stream Confluences and Reaches Between U.S.G.S. 1:250,000 and 1:24,000 (7.5-minute Quadrangle) Maps.

result in additional cartographic errors in reach enumeration due to the increased number of map boundaries, thus making it impractical to develop a quality assured list frame based on 7.5-minute quads.

The 1:100,000 maps were also compared with the 1:250,000 maps. Generally, equivalent or fewer numbers of reaches were found on the 1:100,000 maps. This map base was thus considered less desirable than the 1:250,000 map base for defining the population of streams of interest.

The 1:250,000 maps will be used as the map base for the MSSCS, for the following reasons:

- Blue-line streams on the 1:250,000 maps generally represent streams that flow year-round, thus having a high potential for containing important biological resources.
- Only five maps are required to cover the State of Maryland, thus reducing the potential for variation among maps resulting from differences in feature interpretation among cartographers.
- The 1:250,000 maps are logistically tractable for developing a list-frame random sample.
- The 1:250,000 map base was used in the NSS, thus providing the only valid basis for comparing the results of Maryland's assessment of stream resources at risk with the national assessment.

Exclusion Criteria

The map base selected provides a major basis for defining the population of interest by determining what reaches may potentially be included in the population sample. It is, however, desirable to remove from this potential population those stream reaches that are not part of population of interest (i.e., potentially the susceptible to acidification from atmospheric sources). For this reason, several exclusion criteria were developed. Exclusion criteria are employed instead of selection criteria because all streams not specifically excluded are included in the sample. This approach allows the sampling

program to be representative of all streams belonging to the population of interest.

Reach Size

There are two aspects of reach size considered in the exclusion criteria. The first, based on the consensus reached at the Design Workshop, is that large streams, with the exception of a few Eastern Shore rivers, are unlikely to exhibit the effects of acidification. The NSS also recognized this and excluded reaches with watershed areas of greater than 60 mi² (155.4 km²) from the sample.

An alternative approach is to exclude reaches with stream orders greater than some pre-determined value. Originally, fourth order (Strahler method) or larger reaches were recommended for exclusion from the MSSCS sample. An exclusionary criterion based on reach order is difficult to apply uniformly, however, because reach order depends on both the reach order definition used and the map base used to define the stream population. The size of streams of similar order may also vary greatly among different geographic regions due to differences in drainage patterns.

Use of a drainage area criterion to exclude large streams from consideration was deemed preferable. A maximum acceptable drainage area size of 100 km² (38.6 mi²) was chosen for the MSSCS. Based on the drainage area to flow relationships of gauged Maryland streams (Carpenter 1983), this drainage area criterion is expected to result in exclusion of reaches having annual average flows in excess of 1.5 m³/s (50 cfs).

A second reach size criterion was proposed at the Design Workshop. Reaches less than 300 m (1000 ft) in length will be excluded from the MSSCS sample. This criterion is intended to remove from the sample those reaches with heterogeneous water chemistry caused by incomplete mixing of the waters from the reaches forming the upstream confluence.

Tidal Areas

Exclusion of tidal waters from the MSSCS was required. Two alternative methods for eliminating tidal influences were considered. First, the use of a contour line ten feet above mean sea level was considered. This method requires interpolation between the lowest contour line (20') of a 7.5-minute quadrangle map and the coast-line to delineate the head-of-tide location on coastal stream reaches identified on the 1:250,000 scale maps. A second alternative was to transfer head-of-tide locations indicated on large scale (1:2400) aerial photomaps to the 1:250,000 scale maps. Approximately 2000 of these photo maps cover the entire coastal area. They were prepared by experienced photo interpreters for the Maryland DNR Critical Areas Program. Head-of-tide delineation will be accomplished using these aerial photomaps, because the original delineations are based upon site-by-site analysis using established criteria, as opposed to delineation at an arbitrarily chosen contour line.

Chemically Affected Reaches

Stream reaches affected by acid mine drainage (AMD) are highly acidic and as a result, acidifying effects of atmospheric or other weak acid inputs are usually undetectable. Reaches affected by AMD can be identified using data available from the Maryland Bureau of Mines. Stream reaches affected by chemicals from sources other than AMD also may resist acidification caused by weak acid inputs. However, such reaches may be more difficult to identify. Chemically affected reaches will be identified using available data, including discharge permit data and personal knowledge of volunteer samplers or the personnel obtaining site access permission. If the presence of a major point source can be confirmed prior to sample collection, the reach will be excluded from the sample and an alternate reach selected in its place. If a chemical discharge is discovered to affect a stream reach after it has been sampled, the data from that sample will be flagged in the data base.

Impoundments

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Water quality in tailwater streams from large impoundments (reservoirs and lakes) is often more similar to the quality of the impoundments at the level of the discharge inlet (surface, mid-depth, or bottom) than to the quality of the influent streams to the impoundment. In addition, because impoundments integrate temporal variations in tributary water quality, tailwater streams from large impoundments may not be representative of regional stream resources. For these reasons, stream reaches that represent tailwaters from reservoirs shown on 1:250,000 maps will not be sampled during the MSSCS.

Sampling Strata

The primary objective of stratified sampling for the MSSCS is to increase the precision of the estimate of the number of stream resources at risk from acidification. Cochran (1977) observes that large gains in precision can be obtained when differences in the parameter of interest are great among strata. Several sources have indicated that the distribution of acidic streams varies greatly among regions of the State (Harman 1984, Janicki and Greening 1986). In general, Maryland streams sensitive to acidification are more prevalent in the Appalachian Plateau and Coastal Plain physiographic provinces than in the Piedmont and Valley and Ridge provinces (Janicki and Greening 1986, Harman 1984). (The Blue Ridge province was incorporated into the Valley and Ridge province in the foregoing water quality studies due to its small size and the relative scarcity of data for this province.)

Physiographic provinces provide one of many possible frameworks for stratification of sampling in the MSSCS. Other stratification schemes may be based on geology, soils, known patterns in surface water quality, vegetation, and political units such as counties. In Maryland, the physiographic provinces reflect and integrate, to some extent, geology, soils, and vegetation. Surface water quality is grossly related to these physiographic regions in terms of potential susceptibility to acidification. In summary, physiographic regions provide a reasonable

preliminary definition of sampling strata. However, a review of the geology and soils of the physiographic provinces indicates that in some cases the province boundaries separate regions of similar geology and soils, but in other cases they combine regions with very different characteristics. Therefore, the physiographically defined strata boundaries described above are modified in two areas of the state: Western Maryland and the Coastal Plain.

Western Maryland

The western Valley and Ridge province has a geology very similar to the Appalachian Plateau. Because geology is extremely important in determining the sensitivity of surface waters to acidification in western Maryland, the stratum representing the Appalachian Plateau includes the western portion of the Valley and Ridge province for the MSSCS. Although, as previously noted, recent classifications of geographic regions with respect to their sensitivity to acidification have tended to incorporate the Blue Ridge into the Valley and Ridge province, geology of the Blue Ridge is sufficiently different from the Valley and Ridge to warrant its treatment as a distinct stratum.

Coastal Plain

In the Coastal Plain province, soil acidity and relative base saturation provide indications of surface water sensitivity to acidification. Coastal Plain soils tend to be shallow, and underlain by deep, unconsolidated sedimentary deposits. Bedrock is deeply buried and probably does not affect surface water quality. A review of average soil pH maps and percent base saturation maps for Maryland (PPRP 1987) indicates that soils in the southern portion of the Coastal Plain are more acidic and have lower base saturation values than soils in the northern Coastal Plain. Thus, the Coastal Plain is divided into two strata for the MSSCS.

The MSSCS sampling design therefore contains six strata (Appalachian Plateau and Western Valley and Ridge, Eastern Valley and Ridge, Blue Ridge, Piedmont, Northern Coastal Plain, and Southern Coastal Plain), as



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shown in Figure II-2. The strata are based on the physiography of Maryland, with modifications to account for geology and soils information. Because these strata reflect regional differences in surface water quality reported by previous studies, a gain in the precision of the estimated number of Maryland streams susceptible to acidification can be expected. These strata also will help assure ample geographic dispersion of sampling effort in the MSSCS and allow development of regional estimates of resources at risk for the Coastal Plain, Piedmont, and Western Maryland.

PHYSICAL AND CHEMICAL PARAMETERS

Six parameters (pH, ANC, dissolved inorganic carbon, dissolved organic carbon, conductivity, and color) will be measured routinely in MSSCS water samples. This suite of parameters allows identification of reaches that are acidic (pH) or potentially acid sensitive (ANC). The use of dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), conductivity, and color measurements provides an opportunity for identification of those reaches in which acidity may be derived from sources other than atmospheric deposition. DIC and DOC will be used as Quality Assurance and Quality Control (QA/QC) parameters, to assist in interpretation of pH, ANC, and conductivity data. Conductivity will be used to indicate the presence of marine influences, drilling brines, point sources of pollution, or AMD. DOC and color will be used as indicators of organic acidity. If a sample pH value is below 4.5, a strong mineral acidity titration will be performed as a QA/QC procedure to assist in identification of the source of acidity. Analytical protocols to be used for these procedures are specified in Table II-1.

QUALITY ASSURANCE AND QUALITY CONTROL SAMPLES

The MSSCS sampling design requires that data with known statistical properties be produced. The sampling design thus incorporates several types of Quality Assurance and Quality Control (QA/QC) samples, in addition to QA/QC measures applied at each step in the implementation process, as discussed in Chapter III. QA/QC sampling is designed to meet the following objectives:



Parameter	Units	Detection Limit	Precision Goal (%RSD)*	Accuracy Maximum Absolute Bias (%)	Maximum Holding Time (Days)	Method	Reference
рН			0.10 units	±0.1 units	1.5	Potentiometric, unequilibrated	Hillman et al. 1986
Conductivity	uS/cm	0.9	10	5	7	Wheatstone Bridge	EPA 120.1
ANC	ueq/1	**	10	10	14	Titration (modified Gran Analysis)	Hillman et al. 1986
DIC	mg/1	0.05	10	10	1.5	Infrared Spectro- photometer	EPA 415.2 modified
DOC	mg/l	0.1	5(≥5.0) 10(<5.0)	10	14	Infrared Spectro- photometer	EPA 415.2 modified
True Color	PCU		5		7	Color comparator	EPA 110.2 modified
Acidity***	mg/1	10.0	10	10	14	Potentiometric	EPA 305.1

TABLE II-1. PARAMETERS FOR WATER ANALYSIS, MSSCS

Computed as %RSD at 10 times the instrumental detection limit Blank titration \leq 10ueq 1⁻¹ *

* *

Performed as quality assurance analysis on samples with pH \leq 4.5 ***

- Evaluation of the error associated with sample collection and analysis
- Evaluation of analytical precision
- Evaluation of analytical accuracy

Three distinct types of QA/QC samples are employed to meet these objectives. Duplicate samples collected in the field are employed to evaluate the error associated with the sampling system (i.e., preparation of sample containers, sample collection, micro-scale temporal and spatial variability in the water quality of the reach being sampled, sample handling and transport to the laboratory). A minimum of 10 percent of the sampled reaches will be randomly selected for duplicate sample collection. When samples enter the laboratory they are organized into analytical batches. At this point 5 percent of the incoming samples (a minimum of 3 per batch) are selected for duplicate analyses. These samples are considered laboratory duplicates (or splits), and provide a means of assessing the precision or repeatability of an analytical procedure. If precision goals are not met for split samples, a series of quality control procedures are instituted as prescribed in the IS&T Laboratory Standard Operating Procedures Manual (Filbin and Turner 1986) to identify the cause of decreased precision and, if necessary, to flag data in the database. In addition to split sample analyses, audit samples of known chemical composition are inserted in the sample batch. Five percent of the samples analyzed (a minimum of 3 per batch) will be audit samples. These samples are used in addition to quality control check solutions and calibration standards to assure the accuracy of analytical measurements. As in the case of split samples, quality control procedures are instituted if accuracy goals are not met.

SAMPLING FREQUENCY AND INTENSITY

It is necessary to specify the number of samples to be collected from a reach (intensity) and, if more than one sample is to be collected, the time between sample collections (frequency). In addition, sampling intensity has a spatial context when discussing samples taken from a population of reaches. Sampling frequency and intensity are integral to sampling design and must reflect the objectives of the sampling program. In the MSSCS, the major objective of sampling is to develop information on the population of Maryland stream reaches of interest. It is important to note that the MSSCS has not been designed to establish the extent or potential extent of extreme conditions that may occur for very short periods of time. Instead, sampling for the MSSCS will provide information on the extent of conditions likely to result in the occurrence of extreme pH conditions within the population. Intensive data collection to document the occurence of extreme conditions will be addressed during the long-term monitoring program design process.

Individual streams may exhibit a great deal of variability in water quality annually, seasonally, and during very short periods associated with rain events. This variability makes it very difficult characterize water quality in an individual stream, even when a large number of samples is collected during a limited time period. Because the maximum number of samples that can be collected is fixed, collection of multiple samples on individual reaches (increased temporal intensity) reduces the total number of reaches (spatial intensity) that can be It was agreed at the Stream Survey Design Workshop that sampled. limiting the number of reaches sampled, in order to collect multiple samples from each reach, would not appreciably improve the precision of water quality estimates for individual streams over estimates based on collection of single samples. Additionally, the precision of estimates for the entire population might be significantly reduced by increased temporal sampling intensity on individual streams. For those reasons it was determined that the number of reaches sampled should be maximized by collecting a single sample from each reach during the MSSCS. Increased precision of estimates of water quality conditions in individual streams will occur as a result of implementing a long-term monitoring program.

To illustrate the effect of increased temporal sampling intensity, the initial estimate of the number of stream reaches in Maryland, after application of exclusion criteria, is approximately 6000. If 25 percent (1500) of the reaches sampled were considered sensitive to acidification,

then the variance of the estimated number of sensitive reaches (assuming simple random sampling) is given by Cochran (1977) as:

$$v (\hat{A}) = \frac{N (N-n)}{n-1} P q$$
⁽¹⁾

Where:

v = estimated variance A = estimated number of sensitive reaches N = total number of reaches in the population n = number of reaches sampled p = the proportion of sampled reaches considered sensitive q = 1-p

Assuming that 600 samples are collected during the MSSCS, the formula above indicates that $v(\hat{A})$ would more than double if two samples per stream were collected instead of one sample per stream. Thus the increase in precision of population estimates obtained by single samples from each stream is quite large relative to the likely precision increase for individual streams.

Timing of Sample Collection

It is desirable to ensure that the MSSCS data base represents the condition of the biologically important resource base consistently throughout the state. Seemingly, if all samples could be collected on the same date, this "snapshot" would allow for valid statewide characterization of resource conditions. However, both theoretical and practical considerations argue against such an "instantaneous" sampling effort, whether it was implemented statewide or regionally.

Statewide

Due to Maryland's physiographic diversity, similar seasonal conditions do not occur simultaneously throughout the state. The date of last freezing temperatures in spring, for example, varies from April 10 to May 30 from the extreme southeastern coastal areas to the highest elevations in western Maryland (Figure II-3). Thus the sampling effort must be scheduled to account for differences in phenology among different regions of the State.

Scheduling the sampling effort to accommodate differences in phenology among different regions also provides logistic benefits in use of personnel and equipment and in quality of training and support for samplers. Logistic considerations associated with a single, statewide, sample collection date would include coordination of large numbers of samplers without use of direct supervision, sampler training without instructor contact, reliance on couriers or commercial carriers for sample shipment, and high peak load demands on laboratory personnel and equipment.

The NSS used a sample collection period that covered the dates from March 15 to May 15. This period was selected for several reasons (USEPA 1985):

- Alkalinity and pH are typically low in streams during this period
- Spring pH depressions occur more ubiquitously than fall or winter depressions
- Acid sensitive life stages of important fish species are more commonly present during spring than during other seasons.

Based on these considerations, and the knowledge that anadromous spawning runs may begin in southeastern coastal streams during late February or early March, the sampling period selected for the MSSCS is March 1 through May 15. Sampling efforts will be regionally implemented to maintain reasonably constant phenological conditions.

Regional

At any moment, stream water quality reflects the antecedent climatological conditions and processes in the watershed or aquifer. Samples collected immediately after low pH rains have contributed to streamflow will reflect precipitation quality much more than samples



collected following an extended precipitation-free period in which ground waters provide the major contribution to streamflow. If samples within each region are collected on single dates, and samples from adjacent regions are collected following different weather conditions, differences in water quality observed between the regions may be solely artifacts of the differing antecedent conditions.

To reduce the potential influence of differing antecedent conditions, sampling regions will be delineated so that multiple strata are sampled on the same date, and no more than 50 percent of the selected reaches in any one sampling region will be sampled on the same date.

Number of Reaches Sampled

The maximum number of routine samples that will be collected is 600. This number is the maximum number of reaches that can be handled logistically, and represents approximately 10 percent of the expected population of interest after application of exclusion criteria. With the addition of field and laboratory QA/QC samples (discussed below) and special interest reaches, the number of samples actually analyzed will exceed 700, and possibly approach 750.

Precision of Statewide Estimates

A preliminary determination of the utility of any desired sample size can be obtained using the estimated total population size and making some assumptions concerning the true percentage of streams in the state that might be considered acidic. The relative error of estimates obtained using a sample of (n) reaches from a population of (N) reaches can be calculated for a given proportion (P) of reaches falling into a "sensitive" category using:

$$r^{2} = \frac{t^{2} (1 - \alpha/2)(N - n)}{n(N - 1)} \qquad \frac{Q}{P}$$
(2)
r	=	the relative width of a confidence interval about P	
Р	z	the true proportion of reaches falling into the sensitive	
		category	
Q	=	1-P	
n	=	the number of reaches sampled	
N		the total number of reaches in the population	
$t_{(1-\alpha/2)}$ = the value of the abscissa of the normal curve for		the value of the abscissa of the normal curve for a	
•		confidence interval containing 1-g of all estimates of P	

Thus for a P of 0.25 with 95 percent confidence ($\alpha = 0.05$), an estimate based on 600 samples from 6000 reaches can be expected to fall within <u>+</u> 13.1 percent of P. In this case, 95 percent of the time the estimated percentages of sensitive reaches would fall in the range 25 <u>+</u> 3.3 percent. The relative precision of the estimate improves as the proportion in the sensitive category increases.

Despite the fact that the data presented by Janicki and Greening (1986) do not represent a statistically valid sample for a comparable population of interest (larger streams were included), those data can be used to indicate the relative error that can be expected for estimates of proportions of sensitive stream reaches in Maryland. A review of these data indicates that the proportion of sensitive reaches in the population of interest is likely to exceed 20 percent thus resulting in a relative error of \pm 15 percent or less. This analysis indicates that a sample size of 600 is adequate to produce a fairly precise estimates of the resources at risk in Maryland.

Precision of Stratum Estimates

An analysis similar to the one above was performed for each of the sampling strata assuming proportional allocation of sampling effort and using preliminary estimates of the number of streams in each stratum. This analysis indicated that the relative error of estimates of proportions of sensitive reaches in areas such as the Coastal Plain and Appalachian Plateau would be acceptable, on the order of \pm 30 percent or less. However, in areas where few sensitive streams are expected, such as the Piedmont and Eastern Valley and Ridge, the relative error of estimated proportions could approach \pm 100 percent. In this case the interval in which an estimate is likely to fall is a better guide to the appropriateness of sample size. For example, if the proportion of sensitive streams in the Piedmont is on the order of 5 percent, then the estimated percentage of sensitive streams might be expected to fall between 1.5 percent and 10.5 percent. Thus, although the relative precision seems to be poor, the interval in which the estimate occurs is relatively narrow.

In the Eastern Valley and Ridge and Blue Ridge strata relatively few reaches would be sampled if all effort were allocated in proportion to the total number of reaches in each stratum. For these strata a minimum of 50 reaches will be sampled.

Optimum Allocation of Sampling Effort

The simplest method for allocating sampling effort among strata is proportional allocation. In this type of sampling, the proportion of the total sample size that is allocated to a stratum is equivalent to the proportion of the total stream population that is present in that stratum. In the absence of information on differences in the proportions of acidic or sensitive streams among strata, this approach is useful. Proportional allocation among geographic strata also helps assure a good geographic distribution of samples.

In Maryland, previous studies have indicated that large differences exist in the proportions of acidic and acid sensitive streams among strata (Harman 1984, Janicki and Greening 1986). Although the previous studies do not base their results on random probability samples and do not represent the population of interest defined for this study, these studies do provide data that can be used in developing a sample allocation scheme that will reduce the variance on the estimated proportion of affected or sensitive reaches in the population. Assuming

that cost per sample is the same for all strata, the following equation can be used to establish the optimum sample size for a stratum given a fixed total sample size:

$$n_{h} = n \frac{N_{h} \sqrt{P_{h}Q_{h}}}{\sum_{h=1}^{L} N_{h} \sqrt{P_{h}Q_{h}}}$$
(3)

Where:

ⁿ h	=	the number of reaches to be sampled from stratum h
n	=	the total number of reaches that can be sampled
N _h	=	the total number of reaches in stratum h
P _h	=	the proportion of sensitive reaches in stratum h
0 _h	=	1-P _h
L	=	The total number of strata

To develop a sampling allocation scheme for MSSCS, data from Janicki and Greening (1986) will be used to estimate P_h for the MSSCS strata. Although use of these data will not result in optimal allocation, this approach will reduce the variance in the estimated proportion of sensitive streams. When they become available, the actual numbers of streams identified for each stratum and for the statewide total will be used to determine the proportional distribution of samples among strata (minimum 50 reaches per stratum).

SUMMARY OF SAMPLING DESIGN

The sampling design for the Maryland Synoptic Stream Chemistry Survey is a stratified random design. Six sampling strata were selected based on physiography modified by geology and soils information:

- Northern Coastal Plain
- Southern Coastal Plain
- Piedmont
- Blue Ridge
- Eastern Valley and Ridge
- Appalachian Plateau/Western Valley and Ridge.

The population of Maryland streams of interest is defined as the population of all blue-line stream reaches on USGS 1:250,000 scale maps that are non-tidal, have drainage areas of less than 100km^2 , reach length greater than 300m, are unaffected by acid mine drainage or major point source discharges, and are not the tailwater streams for large impoundments. All stream reaches on the 1:250,000 scale maps will be listed and a stratified random sample of 600 reaches will be selected using this list frame.

One routine water sample will be collected from each of the 600 reaches during the course of the study. Each routine sample will be analyzed for pH, ANC, DIC, DOC, conductivity, and color. If sample pH is below 4.5, a titration for strong mineral acidity will be performed to assess the possible presence of acidity from terrestrial sources. Sampling and analytical QA/QC includes collection of duplicate samples at 10 percent of the reaches, analysis of split samples for 5 percent of the reaches (minimum of 3 per analytical batch) and analysis of audit samples added at a rate of 5 percent of the sample load (minimum of 3 per analytical batch). All duplicate, split, and audit samples will be analyzed for the same parameters as the routine samples.

The target precision for statewide estimates of the proportion of resources affected by, or sensitive to, acidification is a relative error \pm 15 percent. Precision of estimates for sampling strata will be somewhat less, but should be adequate in terms of absolute precision of the estimates.

CHAPTER III

SURVEY DESIGN IMPLEMENTATION

IMPLEMENTATION CONSIDERATIONS

Converting the sampling design into a field program to collect and analyze water samples from selected stream reaches requires coordination of several distinct activities, including: developing a data base and selecting streams for sampling, preparing for all aspects of field sampling, conducting field and laboratory operations, and maintaining high standards of quality assurance and quality control throughout the process. Each of these activities, while not strictly design elements, must be clearly prescribed and uniformly implemented to ensure that the MSSCS will produce a data base that ultimately will allow the design of an effective long-term monitoring program. The following sections discuss approaches that will be used to implement the MSSCS.

IMPLEMENTATION OF SAMPLING DESIGN BLEMENTS

To implement the survey design, the sampling design framework developed in Chapter II must be applied to generate Statewide and stratum-specific lists of stream reaches from USGS 1:250,000 maps. These lists will represent the stream reach population mapped prior to sample selection, and therefore must be complete and accurate. The approaches that will be used to develop the list frame data base (containing lists of stream reaches and their locations and lengths) and provide quality control during development of this data base are described below, followed by a discussion of the methods that will be used to select streams for sampling.

List Frame Data Base Development

A list identifying all non-tidally influenced stream reaches in Maryland will be created through a two-stage mapping exercise. First, all coastal stream reaches indicated on the 1:250,000 scale USGS

topographic quadrangle maps covering portions of Maryland will be marked to indicate the upper limit of tidal influence, using wetlands boundary maps supplied by the Wetlands Division, Maryland Department of Natural Resources. Second, the length and location (using UTM grid coordinates) of all non-tidally influenced stream reaches indicated on 1:250,000 scale USGS topographic maps throughout the state will be digitized (i.e., measured and recorded electronically) and stored in a computerized data base. This data base will be used in selection of stream reaches and some analyses of statewide or regional stream population characteristics, such as calculating total stream miles and estimating stream order frequencies. Stream reaches will be included in this data base if they flow into a confluence that lies within Maryland, or if they flow into tidal waters in Maryland.

Following stream reach digitization, the boundaries of each stratum identified in the Stream Survey Design Workshop will be digitized. Each stream reach then will be assigned to the stratum containing the confluence at the lower end of that reach. State and county boundaries also will be digitized and recorded in the data base. Additional mapped information including geological substrate, soil type, watershed area, vegetation cover type, and land use type may be added to this data base, if subsequent data analysis requires the use of these data.

To ensure the completeness and accuracy of the stream reach list, three quality control steps will be taken. The first will involve plotting each reach and manually checking to verify the continuity of all stream drainages. Reaches that are inadvertently omitted will be added to the data base to connect headwater systems with their downstream components. The second step will involve comparison of each digitized reach (plotted from the data base) with the same reach as it appears on transparent copies of drainage system overlay sheets of the five USGS 1:250,000 maps covering portions of Maryland. This process will allow evaluation of the adequacy of recorded location and length data. Streams that have been inaccurately recorded in location or length will be re-digitized, and reaches that have been omitted will be added to the data base. Finally, reaches in all coastal areas will be checked for

completeness of head-of-tide information by comparing reaches plotted from the data base with the head-of-tide maps to ensure that each coastal stream is terminated at a head-of-tide boundary. Each of the quality control steps described will be completed prior to reach selection. All errors that are detected after reaches have been selected will be recorded as mapping errors in one of three categories: original cartography, digitization, or head-of-tide delineation. These error statistics will be used in developing the quality assurance statistics for this project.

Sample Selection

Stream reaches to be sampled will be identified after all non-tidal streams are digitized and the stream data base is complete and quality checked. Reaches will be selected randomly, with no categorical exclusion of reaches prior to reach selection (other than tidal influences). After reaches have been selected, certain undesirable (non-target) stream types will be excluded, as discussed in Chapter II. Exclusion of these streams after selection will allow use of the exclusion rate to estimate the statewide number of stream reaches of the type excluded.

Random Numbering of Reaches

The selection of reaches for sampling will be done through a random ordering of reaches within each stratum. This will be accomplished by randomly assigning the number 1 to N_h , where N_h is the total number of reaches in the stratum, to all reaches in the stratum. A six-digit stream identification number will be assigned to each stream reach. The first two digits will be the county code, the third will be the stratum code, and the last three will be the random number assigned to that reach. For each stratum, the required number of streams will be obtained by simply taking that number of reaches from the ordered list for that stratum. If any of those reaches is subsequently excluded from sampling, the next reach selection.

Application of Exclusionary Criteria

Non-target stream reaches will be excluded from sampling. If the discovery that the reach is a non-target reach occurs after sample collection, flags will be added to the data base. Each excluded reach will be identified and the number of reaches excluded for each reason will be totalled. These data will provide estimates of the statewide and regional abundance of such non-interest reaches.

<u>Watershed Size.</u> Reaches with a watershed size greater than 100 square kilometers will not be sampled. Most reaches will drain watersheds that clearly differ from 100 km^2 , and manual inspection of the mapped reach, its tributary drainage system, and watershed topography will reveal this fact. However, for those reaches where watershed area is not easily discernible by manual inspection, the watershed as shown on a topographic map of suitable scale will be digitized to determine the watershed area.

<u>Acid Mine Drainage.</u> Reaches with known sources of acid mine drainage will not be sampled. Data available from the Maryland DNR, Bureau of Mines, and historical water quality data will be used to identify acid mine drainage affected sites. The data for reaches found to be affected after sampling will be so identified (flagged) in the data base.

<u>Chemically Affected Reaches.</u> Reaches with known point sources of chemicals (such as sewage outfalls and permitted discharges) will not be sampled. Such reaches will be identified by samplers and personnel obtaining site access permission, prior to initiation of sampling. Data from reaches discovered to be affected by chemical discharges after sample collection will be flagged in the data base.

<u>Impoundments.</u> Reaches serving as outlets for impoundments that appear on 1:250,000 scale maps will not be sampled. Small impoundments flush rapidly during elevated flow periods. For this reason, tailwaters from impoundments that appear only on 7.5-minute topographic maps, or that are detected during the sampling visit, may be sampled as described in the sample collection location rules described below.

<u>Unmixed reaches.</u> Extremely short reaches may not mix sufficiently to establish uniform water quality conditions. Therefore, any reach less than or equal to 0.3 km in length will not be sampled.

Special Interest Reaches

Special interest reaches are those which have been the subject of extensive research or monitoring in the past. No consideration of special interest reaches will be made during the random reach selection process. Some reaches that would qualify as special interest reaches may be selected for sampling during the random reach selection process. Data from any randomly chosen special interest reaches will be treated as any other data from randomly selected reaches. Special interest reaches that are not randomly selected, however, will be sampled as part of an additional study, at the same time as routine sampling. The data from non-randomly chosen special interest reaches will not be used in development of population estimates. These data will be used to relate the results of the MSSCS to known characteristics of streams that have been monitored for long periods.

FIELD SAMPLING PREPARATIONS

Samples will be collected from the selected streams by a volunteer workforce directed by the staff of IS&T. Before volunteers can collect samples, however, several additional tasks must be accomplished:

- Develop a sampling itinerary
- Prepare site information packets
- Obtain permission from land owners to collect samples
- Develop field protocols
- Recruit and train volunteer samplers

Each of these tasks of field preparation involves several components. The following description of these elements presents the final logistical design that will be used to implement the field sampling program.

Sampling Itinerary

Two objectives govern the itinerary for sample collection: maintenance of reasonably constant phenological status for all sampling efforts, and avoidance of sampling bias created by regional differences The date of last expected freezing in antecedent precipitation. temperatures and the strata developed in Chapter II were used to identify regions within the state where sampling operations could be centralized and conducted efficiently (Figure III-1) and to develop a schedule for sample collection within each of these regions (Table III-1). Within each of the sampling regions, only a randomly chosen 50 percent of the streams will be sampled during the first scheduled sample date. The remaining 50 percent will be sampled on the second date, to minimize the possibility that differing antecedent conditions could be statistically indistinguishable from differences among strata.

Site Information Packets

To assist in the process of obtaining site access permission, site information packets will be prepared. These packets also will assist field personnel in locating assigned sites for water sample collection. One packet will be prepared for each reach to be sampled, including both randomly selected reaches and non-randomly selected special interest reaches. Duplicate information will be maintained at the IS&T offices in case the original packet is lost or destroyed. Site information packets will contain the following items:

- A large-scale (USGS 7.5-minute topographic quadrangle) map with the selected stream reach indicated, a preferred sample location marked on the stream reach, and the stream reach identification number marked alongside the preferred sampling location.
- A site access permission form. A copy of this form will be completed for each site by the individual who obtains site access permission, to provide documentation of that process. It will be used by samplers to identify preferred access routes to the sample site and to verify site access permission, if required.



Figure III-1. MSSCS Field Sampling Regions.

TABLE III-1.

REGIONAL SAMPLING SCHEDULE

SAMPLE DATE	REGIONS TO BE SAMPLED
3-7-87	
	I
3-14-87	I, II
3-21-87	II, III
3-28-87	III, IV
4-4-87	IV, V
4-11-87	V, VI
4-18-87	Holiday, no sampling
4-25-87	VI, VII
5-2-87	VII, VIII
5-9-87	VIII

- A set of sampling instructions to reinforce the sample collection training program.
- Background information about the MSSCS to allow samplers to provide accurate information on the program to interested parties.
- A medium-scale, regional map to assist samplers in locating the selected reach.

The USGS 7.5-minute quad map (1:24,000 scale) that indicates the selected stream reach and preferred sampling location will be prepared from a list of the coordinates of selected stream reaches stored in the digitized data base. The preferred sampling location on each reach will be indicated, based on criteria described below, and the stream reach identification number will be indicated next to the preferred sampling location. If any route other than the most obvious route to the site is desired (e.g., due to property owners request) it will be indicated, Selected reaches shown on 1:250,000 scale USGS topographic maps also. will be compared with the same reaches as shown on 7.5-minute maps, for QA/QC. The 1:250,000 maps will be used in logistics planning and coordination of field sampling. The 7.5-minute maps will be used in the field, as aids in obtaining site access permission, and in sampling efforts.

Site Access Permission

Permission to collect samples from selected streams will be obtained from land owners of adjacent properties. On State and privately owned land, this process will be facilitated by personnel from the Maryland Forest, Parks, and Wildlife Service (FPWS). The FPWS is organized into districts (Southern, Eastern, Central, and Western), each of which includes several counties. Site information packets will be sent to designated FPWS personnel in each of these districts to assist in obtaining access permission in advance of sampling efforts in each region of the state. On Federally owned property, site access permission will be obtained by IS&T personnel. Many sites will not require that site access permission be obtained prior to sample collection, because they can be accessed easily from U.S., Maryland, or county roads without the sampler having to leave the right-of-way. State personnel from the FPWS will assist in identifying sites where access permission is not required.

Where it is necessary to obtain access permission, the following tasks will be performed:

- Identify the owner of the property surrounding the selected sampling point and any property intervening between it and the nearest public access point.
- Contact the owner to introduce the program and request permission to cross the property to collect samples.
- Document the site access permission process.

On State owned land, site access permission will be obtained by requesting the right to collect samples from the manager of the property, whether these lands are parks, forests, wildlife management areas, or other State lands. This process may be completed by FPWS personnel or by representatives of IS&T, depending upon the circumstances associated with each case.

On Federal lands, IS&T personnel will seek site access permission from the local manager of the property. This manager will be identified and contacted through the Federal agency managing the property. Where necessary, arrangements will be made to allow specific samplers to meet with Federal agency representatives to be escorted to sampling locations.

Once site access permission is obtained, all information that is pertinent to gaining access to the sample location is recorded on a site access information form, the site information packet will be returned to IS&T to be used in the field sampling program. All information in the packet will be identified with the stream reach identification number and will be copied and stored at IS&T to ensure the availability of back-up copies of critical information. If access permission is denied, then an alternative sampling point on the reach will be selected. If, after all reasonable sampling points have been investigated, site access permission cannot be obtained, then a replacement reach will be selected from the randomly ordered list of stream reaches within each stratum. Site access permission will be sought until the desired number of stream reaches is obtained in each stratum.

Field Protocols

During each field sampling effort, several judgements are required from each volunteer sampler. These judgements are necessary for the samplers to arrive at the selected stream reach, select a suitable sample collection location on the stream, collect a representative sample of the stream water, and appropriately label and handle the sample to return it to a sample receiving location. Protocols will be developed to regulate each of the judgements and procedures that are critical to the quality of the data base, namely: selecting a proper place in the stream to collect the sample, collecting and labeling a sample, and handling the sample after it has been collected. Each sampler will be trained in these protocols prior to collecting samples.

Sample Collection Site Rules

The preferred location where streams should be sampled will be marked on the 7.5-minute quadrangle map depicting the stream reach. This location will be selected using the following criteria, as applied to the stream reach as depicted on the 7.5 minute map:

- If a road bridge crosses the reach at any point, the sample will be collected approximately 100 feet upstream of this bridge.
- If multiple roadway bridges cross the reach, the sample will be collected approximately 100 feet upstream of the bridge at the lower end of the longest unobstructed segment of the reach.
- If no bridges cross the reach, the sample will be collected at least 100 feet upstream of the confluence at the lower end of the reach.

- Where the lower end of most stream reaches are flowing through limestone substrates in the limestone outcrop regions of Western Maryland, the sample will be collected at a location slightly upstream from the break in slope from ridge to valley. Where agricultural land in these areas creates a tree line at the base of slopes, the sample will be collected slightly upstream from the line of trees marking the toe of the ridge and the edge of agricultural land.
- If impoundments appear in the middle of reaches shown on the 7.5-minute maps where no impoundments were shown on the 1:250,000 scale maps, then the sample will be collected upstream of the impoundment. If no segment of the selected reach drains into the impoundment, then the sample collection point will be located 100 feet upstream from the downstream termination of the reach (confluence, impoundment, head-of-tide), or at the lowest point on the reach that conforms to the previous sample collection site rules.

If no sample collection point is identifiable using these criteria, then a new reach will be selected.

Samplers will be instructed to move upstream or downstream from the preferred sampling location marked on the map, if a sample cannot be collected at that location. In the field, the precise location for sample collection will be chosen by the volunteer samplers. The criteria for choosing sample collection locations on stream reaches are as follows:

- Samples will be collected from flowing stream water. Swirling, eddying, or slack water areas are to be avoided.
- Samples will be collected at least 100 feet upstream of any bridges or channel obstructions.
- Samples will be collected at least 100 feet upstream of the downstream confluence of the reach.
 Samples will be collected from, or at the lower end of, riffles in the stream, where possible.

- Samples will be collected upstream from actively eroding stream banks, where possible.
- Samples will be collected on the upstream side of any metal or organic debris in the water.

A list of these criteria will be included in the site information packet.

Sampling Protocols

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To ensure that all samples are collected uniformly and to minimize the possibility of contaminating samples, samplers will be trained in sample collection protocols. In addition, a list of these protocols will be included in the site information packets for each site. The sample collection protocols are as follows:

- If possible, collect the sample without entering the flow. If the sampler enters the stream to collect the sample, collect the sample on the upstream side of the sampler, in a region of uniform flow that is not disturbed by the presence of the sampler.
- Do not disturb bottom sediments. If bottom sediments are disturbed, move upstream to collect the sample in an area of flow that is not disturbed by the presence of the sampler.
- Wear disposable gloves during the entire sample collection process.
- Hold the sample bottle with the hand well back from its mouth.
- Prior to sample collection, completely rinse the sample bottle, cap, and beaker (or second sample collection bottle) at least three times with stream water from the sample location. Discard all rinse water on the downstream side of the sample collection location. (Note: All samplers will be provided with spare sample bottles and clean disposable beakers for use in collecting samples from shallow water, and to assure sample collection if the primary bottle is lost or contaminated.)

- If possible without disturbing bottom sediments, immerse the bottle completely in the flow and fill it completely. If the bottle cannot be completely immersed, use a beaker or spare sample container (rinsed three times) to completely fill the sample bottle. Use great care to avoid disturbing bottom sediments.
- Fill the sample bottle completely with stream water. Rinse the cap and, if possible, screw it onto the sample container while holding both cap and bottle underwater. Do not place either hand in front of the sample bottle opening.
- Turn the sample bottle upside down and check to see if an air bubble is present. If an air bubble larger than about 10 cc (one teaspoon) is present, discard the sample, rinse the container three times, and collect a fresh sample.
- If, at any time in the sample collection process, the sample collection bottle becomes contaminated with sediments generated during the sampling process or by having a hand in front of the sample opening, discard the sample, rinse the container three times, and collect a new sample. Move upstream a short distance, if necessary.
- If the sample is grossly contaminated (for example, by being dropped and spilled) use a spare sample bottle to collect a new sample.
- Collect duplicate samples immediately following the routine sample at the same location as the routine sample. Move upstream a short distance, if necessary.
- In the notebook provided, record observations regarding site conditions, presence of sediments or turbidity in the stream, and a description of the route traveled to reach the site.

Sample Labeling and Handling Protocols

All samples will be identified using a gummed, waterproof label. The site identification number and stream reach name (if any) will be entered on the label prior to sample collection. Immediately before sample collection, the date, and time of sampling, and the samplers name will be added to the label.

Following sample collection, the sample bottle will be placed in a sealed plastic bag and placed in a cooler with ice for transportation to a sample receiving facility. An IS&T representative will sign the label when the sample is received. All samples collected on a single day will be placed in iced coolers for transportation to the IS&T laboratory in Sterling, VA, where they will be received the same day they were collected.

Volunteer Sampler Recruiting and Training

The sample collection effort requires the availability of a large number of samplers to collect a sample from each of the selected reaches. Volunteers will be recruited, organized and trained to perform the duties of field samplers for the MSSCS. Volunteers will be recruited through the use of press releases about the survey and presentations to volunteer organizations such as Trout Unlimited and Maryland Save Our Streams. Volunteer recruitment will be coordinated by Mr. James Gracie of James W. Gracie and Associates. The recruitment effort is intended to enlist volunteers in all areas of the state. When sufficient numbers of volunteers have been recruited for sample collection in each of the sampling regions, these samplers will be organized into "telephone trees" for information exchange.

To ensure a high quality data base, all samples must be collected using uniformly applied collection protocols and they must be representative samples of the stream reaches where they were collected. A training program will be conducted to ensure that all volunteers are properly trained and competent in sample collection procedures. This training program will consist of three components: an introduction to the MSSCS, presented at volunteer recruitment meetings; mailings, to distribute schedules and background information; and a training session covering sample collection protocols, held on the day of sample collection.

Presentations made at meetings of volunteer organizations will include a preliminary discussion of acid rain, followed by an overview of

the MSSCS and an introduction to the use of volunteers in the sampling program. A slide show will illustrate the types of conditions to be expected in the field and will present an introduction to sample collection methods.

Before the sample collection day, written procedures and sample collection protocols will be mailed to volunteers. These procedures will include simple directions for implementing each step of the sample collection process. Illustrations will be used where necessary to clarify the instructions.

At the start of each sample collection day, a sample collection training session will be held at the field headquarters site. All volunteers who will be collecting samples that day must attend. This session will include individual instruction in sample collection, handling, and transport, and will involve sample collection practice on a stream near the field headquarters. Volunteers also will be given a briefing on the goals and objectives of the MSSCS, including the importance of the synoptic sampling program to establishment of a long-term monitoring program for the state. Each sampling team will have a copy of sample collection protocols for reference if questions arise in the field.

FIELD OPERATIONS

Field activities will be organized around a regional field headquarters that is centrally located within each of the sampling regions. As the logistical center for field coordination, these headquarters locations will be the place where samplers gather to receive instruction in sample collection protocols, sample collection site assignments, site information packets, and necessary supplies. An additional field headquarters may be established within a remote part of a region. In addition to pre-sampling activities, field headquarters locations will be the final drop-off point for collected samples.

At least one IS&T representative will remain at each headquarters throughout the time that volunteers are in the field. When a sample is brought to the center, the IS&T representative will sign the label and place the sample in a cooler at 4°C for shipment. When all samples have been received, the field coordinator will inform the IS&T laboratory of the number of samples collected and the expected arrival time at the laboratory. Samples will be driven from the headquarters to the IS&T laboratory in Sterling, VA.

All volunteers will receive the phone number and directions to the headquarters prior to sample collection. The field coordinator will have topographic and highway maps for the particular region, to address questions that may be received by telephone from samplers regarding access routes, stream locations, or other logistical problems. The field coordinator will also have names, social security numbers, and descriptions of all samplers; telephone numbers of all parties contacted for access permission in that region; and telephone numbers for search and rescue and other emergency services for the region. All field samplers will be required to sign a register and provide a social security number to enable the State to provide liability insurance.

LABORATORY OPERATIONS

All analyses of sample parameters will be conducted at the IS&T laboratory. Samples (routine and duplicate) will be received at the laboratory on the same day as they were collected. Batch and sample identification numbers will be assigned to each sample. At this point, a number of audit samples equal to 5 percent of the batch (or a minimum of 3) will be inserted at random into the batch. The batch and sample numbers of all samples will be copied onto the field labels, then the portion of the field labels that show the sample site identification data will be removed and archived. All analysts will be "blind" to whether a particular sample is a routine stream sample, an audit sample, or a duplicate stream sample. Immediately following assembly of the batch of samples, 10 percent of the samples (or a minimum of 3) will be chosen at random and identified for duplicate analysis of all parameters for quality assurance.

Each sample will be opened in a clean work station and two closed aliquots will be withdrawn into 60 ml syringes that will then be sealed using syringe valves. These aliquots will be used for non-air equilibrated determinations of pH and DIC. The sample bottle will be recapped tightly. The syringes will be labeled with batch, sample, and analysis identifiers. All aliquots will be stored under refrigeration until used, except that the pH aliquot will be allowed to equilibrate to laboratory temperature prior to measurement (which must be within 24 hours of collection).

The following water chemistry parameters will be measured on samples from all streams: non-air equilibrated pH, acid neutralizing capacity (ANC), dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), conductivity, and true color. The analytical methods, accuracy, precision, detection limits, and maximum permissible holding times for each of these parameters and the quality assurance parameters are presented in Chapter II.

QUALITY ASSURANCE AND QUALITY CONTROL

Each element of the design implementation program will be quality controlled (i.e.: correctible errors will be corrected) to the greatest extent possible. Whenever possible, independent processes will be utilized to detect errors in mapping, sample selection, and calibration of analytical instruments. Where error correction is not possible, or would affect the consistency of the data base, errors will be recorded without correction, and the appropriate data will be flagged, to provide quality assurance (i.e.: quantification of the quality of the data base). Additional quality assurance will be provided through the analysis of dissolved inorganic and organic carbon in all samples. Strong mineral acidity will be determined in samples with a pH of less than or equal to 4.5. Table III-2 lists the quality control steps that will be taken and the quality assurance measures that will be employed throughout the survey. In addition, the analytical methods, accuracy, precision, detection limits, and maximum permissible holding times for analytical quality assurance parameters were previously specified in Table II-1.

Process	Quality Control Steps	Quality Assurance Measures
Map Digitizing	 Manual and electronic inspection of drainage system plots for continuity and duplication 	1) Documentation of errors detected after reach selection
	 Manual comparison of digitized stream system plots with USGS 1:250,000 drainage system transparencies for completeness and accuracy 	
	3) Manual comparison of coastal streams with DNR Critical Areas Program head-of-tide aerial photomaps for completeness and accuracy	
	 Hanual and electronic inspection of stratum boundary and political boundary plots for accuracy 	
Reach Selection	 Digitization, prior to sample collection, of watershed area for reaches with watersheds of approximately 100 km² 	 Documentation of errors in identifying large watersheds when detected after reach selection
	 Manual screening of known acid mine drainage locations 	2) Documentation of all AMD or chemically affected sites discovered during or after sampling
	 Expert and knowledgeable local individual review of acid mine drainage and chemically affected reaches. 	 Documentation of cartographic errors observed by samplers during sampling
	 Preferred sample location criteria and field sampler training to avoid impoundment tailwaters 	4) Documentation of sampling errors observed in IS&T audit visits during sampling operations

TABLE III-2 QUALITY CONTROL AND QUALITY ASSURANCE MEASURES

TABLE III-2 (CONCLUDED) QUALITY CONTROL AND QUALITY ASSURANCE MEASURES

Process	Quality Control Steps	Quality Assurance Measures
Sampling Program Logistics	 Manual checking of downstream confluence coordinates of selected reaches as mapped on 7.5-minute maps versus their downstream confluence coordinates from the data base 	1) Documentation of erroneous mapping when discovered after sampling
	2) Training program for samplers to ensure orienteering ability	2) Field audits, using IS&T personnel, to detect and document sampling team errors in locating indicated reaches, locating sampling sites on those reaches, and applying sample collection and handling protocols accurately
	3) Training program to ensure uniform sample collection methods, labeling, and sample handling	
Analytical Procedures	 Indivídual copy of calibration protocols and analytical procedures for each analyst 	 Log books maintained by each analyst, to record all calibration values, instrumental problems, and observations
	 Field duplicate samples collected at 10% of streams 	2) Documentation and analysis of field duplicate values
	3) Laboratory duplicate (split) samples analyzed for 5% of each analytical batch (minimum 3)	 Bocumentation and analysis of laboratory duplicate and audit sample results
	 Audit samples inserted in each analytical batch (5% of batch size, minimum 3) 	
	5) Strong mineral acidity titration for all samples with pH less than 4.5	

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CHAPTER IV

ANALYSIS OF SURVEY DATA

INTRODUCTION

Preliminary analysis of data collected during the MSSCS will develop population estimates to meet the design objectives of the survey, as described below. In addition to population estimates, classification analyses will be used to identify groups of streams with similar characteristics. Following initial development of population estimates and classification analyses, a data analysis report, comprising the preliminary study results and recommendations for further analyses, will be submitted to PPRP for peer review. The objective of peer review will be to identify the nature and scope of further data analyses required to develop the Long Term Monitoring Program. Following these analyses, a workshop will be held to complete the data analysis review and to develop the Long Term Monitoring Program.

POPULATION ESTIMATES

In a stratified random sampling design where the total number of reaches in the population of interest within each stratum is estimated, the estimate of the proportion of streams in a sensitivity category is:

$$P_{st} = \sum_{h=1}^{L} \frac{N_h a_h}{N_h n_h}$$
(4)

L = the number of strata

The variance of \mathbf{p}_{st} is estimated as:

$$v (p_{st}) = \frac{1}{N^2} \sum_{h=1}^{L} \frac{N_h^2 (N_h - n_h)}{N_h^{-1}} \frac{p_h q_h}{n_h}$$
(5)

Where:

N,
$$N_{h}$$
, n_{h} , and L are as above

and,

 $q_h = 1-p_h$

The total number of streams in a sensitivity category and the confidence interval about that total can be estimated using p_{st} and $v(p_{st})$.

The variance estimator presented in equation (5) is a simplified form of the variance estimator that will be used to develop confidence intervals about population estimates. Equation (5) ignores sources of variance (e.g., analytical imprecision, temporal variability in regional stream hydrologic state) other than the variance introduced by random selection of reaches. A refined variance estimator will be developed to account for other sources of variation prior to analysis of the MSSCS data.

Estimating the number of stream miles affected by or sensitive to acidification requires that some assumptions be made about the water quality of reaches upstream from a sampled reach. Several approaches may be utilized. In the simplest approach, it will be assumed that reach water quality measurements apply only to the sampled reach. Another approach may use the assumption that water quality of a reach reflects the water quality of all reaches upstream (i.e., the drainage length for that reach). In this instance, all reaches upstream of a sampled reach will be considered to belong to the same sensitivity category as that reach. Additional approaches may utilize the data from groups of upstream tributary reaches and downstream receiving water reaches to estimate the relationship between upstream and downstream acidification sensitivity.

For each of these approaches, the population parameter that will be estimated is the proportion of resources (i.e., stream miles) presently affected by, or at risk from, acidic deposition. This parameter will be estimated by the proportion of stream miles in the population of interest that are acidic or acid sensitive. This quantity and its variance will be estimated using methods for ratio estimators presented in Cochran (1977).

CLASSIFICATION ANALYSIS

The population estimation techniques discussed above all involve classification of reaches according to some parameters or combination of parameters. The classifications are assumed to be binary; that is, reaches will be classed as either "sensitive" or "non-sensitive." In estimating the resource potentially at risk, individual estimates of p_{st} (and its 95 percent confidence interval) will be developed for several classifications. For example, the class containing reaches considered to be acidic might be defined at four different pH values (eg. pH equal to 5.0, 5.5, 6.0, or 6.5). A separate estimate of p_{st} and its confidence interval will be developed for each binary classification.

This approach allows organization of data according to our present knowledge of the sensitivity of various biological resources to acidity. This type of a priori classification has the disadvantages of potentially separating similar stream types or, conversely, of grouping dissimilar types. Usually such classifications are based on few variables. As a result, much of the information available for classification may be ignored. Exploratory multivariate analyses such as cluster analysis and discriminant analysis provide a means by which all the information available, including water quality and watershed data, can be employed in classification. It should be noted that a priori classifications are required for discriminant analysis, and are often useful in certain types of cluster analysis. A priori classifications based on few variables and exploratory multivariate analyses complement each other in developing a thorough understanding of the factors governing classes of streams. The information provided by such analyses may be of great utility in designing the long-term monitoring program, by helping to identify streams considered typical of general categories of Maryland streams.

CHAPTER V.

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