Massachusetts Water Watch Partnership
Volunteer Water Quality Monitoring Manual

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Principal Authors: Geoff Dates, River Watch Network; Jerry Schoen, MassWWP, Paul Godfrey and Mark Mattson, UMASS Water Resources Research Center; Karen Pelto and Maria VanDusen, Massachusetts Department of Fisheries, Wildlife and Environmental Law Enforcement Riverways Programs.

Reviewers: Kevin Curry, Greater Springfield Riverwatch; Carolyn Somes, North and South Rivers Watershed Association; Bill Dunn and Paul Hogan, Massachusetts Department of Environmental Protection, Technical Services Branch; Carmen DiFillipo, Pepperell Wastewater Treatment Plant.

Additional Assistance: Jacob Tinus, Riverways intern; Barbara Offenhartz, Organization for the Assabet River, Gene Berkowitz, technical support.

Compiled and Edited By: Karen I. Pelto, Stream Ecologist, Massachusetts Riverways Program.

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The Massachusetts Water Watch Partnership
Jerry Schoen, Coordinator
Blaisdell House
University of Massachusetts
Amherst, MA
(413) 545-5532

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i. Why Monitor?

You are your local river or stream's greatest resource and closest ally. Whether aimed at pinpointing trouble spots, restoring fish or shellfish, or evaluating overall river health, water quality monitoring as a tool for river or stream protection is well within your grasp.

Every river is a reflection of the land it flows through. The natural chemistry of your stream is influenced by factors such as geology, climate, and vegetation, and, in part, determines what types of plants and animals will live and thrive there. Human activities can alter natural stream chemistry and biological communities. Water quality monitoring can provide you with an understanding of your river's natural conditions and constraints as well as human-caused changes.

Our best hope for retaining wonder and a sense of place in the natural world is to protect and bring back to life those systems which we've impoverished and abused. Water quality data gathered by trained volunteer monitors can augment the assessments performed during the Commonwealth's basin permitting process and be useful locally for increasing public awareness and informing board decisions. Sound solutions to water quality problems depend upon a knowledgeable and concerned public. A great way to start the job is to train ourselves to listen to the river, to learn its needs, and to heed its voice.

"Monitoring" is flush with opportunities - let the river tell you what to look for! Many kinds of monitoring are available to help you evaluate your stream, including chemistry and aquatic macroinvertebrate surveys through the MassWWP, land use through Riverways' Shoreline Survey, discharges through an NPDES inventory, or fisheries through a Physical Habitat Survey. A bit of research by you at the outset about your river's character and your group's financial and people resources will help guide you toward the type of monitoring that will yield the most helpful information.

Whether you decide to do chemical, physical, biological, or land use monitoring, any form of data collection that is done systematically over time will begin to show trends in stream health. Persistence and consistency are the bywords.

This *Manual* offers technical guidance on basic chemical and bacterial indicators, including dissolved oxygen, pH, alkalinity, and fecal coliform. Macroinvertebrate survey training is a companion service of the Massachusetts Water Watch Partnership. A Guide for macroinvetebrate monitoring is also available through the MassWWP. Shoreline Survey manuals and training, NPDES brochures, and Physical Habitat Survey guidelines and training are available through the Massachusetts Riverways Programs. Contact them at 617-727-1614 ext. 359.

ii. Introduction

Welcome to the Massachusetts Water Watch Partnership!

The Massachusetts Water Watch Partnership is a statewide collaboration of citizen volunteers, environmental organizations, state agencies, schools and universities, and industry formed to foster lay monitoring of river and lake water quality. Using a combination of public and private resources, MassWWP provides study design, training, equipment advice, quality control assistance and help on data interpretation and use to volunteer water quality monitoring programs.

By participating in MassWWP, you will become part of a network of citizens mobilized to collect, evaluate, and act on scientifically credible water quality information for the benefit of Massachusetts rivers and streams.

Founded in 1990, MassWWP continues to grow. To date, principal planners and supporters include the University of Massachusetts Water Resources Research Center, the River Watch Network, Riverways Program of the Massachusetts Department of Fisheries, Wildlife and Environmental Law Enforcement, Massachusetts Department of Environmental Protection's Technical Services Branch, Congress of Lakes and Ponds, Trout Unlimited, Millipore Corporation, and Monsanto Chemical Company. It has evolved from citizen interest and a number of monitoring efforts on rivers across the state.

Please use this *Manual* to introduce yourself and your river group to water quality monitoring. It contains information on key aspects of launching a successful monitoring program, including study design, building a successful program, field and lab techniques, and quality control. Detailed protocols are provided for sampling and measuring dissolved oxygen, pH, alkalinity, and fecal coliform. These protocols reflect MassWWP's data quality requirements. They do not represent the only way to take and analyze water samples, nor are they the only parameters you may want to measure. MassWWP can offer advice and guidance on methods for other water quality indicators. A matrix of options is provided in Appendix E.

How Do You Get Involved?

While the needs of each river and river group are different, getting involved with the MassWWP is a straightforward process. The time commitment involved depends upon the resources and interest of your group and complexity of your river's needs.

First, an informal meeting is held to explore freely your concerns about the river and dreams for its future. We will help you set goals and make plans to achieve them. To decide what type of monitoring is right for you and your river, you will review existing water quality data and collect initial land use and landowner information, perhaps through a Shoreline Survey. This is a time for you to discuss options available to your group, including chemical and biological monitoring with MassWWP's assistance.

Following this, a scoping session is held to outline services that MassWWP can provide to your group, and to discuss the types of information provided by water quality monitoring that can help meet your river's most

pressing needs.

A subcommittee of your group will then work with MassWWP to develop a series of questions about your river's health that will form the basis of your study design. This is the time for evaluating available resources and setting priorities.

Focussing on the top river needs, MassWWP will help you choose sampling sites and water quality indicators that you can measure. Finalizing the study design involves developing a monitoring schedule, recruiting volunteers, and performing public outreach.

The final step before you will be ready to take to the river is attendance at a MassWWP training session, where you will learn the proper way to take samples in the field, analyze them in the lab, assure quality control, and monitor safely.

How To Use This *Manual*

This *Manual* is intended to be used in conjunction with training, advice, and assistance from MassWWP. However, you will find it a useful tool to become familiar on your own with the process of developing a volunteer water quality monitoring program, as it provides many opportunities for research and "homework." The better prepared you are, the better able MassWWP will be to assist and advise you.

Part One: Getting Ready provides important background information that you will need in order to understand why you will be sampling your river and what your investigations can tell you. A water quality monitoring program is only as good as your preparation. Attention paid at the start to study design, a healthy organization, and quality control will yield rewards for your river and the people involved in your program. We urge you to read this carefully before you immerse yourself in the "nuts and bolts" of how to take and analyze a water sample.

Part Two: Getting Underway describes water quality indicators and MassWWP procedures for field sampling and lab analysis, including critical safety guidance. Equipment checklists, field and lab data sheets are provided.

The **Appendices** include a copy of the 1990 Massachusetts Surface Water Quality Standards, equipment and supply lists for the parameters described in the *Manual*, references for further reading, and additional information on indicators beyond those described in this *Manual*.

To the Reader:

This *Manual* is designed for easy reference and frequent use. Please feel free to photocopy procedures, worksheets and data sheets. If you have any questions or suggestions for future editions, please let us know!

How did you learn about this *Manual*?

Are you a new ___ or established ___ group?

Comments on the First Edition:

Suggestions for future Editions:

Mail your comments to:

Massachusetts Water Watch Partnership
Blaisdell House
University of Massachusetts
Amherst, MA 01003

Thank you!

Part One: Getting Ready

I. River Ecology

Rivers offer areas for swimming, boating, fishing, or waste disposal, and sources of water for generating energy, drinking, snowmaking, irrigating crops or fighting fires. But they are more than their sum of human uses. They are "home" to an interconnected web of creatures, many of which we never see and rarely think about. Yet, many of the uses we make of rivers have tremendous impacts on natural communities, making the health of rivers our responsibility. This section will explore our rivers as natural communities and describe how human land and water use affects them.

The River As A Community

Once we begin to consider the river as a web of living organisms bound together by water, we should begin to wonder how river users affect how that biological community functions.

We can think of river communities as having physical, chemical, and biological attributes:

The **physical** layout and foundation for a river community is flowing water and its relationship to the land area that drains into the river - its watershed. It's water rushing through a gorge, or flowing lazily through a farm meadow. It is a physical process, as runoff flowing over land and groundwater flowing underground replenish the river with water, sediment, and nutrients. In turn, the river influences the land by cutting its channel through rock and soil, and carrying the eroded material downstream. Shallow rapids where water flows over submerged rocks or *riffles*, calm gentle *glides*, deep slow *pools*, and stagnant waters along the river margin or *backwaters*, provide a variety of habitats for fish, waterfowl, and aquatic invertebrates.

The river's **chemical** characteristics are the basic building blocks for river life. These are the water's oxygen content (dissolved oxygen or DO), acidity (pH), ability to neutralize acid (alkalinity), nutrients, metals, and other constituents. In the absence of human influence, the water chemistry is determined by the soils and rocks in the watershed, the chemistry of the precipitation, and interaction with plants and animals on land and in the water. It profoundly affects, and is affected by, aquatic organisms.

The **biological** inhabitants of river communities are wonderfully varied - from single-celled plants and animals, aquatic insects, and other small residents, up through large fishes and waterfowl. Flowing water is the thread that binds this living community together within itself and with the surrounding land.

How does this web of life work?

A leaf falls into a small stream high in the mountains. It is quickly attacked by bacterial, fungal, and macroinvertebrate *decomposers.* Some of the nutrients in the leaf are dissolved into the water, and flow downstream until taken up by aquatic plants.

Aquatic insect *shredders* (such as caddisfly larvae and snails) feed on the leaf and its attached "frosting" of decomposers.

Meanwhile, *grazers* (such as mayfly nymphs), feed directly off living aquatic plants. Grazers and shredders reduce plant tissue to smaller particles, some of which is used by the insect to grow. Excreted or unused food is washed downstream.

This "detritus" provides food for the *collectors* such as black fly larvae and worms, which are waiting downstream to catch a meal. The insects themselves provide food for other predatory insects and fish. As the river flows downstream, some organic material is stored (as insect or animal tissue), some is cycled (changed to different forms), and some is released. Downstream, aquatic communities take advantage of inefficiencies upstream.

As you can tell from the above cycle, river communities are not homogeneous, nor are they static. A river community changes dramatically from its headwaters to its mouth, from season to season, and from year to year. However, healthy rivers are remarkably stable communities due to the diversity of organisms living there. A diverse river community indicates that a menu of food choices is available. Reducing these choices by physical or chemical alteration decreases community diversity. Since many aquatic organisms are opportunistic, they can adapt to changes in the food supply. Organisms that are most effective at using the remaining food sources will dominate, others may disappear. Serious disruptions may eliminate large segments of the community. This is what is meant by loss of biodiversity.

Human Impacts on River Communities

People can affect rivers directly by dumping things in them or changing their channels or indirectly by changing the land through which the rivers flow. To see how, let's assault a hypothetical river.

First, we'll cut down the trees along the banks and pave the watershed. Then we'll add sediment and nutrients from urban areas, crop land, lawns and golf courses. We'll dam the river, dump sewage into it, pump water out of it, and, for good measure, excavate the bed for sand and gravel. What have we done to this river community? A whole chain of events is set in motion throughout the aquatic ecosystem.

Removing trees from the banks means less food from leaf fall, and warmer water temperatures as the sun strikes and heats more of the water surface. Since most biochemical processes speed up as the temperature increases, warmer water can push the system into high gear. Decomposers work and use oxygen at a faster rate. To compound the problem, warm water holds less oxygen than cold water. Some species can't survive in warm water, either due to lower oxygen levels, or because they are sensitive to heat. Also, loss of large woody debris such as fallen logs and root wads removes hiding and resting areas for fish, known as "cover."

Impervious road, parking lot, and roof surfaces speed up the over-land flow of water, which means more water gets to the river faster. Higher flood flows during spring and fall, more channel scouring, and more erosion (since there's more energy and soil particle-disloging potential) are the result. Less water is able to infiltrate the soil to replenish groundwater, so lower summer flows occur. Asphalt surfaces also heat the water entering the river. Pollutants such as oils, trash and even dirt are washed right into the river instead of being filtered through the soil.

Now let's add some **sediment** from eroding crop land, construction sites, logging areas, and bank erosion. Sediment buries the homes and clogs the gills of many aquatic organisms, and catches and holds heat from the sun, causing warmer water temperatures. Often, nutrients and other pollutants, including heavy metals and toxics, attach to sediment, adding to the damage it causes when washed into streams. Habitat alteration from sedimentation is one of the leading causes of fishery decline.

Adding **nutrients** to a river encourages aquatic plant and algae growth. These plants may create wild swings in oxygen levels, as they release oxygen during the day and along with aquatic animals and decomposers consume it at night. When the plants and algae die and decompose, more oxygen is used. Again, aquatic

organisms may suffocate, especially in the dark hours of early morning.

A **dam** changes the physical foundation of the river when it replaces rapids and cascades with a reservoir. Above the dam, water velocity is slowed, causing soil particles and organic material to settle to the bottom and cover the river bed with mud. Oxygen levels are reduced as the organic material, which previously flowed downstream, decomposes. At the same time, oxygen is not replenished as quickly in the reservoir as it was in the rapids. Downstream of the dam, the flow and oxygen levels may fluctuate dramatically, if water is daily stored and released. The food supply from upstream is reduced. Temperature changes may cause a trout fishery to be succeeded by a warmwater bass population.

Sewage means decomposing organic material, which cosumes oxygen and adds nutrients to the water. The decomposers go to work. As they work, they breathe in oxygen, breathe out carbon dioxide and create an oxygen demand. If we put too much organic material in, the river can't replace oxygen fast enough and the demand exceeds the supply. Fish like salmon and trout need high oxygen levels in the stream to survive. So do the egg and juvenile life stages of other fish species. Aquatic organisms that need the most oxygen will suffocate first, reducing the food choices for surviving species. If the oxygen drain continues, more species will perish, reducing the food choices further. In Massachusetts, late summer is a stressful time for fish, as water levels drop, water temperatures rise, and dissolved oxygen levels decrease. Added organic or nutrient loads can cause fish kills. Sewage also brings in bacteria and pathogens, making the water unsafe to drink or swim.

Natural **droughts** in late summer can be exacerbated by withdrawals of water from the river directly or through groundwater wells. Shallower waters and lower flows mean less living space is available to fish and other aquatic organisms, increasing competition for food and predation. Lower oxygen levels and increased temperatures stress fish, making them more susceptible to bacterial infections.

The **bulldozer** or bucket loader pulling gravel out of the stream changes the physical habitat available for some insect and fish species in addition to causing sedimentation by stirring up the streambed.

Not only do these individual actions cause impacts, there is a cumulative impact that may go far beyond the sum total of the individual impacts. Most any river in Massachusetts has been subjected to this treatment at some time it its relationship with humans. This not-so-hypothetical river can no longer support the same aquatic community it once did. Monitoring will help you identify the changes that may be occurring in your river or stream as well as lead you to ways to protect and restore it.

II. How To Design a River Water Quality Monitoring Study

Building credibility begins before you collect your first river sample. It begins with the study design process: deciding and documenting the why, what, where, how, and when of your monitoring effort. In many ways, study design is the most important step in your whole monitoring program. If you don't do this step, then

you may spend a whole lot of time and money on equipment and procedures that are inappropriate

you may look at the wrong things at the right places or the right things at the wrong places

you may end up not answering the question you asked, or you may answer a question you didn't ask, or worst of all, you may not answer any questions at all

you may find that decision-makers are reluctant to use your data, since they won't know how good it is

Designing the study and preparing a written plan go hand in hand, since the process of writing the plan forces you to completely think through each aspect of the design.

Why Are You Monitoring?

The first step in designing your study is to define the reasons for it. What do you value most about your river? What are the threats facing it? What are your organization's long and short-term goals for the river and what information do you need to achieve those goals? What information is already known and where are the gaps that volunteer water quality monitoring can help fill in? Who will use the information you collect?

To help answer these questions, we recommend holding meetings at which representatives of the whole range of river interests identify issues and work with topographic maps and aerial photos to locate pollution sources, river uses, and problem areas. Then guide groups through a structured process of identifying and prioritizing issues and program goals. Please use Worksheet # 1 found at the end of this section as a guide for this process.

Once you've identified issues, goals, and information needs, it's time to pose one or more specific questions that your monitoring effort will address. For example,

Is the water safe to swim in?

Does the river meet state water quality standards for bacteria, dissolved oxygen, temperature, and aquatic life?

What are the impacts of a wastewater treatment plant (or some other human alteration) on the physical, chemical, and biological integrity of the river?

What are the impacts of non-point source pollution on the river?

Does the river support a healthy aquatic community?

What is causing shellfish bed closures?

Can trout be restored to the stream?

What Water Quality Indicators Will You Measure?

As we illustrated earlier, rivers are complex systems of interrelated physical, chemical, and biological characteristics. We can't measure them all, so we use water quality indicators - selected characteristics that tell us about the river's basic health. Some examples of commonly used indicators are:

Physical: temperature, depth, flow, bottom composition, water clarity, suspended solids

Chemical: dissolved oxygen, pH, alkalinity, nutrients, conductivity, salinity

Biological: benthic macroinvertebrates (such as aquatic insect larvae), fish, algae, rooted aquatic plants

"Monitoring" covers a broad array of projects and the program you design should help you answer the questions you've asked about your river. For example, if you want to know if the water is safe for swimming or shellfishing, you would analyze for bacteria. If you want to know the health of a stream's aquatic biological community and the impact of various human activities, you would sample benthic macroinvertebrates. If you want to know more about fish habitat, document temperature and bottom substrate along a stream's length. Shoreline Surveys are a means of visually documenting riparian corridor land use, habitat, potential pollution problems and public access. Remember, you choose water quality indicators to round out your investigation, rather than build a program around indicators.

Many water characteristics and problems are observable as well as measurable. A camera can be a very useful tool in documenting changes in water clarity before, during, and after a storm. Groups collecting benthic macroinvertebrate samples also observe and record surrounding land uses, bank erosion, degree of shading, and the presence of pipes emptying into the water. Certain problems such as sediment may be better documented by frequent observations than by infrequent (though more precise) measurements. Ultimately, which indicators you will choose will also depend upon your available human and financial resources.

MassWWP recommends a minimum set of indicators for rivers: temperature, pH, total alkalinity, bacteria, and dissolved oxygen. MassWWP also recommends sampling and analysis for benthic macroinvertebrates, where appropriate. You may decide to analyze other indicators such as turbidity and conductivity, but bear in mind that the MassWWP's quality assurance procedures are for the recommended minimum indicators only. Please refer to Section IV for a discussion of designing a quality control program for other indicators. For your reference, Appendix E of this *Manual* describes in brief additional parameters and their field, lab and quality control requirements.

What Are Your Data Quality Objectives?

Data quality objectives are narrative statements that link the quality of data with the intended use of the data. Data quality requirements refer to how precise, accurate, and sensitive your methods and equipment need to be and how complete, representative, and comparable your data need to be in order to meet your data quality objectives. Key to determining your objectives are the audience you are trying to reach and the technical and financial abilities of your group.

For example, suppose your program goal is to restore an alewife run to your river. A data quality objective

would be to produce data that the Massachusetts Division of Marine Fisheries would accept as an indication of the conditions suitable for anadromous fish survival. You then select a set of water quality indicators to meet that objective, and for each one you determine data quality requirements. For example, you may monitor chemical conditions such as temperature and dissolved oxygen, as well as inventory physical habitat conditions such as bottom substrate. The Division of Marine Fisheries relies on a sediment particle size scale developed by **Wentworth** to evaluate bottom substrate. For further discussion of data quality requirements, please see Section IV, "The Importance of Quality Data."

Where Will You Sample?

Where you sample is critical to the validity of your study. Locations are determined by what you want to know, what indicators you are measuring, the nature of the stream in the study area, and your program resources. First, use a USGS topographic map for a preliminary selection of sites that appear to meet your criteria. Following preliminary site selection, all sites should be verified in the field. (This may already have occurred as part of a Shoreline Survey.) The monitoring coordinator should visit each site to ensure that they meet basic safety and accessibility criteria, using photographs and the Sample Site Evaluation Sheet (Worksheet # 2). Then, prepare detailed site maps and site location sheets for each volunteer team that show monitors how to get to the site and where at the site sampling should occur. The latter are important for three reasons: one, if the monitoring team needs a replacement, another volunteer can easily find the site; two, others may visit the site to collect additional samples for quality control purposes, and three, in case of an emergency, others will know where to send help. You may also want to permanently mark each location with colored tape. Archive all Site Evaluation Sheets and photograps in a loose-leaf binder.

Illustrated below are general guidelines for siting sampling locations followed by examples specific to the types of surveys most commonly undertaken by groups who are part of MassWWP.

General Guidelines

Locate sampling stations at a variety of sites that represent the variety of conditions in the watershed and along the river.

Where possible, choose sites monitored historically by the Massachusetts Department of Environmental Protection.

Select sites which are representative of your river. If your river is for the most part lazy, shallow, and bordered by wetlands, don't focus on the one short reach where there is a gorge and faster-flowing water.

Choose only sites which are accessible safely. Avoid steep, slippery, or eroding banks or sites where landowner permission cannot be obtained.

Locate collection sites in the main current and away from the banks. If that is not possible, locate the site next to the bank where homogeneous mixing of the water occurs, such as on an outside bend of the river.

At collection sites, consider variable flow patterns caused by artificial physical structures such as dams, weirs, and wing walls. These may influence the representative quality of the water.

Consider including areas of public use for water-contact recreation.

Consider including habitats of sensitive species, for example, spawning areas important to cold water fisheries.

Survey Types

A characterization survey is designed to establish baseline information on the aquatic system's physical, chemical, and biological characteristics - in other words, the river's overall health. Therefore, sampling stations should be located at a variety of sites that represent conditions in the watershed. These might include:

waters located in areas of different land uses (urban, agricultural, forested)

streams and rivers of different orders (sizes)

waters receiving point source discharges

waters receiving non-point source pollution

An impact assessment survey is designed to measure the impact of a human alteration (such as a pollution discharge or an eroding bank) on a river. Generally, three sites should be chosen to "bracket" the impact. It is very important that each site be similar in all aspects except for the impact being assessed.

a reference or control site immediately upstream of any potential impact

an impact site immediately downstream of the alteration (at the point where an impact is completely integrated with the water)

a recovery site downstream of the impact (where the water has at least partially recovered from the impact)

A tributary impact assessment survey considers tributaries as non-point discharge "pipes" to the main stem. Four sites should be chosen to bracket the tributary confluence.

a reference or control site immediately upstream of the tributary confluence

an impact site immediately downstream of the tributary at a point where the water from the tributary is completely integrated with the mainstem water

a recovery site downstream of the tributary where the mainstem water has at least partially recovered from the impact (for example, where a cleaner tributary has entered)

an "integrator" site in the mouth of the tributary (be sure that you are not sampling a backwater of the mainstem)

A Water Quality Standards Survey is designed to determine whether the river meets Massachusetts Surface Water Quality Standards for its designated uses (such as swimming or habitat for fish and wildlife). Sampling sites should be located where those uses occur. You may want to include sites already established by federal, state and local environmental agencies. For more information, contact your local board of health, water and sewer department, or conservation commission; Massachusetts Department of Environmental

Protection, Fisheries and Wildlife, or Public Health; United States Fish and Wildlife Service, Geological Survey or Environmental Protection Agency.
Sites for **a benthic macroinvertebrate survey** should be shallow (1-2 feet deep), "riffle" areas with a current between 0.4 and 2.0 feet per second, and rocky/gravely stream bottoms.

In addition to the previous examples, there are many other types of surveys, each designed to answer one or more specific questions you have about your river. Whatever type of study you undertake, it is important to ensure that the sites you choose give you samples that are representative of what you are measuring. One of the best ways to identify possible sites for ongoing monitoring is to create a base map of the study area and conduct a Shoreline Survey. This will enable you to record details of the stream's natural characteristics, human uses of the land bordering the stream and potential pollution or problem areas.

Safety and Courtesy

It is important to select sampling locations that are easy to reach safely. If prospective sites are on private property, permission from the landowner must be secured before monitoring can begin. Private property includes river bottoms but not the water. So permission is needed to sample at a private site when wading, while no permission is required when sampling is done from a canoe.

How Will You Collect Samples?

If you're going to collect samples (as opposed to measuring the water directly with a meter) there are a number of decisions to make. Will you take point or "grab" samples? Will you take samples at specific depths or will you combine water from a range of depths to achieve an "integrated" sample? What type of container will you use? (Some chemicals in the water sample may bond to the inner surface of the containers and affect your results.) Do containers require special preparation such as sterilization? How large a sample must you collect to be represenatative and to give enough volune for analysis?

This *Manual* contains sample collection procedures for the recommended indicators which answer these questions for you. Should you choose to measure others, MassWWP is available for advice.

Quality assurance is difficult for sample collection, since this is the one link in the chain that involves many people dispersed over a wide area. To minimize errors, keep sampling procedures simple and foolproof. Put yourself in the place of a volunteer collecting samples on a cold, wet spring morning. How much patience would you have with a complex procedure? Guidelines for sample collection quality control are presented in Part Two, Section III of this *Manual*.

Where Will You Analyze Samples?

Samples may be analyzed either in the field or in a lab. Field analysis is preferred for indicators that will change during transport to the lab (for example, temperature) and often the only choice for monitoring groups without access to lab facilities. For certain indicators, such as dissolved oxygen, samples can be stabilized or "fixed" in the field and analyzed later in the lab. Field meters may be used for some indicators, such as dissolved oxygen, pH, and turbidity. However, meters may be expensive, difficult to operate and/or less sensitive than laboratory methods. Moreover, the number of sites you can sample will be limited by the number of meters you have.

Many groups use field kits to analyze samples at the collection sites. The kits contain all the reagents and supplies needed to perform analysis in the field. MassWWP recommends that, wherever possible, volunteers perform analysis for the basic water quality indicators back in the lab. This makes QC easier, and using a volunteer or staff "lab analyst" to perform the protocols will help limit variability in your results due to error. Field kits are often criticized for being crude, inaccurate, and imprecise and some of them are. However, field kits vary significantly in sophistication, precision and sensitivity. Be sure to match the sensitivity and precision of the kits you buy with your data quality requirements.

For laboratory analysis, you have two main options: you can send your sample to a certified professional lab to be analyzed (usually for a fee); or you can set up your own project lab, hire a lab coordinator and recruit volunteer help for some or all of the analyses. The choice depends on a host of factors such as the difficulty of the analytical methods, equipment required, program resources, availability of labs and experienced personnel, and other program goals such as involving students and volunteers in the lab work. A list of certified labs is provided in Appendix F.

Sending your samples to an outside lab is generally the easier of the two options, particularly for analyses that are complicated and require expensive equipment. A disadvantage is that the lab may not perform analyses on weekends. Some groups have found wastewater treatment plants willing to donate the analysis of a certain number of samples. If the lab is certified by the state or EPA, your data will be more easily accepted by decision-makers. Keep in mind that some indicators, such as bacteria, require analysis within hours of sample collection, which may not be possible if no qualified lab is located nearby.

The expense of setting up your own project lab ranges from buying a few hundred dollars' worth of supplies to spending thousands of dollars on equipment and personnel. Many groups have had good luck with high school or university labs, where basic equipment is generally available and usually at least one teacher is interested and willing to help. Disadvantages include having to work around the academic schedule when classes are in session, the need to design and implement a quality assurance program, and the challenge of establishing the credibility of analyses performed in your project lab.

If you decide to set up your own project lab, you will need to identify an independent lab to perform quality assurance-related activity such as making up known and unknown standard solutions, running duplicate analyses, and trouble-shooting problems. Many groups have worked successfully with state, private, and university labs for this purpose. MassWWP provides this service for dissolved oxygen, pH, and alkalinity.

How Will You Analyze Samples?

This *Manual* contains sample analysis procedures for the MassWWP recommended baseline indicators. For other indicators that you may choose to measure, here are some basic considerations:

The basic reference for methods is the American Public Health Association's Standard Methods for the Examination of Water and Wastewater (generally referred to as "Standard Methods," see Appendix D). In this four-inch thick book you will find various methods and procedures to analyze most any water quality indicator. Often you will find several methods for analyzing a given indicator. How do you choose among them? The methods you choose will be determined by your data quality requirements and by the limits of your human technical and financial resources.

Consider your requirements for how sensitive, precise, and accurate your data must be for each indicator. For example, a change in total phosphorous concentration of as little as 0.01 mg/l can affect a fragile high

altitude stream. If you want to be able to detect such changes, you need to use persulfate digestion, followed by the ascorbic acid method using an infrared-sensitive spectrophotometer. But you can screen for gross problems using a less sensitive method.

The sensitivity of benthic macroinvertebrate analysis depends, in large part, on the taxonomic level (order, family, genus, or species) to which you identify them. Many volunteer programs perform a quick field identification to order. This method, while not highly sensitive, is sufficient to detect relatively dramatic impacts. But to detect subtler effects, you need to preserve the organisms collected in the field and identify them to the level of family, genus, or even species back in the lab.

Once you have identified a method that satisfies your data quality requirements, consider how much time and how many people are needed to perform the method, as well as how much skill is required to complete it well. Will relatively small errors have a dramatic impact on your results? Consider also the equipment required by the method. Do you have it? Can you afford to buy it? Can you seek a donated lab space or equipment? Do you have people with the skills to train volunteers to operate it properly?

In some cases, you may decide that a particular indicator is not worth analyzing because achieving your data quality requirements is too expensive or complex.

When Will You Sample?

When you sample can greatly affect the outcome. Consider the time of day, holding time, frequency, and time of year.

Time of Day: The time of day you collect your samples can affect the results. For example, in waters with dense aquatic vegetation, dissolved oxygen levels fluctuate dramatically over a 24-hour period, with the lowest levels at sunrise and highest levels in mid-afternoon. So if you want the worst-case scenario, sample at sunrise.

Holding Time: For each test, take into account the maximum time a sample collected in the field can be held prior to analysis in the lab. For example, the maximum holding time for fecal coliform bacteria is **6 hours in a container with ice.** If the sample cannot be analyzed within this time frame, the results won't be valid.

Frequency: How often you need to sample depends upon what you want to know. For example, if you want to investigate sources of bacteria causing shellfish bed closures following rainstorms, you will conduct a "wet weather" survey and will most likely take several samples at regular intervals, perhaps hourly, during rain events. Determining a dissolved oxygen profile for your stream will require continous sampling during the day and overnight. On the other hand, if you are performing a characterization survey, gear your sampling to different conditions. Many groups start with a one day per month schedule and then build in more frequent sampling as more volunteers become involved. Benthic macroinvertebrates need only be sampled once or twice per year.

Time of year: In deciding the time of year to conduct sampling, consider the uses of the water. If you want to know if the water is safe to swim in, sample in the summer. Also take into account the ease of field work: do you need to send volunteers out in freezing weather or during rainstorms? In some cases, the nature of the indicator determines the best sampling season. For example, many aquatic biologists suggest that benthic macroinvertebrates be sampled in the spring and fall. During the summer, many members of the

macroinvertebrate community change from the aquatic larval form to the winged adult forms and escape your sampling.

What's Next?

Once you've been through the study design process, you need to document all the decisions in an informative study design plan. This will include a description of why and what you are monitoring, how sites where selected, where the sites are located, who the volunteer teams are, what equipment is being used, how the volunteers will be trained and how quality assurance will be carried out. Someone who is unfamiliar with your work should be able to read it and understand what your study is about. While written, the study design is a flexible document and can be refined as volunteers take to the field and learn more about the river - sites and indicators may change over time.

The study design process may seem like a lot of work. But time spent on designing the study can ultimately save you and your volunteer teams many hours of wasted effort and frustration by assuring that your monitoring matches your goals and resources.

Worksheet #1

ORGANIZING A LOCAL STREAM MONITORING PROGRAM

GOALS OF A LOCAL CITIZEN STREAM MONITORING PROGRAM

Clearly defined goals are essential for establishing a successful chemical stream monitoring program. To define your goals, determine and document the answers to the following questions:

WHY? - Clearly specify and WRITE DOWN the reasons for starting a local stream monitoring program. For example:
determine if the stream meets Massachusetts Surface Water Quality Standards for swimming, fishing or shellfishing
restore the quality of stream for specific recreational or natural purposes
determine the impact of new development along the river
assess the effectiveness of cleanup efforts
collect baseline data to promote better local and state planning for stream protection and clean up
determine the impact of point and non-point pollution sources
assess water quality of stream areas used for water supply, recreation or by sensitive aquatic species

WHAT DO YOU PLAN TO ACHIEVE? - Clearly specify and WRITE DOWN the outcomes that the program is designed to achieve. For example:
educate public officials and local residents & businesses
stop further development/pollution
identify effective cleanup strategies
protect the stream's fish and wildlife
build an informed constituency for stream protection
enhance recreational use
open shellfish beds

WHAT ARE YOU GOING TO DO WITH THE DATA YOU COLLECT?

Clearly specify the frequency and ways in which monitoring data are to be used. For example:
publish quarterly reports in the local newspaper
create education materials for the public
submit yearly reports to local, state and federal environmental agencies
use data to alert environmental officials to potential pollution violations
submit data for inclusion in a statewide stream monitoring database (to be developed)
locate fisheries habitat and stream restoration sites

HOW LONG WILL THE PROGRAM CONTINUE? - Clearly define the duration and frequency of monitoring activities. Consider what can be done to provide long-term baseline monitoring (5 to 10 years) while exploring phases limited to a relatively short time frame (e.g. 1 year). At the end of each phase of your program, review your accomplishments and difficulties and modify goals, activities and time frames if necessary.

Worksheet # 2

III. How To Run a Successful Volunteer Water Quality Monitoring Program

Human and Financial Resources

Once you have shared a vision with people who want to monitor your river or stream and set your stream monitoring goals, you may want to take an inventory of the skills and resources you have available to your group. Volunteer stream monitors need to build a strong organization in order to attract and manage the financial and human resources needed to implement a successful program. Although the human and financial requirements of each program will depend on its size and goals, most programs can use similar methods for recruiting volunteers and raising funds.

Some effective and inexpensive volunteer recruitment methods include: discussing your program with local watershed and environmental groups, advertising in local and environmental publications, and posting flyers at local high schools, colleges, institutions, and other organizations.

Chemical monitoring programs will also need to obtain financing to purchase necessary equipment and supplies. Each organization will have to determine how much it will cost to accomplish their current monitoring goals and develop a plan for raising the necessary funds. Some effective fund-raising strategies include: charging membership dues, organizing fund-raising events (e.g. fishing derby or auction) and soliciting donations from local organizations and businesses. Use Worksheet # 3 to inventory equipment and funding resources.

Several effective ways for volunteer monitoring groups to obtain laboratory resources, either use of space and equipment or actual analysis include:

forming alliances with local wastewater treatment plant operators
getting commercial labs to donate services as a community service
working with interested local high school and college science teachers
working with local, state or federal officials responsible for maintaining water quality in your area

Organizations that may provide volunteer, financial, or space/equipment assistance to a monitoring group include: conservation commissions, local or state governments, land trusts, businesses, civic clubs, fish & game clubs, watershed associations, public health departments, schools, colleges and conservation organizations.

Take A Team Approach

Each successful volunteer stream monitoring program also requires that the workload be distributed fairly. Monitors should feel satisfaction that their results have meaning. The following "job descriptions" are common to the needs of most groups and filling them will serve you well in the long run.

Steering Committee: MassWWP recommends that a volunteer water quality monitoring program involve all users of the river in its design and implementation. Solicit input and help from town boards, local businesses, civic groups, schools, trade associations, sportsmen's groups, and clubs. A point person should be selected to oversee the whole program.

Techical Advisor: This person is responsible for coordinating the training of the volunteers (identifying needs and arranging training and QA/QC "checkups"); equipment maintenance and supplies, and serves as

a point person for sampling and technique questions.

QA/QC Officer: This person works with the technical advisor to develop the QA/QC plan, run lab analysis "checkups," spot checks sampling technique and arranges lab analysis of samples when necessary.

Volunteer Coordinator: This is the "people" person, who recruits and organizes the teams, makes the reminder phone calls, keeps monitors informed of results and interested in the project (through quarterly meetings, events, newsletter, etc.)

Outreach Coordinator: This person writes regular summaries of results, press releases to local papers, landowner education, etc.

Lab Analyst: This person is in charge of performing laboratory procedures for the dissolved oxygen, pH, alkalinity, and fecal coliform tests.

Results/Data Interpretation: This person, or team of people, is responsible for collecting field sheets, entering data into computer system (if applicable), printing reports and/or graphs, and explaining what the results mean for the river. It may be helpful for a science teacher to be part of this team, to provide the necessary data analysis. It need not be too detailed, and these reports may be produced monthly, quarterly, or annually, as your time and budget allows.

In many programs one person will perform several of these tasks. Please rely on Worksheet # 4 found at the end of this section to help you match people's skills and talents with tasks. At the beginning, the most important folks to recruit are the Technical Advisor and Volunteer Coordinator. You may also want to include an equipment manager, legal/liability advisor, computer and graphics experts in your program.

It is important to evaluate your people resources well. There are many folks who are willing to go out once a month to take a sample; there may be other folks in the community who can make a greater time commitment. Be sure not to drain your group's time however, and try to identify a wide range of folks who may be able to fill the above "positions."

Keep the following in mind as you develop and implement your stream monitoring program:

Limit your goals and work plans to make them manageable and measurable - don't take on too much for your group's size or experience

Rotate tasks whenever you can in order to share and build skills among all group members

Where certain tasks require continuity and accountability, assign the work to one or, at most two, people

Watch carefully to see who in your group has special management, technical or outreach skills and draw on them!

Respect people's limits - remember this is a volunteer effort and folks have other commitments as well at home or at work

Set clear expectations for leadership of the monitoring effort

Worksheet # 3

Worksheet # 4

IV. The Importance of Quality Data

Let's face it - quality assurance is probably the least glamorous aspect of any environmental monitoring program. But the scientists, public officials, and members of the public who may use your data have a right to know how accurate and reproducible those data are, and a strong quality assurance program is the only way to convince these people that your data are worth looking at.

Quality Assurance Terminology

The literature on quality assurance is filled with technical jargon, and the definitions of terms vary from paper to paper. We've used the terms given by Keith et. al. (1983) (see Appendix D for citation).

Quality assurance is a broad plan to maintaining quality in all aspects of a program. The quality assurance plan guides:

the selection of parameters and procedures

data management and analysis

the steps taken to determine the validity of specific sampling or analysis procedures. These steps are divided into two categories: *quality control and quality assessment*

Quality control (QC) consists of the steps you take to make your analysis more accurate and precise while you are actually running the analysis or making the measurement. QC procedures let you know right away if you have a problem, so that you can take immediate actions to correct the problem. A standard solution of known concentration that you run along with your samples in a chemical analysis is an example of a quality control sample. As you will see in Part Two, MassWWP provides quality control samples for pH and alkalinity and dissolved oxygen.

Quality assessment (QA), on the other hand, is your "after the fact" assessment of the overall precision and accuracy of your data. Quality assessment samples are often analyzed "blind" - that is, the analyst does not know the expected result. A duplicate sample taken in the field but not obviously labeled as a duplicate is one example of a quality assessment sample. Part Two of this *Manual* offers general guidance for using "blind" samples.

Other terms commonly used in discussing quality assurace include the following:

Replicate samples, or duplicates: Two or more samples taken from the same place at the same time. MassWWP recommends taking one extra sample for every ten sites, or 10% of your sites.

Precision: the reproducibility of your method (how close the results of the replicate analyses of one sample are to each other). Precision is measured by the standard deviation of replicate samples

Accuracy: How close your results are to the true value

Detection limit: The lowest concentration a method can detect as greater than zero

How Much QC?

In order to decide how rigorous your QC program needs to be, you must first answer the question, How good must the data be to serve your purposes? You may already have answered this question through development of your study design, which called for determining your data quality requirements. If your primary purpose is to screen for potential problems so that you can alert agencies to follow up on your findings, you may need only basic quality control for your data. But if you want your data to be used for enforcement or to guide policy decisions, or even to stand up in court, then extensive quality control is essential.

Once you have set goals through your study design and decided how good you want your data to be, you need to weigh the ideal amount of quality control against your resources of time, money, equipment, and personnel. Since higher quality usually costs more, you may find at this point that you have to make some adjustments in your goals for the data.

Sample Collection In the Field

Quality assurance of data does not begin with the lab analysis - it begins with collecting the sample in the field. As we mentioned in the study design section, an important first step is to get volunteers to the correct site. Some volunteers may have difficulty reading maps, so it is best to have a program coordinator assist in locating the site the first time. In some cases it may be possible to affix a marker, such as a staff gage or buoy, in the water at the sample site. The written directions to the site should refer to permanent landmarks.

All information concerning the sample collection (site, date, time, collector, etc.) should be recorded on preprinted data forms. You will find the standard MassWWP data forms for field collection and lab analysis in Part Two of this *Manual*. Your study may also require a *chain of custody* document containing the signature of every person who sampled, transported, stored, or analyzed a sample. The chain of custody document certifies that no switch of samples has occurred.

Physical Data

Quality assurance procedures for physical measurements are generally fairly simple and straightforward. Instruments should be calibrated against a known standard and used according to instructions. For example, thermometers should be checked against a calibrated thermometer. Procedures for calibrating thermometers and pH meters are provided in the lab analysis sections contained in Part Two of this *Manual*. MassWWP offers training sessions where volunteers can learn the proper use of equipment in the field.

Taking replicate samples in the field is important to assuring the quality of physical data. Another check on the quality of physical data is to field-check volunteer measurements by comparing them to side-by-side measurements made by professional staff.

Chemical Data

All those terms you hear for different types of quality assurance samples - like "split sample," "spike sample," "blank," "check sample" - apply mainly to chemical testing. See Table 1 below for descriptions of some of these samples and how each is used.

Table 1. Common Quality Assurance Samples

SAMPLE TYPE	DESCRIPTION	APPLICATION
Quality Assessment		
Field Blank	Deionized water treated as a sample	Use to estimate contamination from sample collection and processing
Field duplicate	Duplicate lake or stream sample	Use to estimate combined sampling and lab precision
Audit sample	Synthetic sample prepared by QC officer or obtained from outside source	Use to estimate accuracy and precision of lab
Quality Control		
Calibration Blank	Reagent-grade deionized water used to zero the instrument	Use to identify instrument signal drift; also, can be compared to field blank to detect contamination of sample
Quality control check sample (QCCS)	Standard solution (source other than calibration standard)	Use to determine accuracy and consistency of instrument calibration
Laboratory duplicate	Sample split in two at the lab	Use to test precision of lab measurements
Matrix Spike	Subsample spiked with known concentration of analyte (susbtance being measured)	Use to determine interference effects in the sample

The samples listed under "Quality Assessment" in Table 1 are usually *double blind* samples - that is, the person performing the analysis does not know the sample's identity or the expected result. These samples are delivered to the lab disguised as regular samples. The results of the quality assessment samples are later compared to the expected results and the comparison is used to assess the overall accuracey and/or precision of the data set.

The samples listed under "Quality Control," on the other hand, are samples whose *identity are known* to the analyst, but whose expected concentration is only known by MassWWP staff. They should be run first, before the real samples are analyzed, and preferably the week before sampling, to check on the accuracy of the analytical procedures and instruments. After the QC samples are run, results are called or mailed in to MassWWP to compare the analyst's results to the expected values. MassWWP provides quality control samples for dissolved oxygen, pH and alkalinity to enable you to detect and correct any problems before the real samples are run.

The *quality control check sample (QCCS)* must originate from a different source than the one used in calibration. Standard solutions sold by scientific supply companies can be used as quality control check samples. MassWWP does not provide QCCS. It is a good idea to plot the QCCS results immediately on

a graph called a quality control chart, so you can tell right away how the result compares to previous results with the same solution. If the QCCS result is outside the upper or lower control limit, you should stop and correct the problem before analyzing the samples.

A *matrix spike* is used occasionally to test for substances in the sample that may interfere with the analysis. Use of a matrix spike does not apply to the basic indicator protocols presented in Part Two of this *Manual.* If you are testing other indicators, such as phosphorous, you should consult with MassWWP for advice.

Audit samples are used to test the accuracy and precision of your lab, either the volunteer run lab or the one the work is sent out to. External audit samples are prepared by an outside agency, while internal audits are prepared from standard solutions by someone in your group. The correct concentrations are revealed after the results are turned in. One way to obtain blind audit samples is to participate in EPA's Water Pollution Performance Evaluation Sampling Program. Twice per year, participants in this program receive a set of audit samples for various chemical parameters from their regional EPA Quality Control Coordinator.

Not all QC procedures are appropriate for all analyses. For example, blanks and standards are not usually used for Winkler dissolved oxygen titrations, due to problems with contamination by oxygen from the air. In this case, there are two options for checking the accuracy of the procedure. In Part Two of this *Manual*, MassWWP has provided instructions for creating an oxygen-saturated sample by shaking and pouring water back and forth through the air, then titrating the sample and comparing the results to published tables of oxygen solubility versus temperature. Another option is to use a standard solution of potassium bi-iodate. A premixed iodate-iodide standard solution can be ordered from the Hach Chemical Company.

For small volunteer programs with limited resources, all the QA/QC procedures for chemical analyses may seem overwhelming. MassWWP recommends that the calibration blank, QCCS, and standards be run with each batch of samples. Other tests, like matrix spikes and field blanks, could be run monthly or yearly. For more information on chemical quality control procedures, see Standard Methods for the Examination of Water and Wastewater cited in Appendix D.

Part Two: Getting Underway

I. Meet the Indicators

This section describes what the water quality indicators recommended by the Massachusetts Water Watch Partnership can tell you about the health of your river or stream. It provides the background needed to understand your river's chemical and biological interactions.

pH and Alkalinity

pH is a measure of the hydrogen ion concentration of the water as ranked on a scale of 1.0 to 14.0. The lower the pH of water, the more acidic it is. The higher the pH of water, the more basic, or alkaline, it is. pH affects many chemical and biological processes in the water and different organisms have different ranges of pH within which they flourish. The largest variety of aquatic animals prefer a pH range of 6.5 - 8.0. pH outside of this range reduces the diversity in the stream because it stresses the physiological systems of most organisms and can reduce reproduction. Low pH can also allow toxic elements and compounds such as heavy metals to become mobile and "available" for uptake by aquatic plants and animals. Again, this can produce conditions that are toxic to aquatic life, particularly to sensitive species like trout.

Changes in acidity can be caused by atmospheric deposition (acid rain or acid shock from snowmelt), surrounding rock, and wastewater discharges. Technically, the pH scale measures the logarithmic concentration of hydrogen (H+) and hydroxide (OH-) ions, which make up water (H+ + OH- = H20). When both types of ions are in equal concentration, the pH is 7.0 or neutral. Below 7.0, the water is acidic (there are more hydrogen ions than hydroxide ions). When the pH is above 7.0, the water is alkaline, or basic (there are more hydroxide ions than hydrogen ions). Since the scale is logarithmic, a drop in the pH by 1.0 unit is a 10-fold increase in acidity. So, a water sample with a pH of 5.0 is ten times as acidic as one with a pH of 6.0. pH 4.0 is 100 times as acidic as pH 6.0.

Alkalinity is a measure of a river's "buffering capacity," or its ability to neutralize acids. Alkaline compounds in the water such as bicarbonates (baking soda is one type), carbonates, and hydroxides remove H+ ions and lower the acidity of the water (which means increased pH). They do this usually by combining with the H+ ions to make new compounds. Without this acid neutralizing capacity, any acid added to a river would cause an immediate change in the pH. Measuring alkalinity is important to determining a river's ability to neutralize acidic pollution (as measured by pH) from rainfall or snowmelt. It's one of the best measures of the sensitivity of the river to acid inputs. Alkalinity comes from rocks and soils, salts, certain plant activities, and certain industrial wastewater discharges. Total alkalinity is measured by collecting a water sample, and measuring the amount of acid needed to bring the sample to a pH of 4.2. At this pH all the alkaline compounds in the sample are "used up." The result is reported as milligrams per liter (mg/l) of calcium carbonate.

The Massachusetts Acid Rain Monitoring Project ranks waters according to their alkalinity as follows:

<0* mg/l: Acidified	>5-10 mg/l: Highly Sensitive
>0-2 mg/l: Critical	>10-20 mg/l: Sensitive
>2-5 mg/l: Endangered	>20mg/l: Not Sensitive

* and pH less than 5.0.

Dissolved Oxygen (DO):

Dissolved oxygen is the oxygen dissolved in the river water. It is an important indicator since most aquatic plants and animals need it to survive. The river system both produces and consumes oxygen. The river gains oxygen from the atmosphere through the aerating action of wind or turbulence (cascading water) and from plants through photosynthesis. Respiration by aquatic animals, decomposition, and various chemical reactions consume oxygen. Decomposition of organic matter discharged in wastewater consumes oxygen. If more oxygen is consumed than is produced, dissolved oxygen levels decline and some sensitive animals may disappear. DO levels fluctuate daily and seasonally. They also vary with water temperature - cold water holds more oxygen than warm water. The most critical time for many aquatic animals are early mornings on hot summer days, when river flows are low, water temperatures are high, and plants have not been producing oxygen since sunset.

We measure dissolved oxygen by collecting a water sample in a special bottle, "fixing" or stabilizing the amount of oxygen in the sample by adding certain chemicals, and then measuring the concentration in the lab. DO is measured in either milligrams per liter or "percent saturation." Milligrams per liter (mg/l) is the amount of oxygen in a liter of water and is the same as "parts per million" or ppm.

Percent saturation is the measured mg/l of oxygen in the water sample relative to the mg/l of oxygen that the water sample is capable of holding at a particular temperature. The amount of oxygen that water can hold varies with temperature. Cold water can hold more oxygen than warm water. At less than 100% saturation, the water will tend to take on oxygen from the air. At greater than 100% saturation, it will give off oxygen to the air. At 100% saturation, the oxygen of the water is at equilibrium with the oxygen in the air and no oxygen will be exchanged. Suppose the measured DO of a your water sample is 5 mg/l. If you measured a temperature of 20 C, your water sample is capable of holding about 9.0 mg/l (this fact is obtained in Table 3 in section IV.A.). Dividing the measured DO by the expected DO gives the % saturation, in this case 55%.

Fecal Bacteria

Members of two bacteria groups, coliforms and fecal streptococci, are used as indicators of possible sewage contamination, because they are commonly found in human and animal feces. Though they are generally not harmful themselves, they indicate the possible presence of pathogenic (disease-causing) bacteria, viruses, and protozoans that also live in human and animal digestive systems. Therefore, their presence in rivers suggests that pathogenic micro-organisms may also be present and that water contact recreation (such as swimming), or eating shellfish, may be a health risk. In addition to the health risk, fecal material can cause a number of impacts on rivers: cloudy water, unpleasant odors, and an increased oxygen demand (see Section I, River Ecology for more details).

It's too difficult, time-consuming, and expensive to test directly for the presence of the large variety of pathogens, so water is routinely tested for coliforms and fecal streptococci as indicator groups, instead.

Sources of fecal contamination to surface waters include wastewater treatment plants, on-site septic systems, domestic and wild animal manure, and stormwater runoff.

Indicator Bacteria Types and What They Tell You:

In the past 50 years, the most commonly tested bacterial indicators are total coliforms, fecal coliforms, E. coli, fecal streptococci and enterococci. All but E. coli are comprised of a number of species of bacteria that all share common characteristics such as shape, habitat, or behavior. E. coli is a single species of fecal coliform.

Total Coliforms is a group of bacteria that is widespread in nature. All members of the total coliform group may occur in human feces, but some may also be widespread in the environment, such as animal manure, soil, submerged wood and other places outside the human body. Thus, the usefulness of total coliforms as an indicator of fecal contamination depends upon the extent to which the bacteria species found are fecal in origin. For recreational waters, total coliforms are no longer recommended as an indicator. For drinking water, total coliforms are still the standard test since their presence indicates contamination of a water supply by an outside source.

Fecal Coliforms is a subset of total coliform bacteria, which is more fecal-specific in origin. However, even this group contains a genus, Klebsiella, with species that are not necessarily fecal in origin. Klebsiella are commonly associated with textile, pulp and paper mill wastes, in the absence of fecal contamination. For recreational waters, fecal coliform was the primary bacteria indicator until relatively recently when EPA began recommending E. coli and enterococci as better indicators of health risk from water contact. Fecal coliforms are still being used in Massachusetts as the indicator bacteria and this *Manual* provides protcols for fecal coliform analysis.

Escherichia coli (E. coli) is a species of fecal coliform bacteria that is specific to fecal material from humans and other warm-blooded animals. EPA recommends E. coli as the best indicator of health risk from water contact in recreation waters and some states have changed their water quality standards and monitoring accordingly.

Fecal streptococci generally occur in the digestive systems of humans and other warm-blooded animals. In the past, fecal streptococci have been monitored together with fecal coliforms and a ratio of coliforms to streptococci calculated. This was used to determine whether the contamination was of human or non human sources. However, this is no longer recommended as a reliable test inthe 20th edition of Standard Methods.

Enterococci are a subgroup within the fecal streptococcus group. They are distinguished by their ability to survive in salt water, and in this respect more closely mimic many pathogens than the other indicators. They are generally more human-specific than the larger fecal streptococcus group. EPA recommends enterococci as the best indicator of health risk in salt water used for recreation and as a useful indicator in fresh water as well.

Which Bacteria Should You Monitor?

Which bacteria you test for depends on what you want to know. Bacteria are commonly used to either determine the health risk of water contact or ingestion of shellfish (through compliance with state water quality standards designed to protect human health) or the presence of fecal contamination from humans or animals to help determine the impact of point or non-point pollution sources on a river.

Studies conducted by the EPA to determine the correlation between different bacterial indicators and the occurrence of digestive system illness at swimming beaches suggest that the best indicators of health risk from recreational water contact in fresh water are Escherichia Coli and enterococci. For salt water, enterococci are the best. Interestingly, fecal coliforms as a group were determined to be a poor indicator of

the risk of digestive system illness. However, Massachusetts continues to use fecal coliforms as their primary health risk indicator. Folks monitoring interstate rivers should obtain information on the bacterial indicators used in neighboring states.

If you want to know whether the water meets state water quality standards, use fecal coliforms. However, if you want to know the health risk from recreational water contact, the results of the E.P.A. studies suggest that you should consider switching to the E. coli or enterococci method for testing fresh water and enterococci for salt water. In any case, it's best to consult with the people at the Massachusetts Department of Environmental Protection, especially if you expect them to use your data. Although the protocols for E. coli and enterococci are not included in this *Manual*, MassWWP can offer training in these methods upon request.

Temperature

Temperature dramatically affects the rates of physical, chemical and biological processes in the water. Some of these are the solubility of compounds in water, the amount and distribution of organisms living in the water, the mixing of the water, the rates of bio-chemical reactions (including decomposition) and others. Cold water holds more oxygen than warm water.

Water temperature fluctuates considerably with the season. In deeper slow moving rivers, surface temperature may be different than bottom temperature. Colder, heavier lower layers may become low in dissolved oxygen if they do not mix with upper layers.

Benthic Macroinvertebrates:

These are bottom dwelling organisms that can be seen with the unaided eye, such as stonefly, mayfly and caddis fly larvae. Benthic macroinvertebrates are good water quality indicators for several reasons: many are sensitive to pollution, the composition of the community is a good reflection of long-term water quality (since they live there year-round), they cannot easily escape pollution, and they are relatively easy to collect.

They are collected from shallow riffle areas by disturbing the stream bottom and catching the dislodged organisms in a net. They are then preserved, picked from the debris, sorted, and identified. The types and numbers found can indicate current water quality and habitat conditions. MassWWP offers training and manuals in macroinvertebrate monitoring.

II. A Note About Safety

Always take time to be careful! Remember, river sampling involves canoeing or wading in flowing water and some of the analyses involve using chemicals - they are laboratory procedures and must be followed with care. Use caution or avoid harsh weather and/or dangerous river conditions. Be attentive during sample collection to prevent loss of balance or injury from equipment. At no time should anyone place themselves in jeopardy for the sake of a sample!

Use the buddy system - sample with a partner.

Plan ahead - Read and know all instructions in this Manual and on your kits/equipment before going out into the field.

Prepare bottle labels before you go out into the field.

Wear rubber gloves when sampling polluted water and handling chemical reagents.

When sampling, wear waders or footwear that can get wet. Don't sample barefoot!

If sampling from a canoe, wear your life preserver!

Note any precautions and first aid information for the reagents contained in the dissolved oxygen kits.

Take along a first aid kit.

Wear rubber gloves and safety goggles when performing lab analyses

Avoid contact between reagent chemicals and skin, eyes, nose, and mouth.

Tightly close all reagent containers after use.

Keep all equipment and reagent chemicals out of the reach of children.

Keep this number close at hand in case of accidental exposure to chemical reagents - Poison Control in Mass: 1-800-682-9211.

III. In the Field/In the Lab: An Overview

As we stated in the Introduction to this *Manual*, these instructions are meant for groups who wish to sample using procedures and equipment in accordance with MassWWP recommendations. We don't mean to suggest these are the only ways to take and analyze river samples. The advantages of using these methods are:

We offer training in the methods.
We will provide quality control (QC) standards for some of the tests.
Standardization makes it easier for MassWWP, state agencies, and others to read, evaluate, and compare your results.

In the Field

The field procedures for collecting samples consist of the following tasks:

1) Preparing sample containers
2) Preparing prior to leaving for the sampling site
3) Preparing at the sample site
4) Filling out field sheet and the label on the sample container
5) Collecting the sample
6) Returning samples and field sheets to the lab or drop-off point

Volunteers should be provided with a sampling schedule, directions to each site, and sampling instructions. They should also have a number to call to verify that the sampling is taking place if conditions become unsafe, such as during electrical storms.

1) Preparing Sample Containers: Make arrangements with the coordinator to pick up sample containers and supplies before the sampling date. Otherwise, pick up your sample containers for the next sampling date each time you drop off your water samples. If any of the sample bottles are not numbered, ask the lab coordinator how to number them. Unless sample containers are to be marked with the site number, do not number them yourself.

2) Preparing Prior to Leaving for the Sampling Site: *Confirm the sampling date , time, and location.* Volunteers should know in advance which sample sites they are covering and the dates they are sampling. They should receive a schedule of the sampling dates and times. If not, confirm with the program coordinator to avoid any misunderstanding about when and where sampling is to take place. Be sure you know which sites you will sample and that you have directions on how to get to each site.

Check Weather Conditions: If there is any question about the weather, if there is heavy rain or wind or other inclement conditions, it is better not to sample. Plan for another day!
Some surveys, such as wet weather studies to determine pollution from stormwater runoff, may plan for sampling during inclement weather. In either case, it is a good idea to check with your program coordinator.

Check Equipment and Supplies:

Sample Containers. Bring one sample container for each site to collect a water sample, one for each field blanks or duplicate, plus an extra container in case something happens to one of the containers.

Small cooler with ice to keep samples cool.

Written procedures and field sheets. Be sure to understand the sampling procedures before leaving. Make sure to bring enough field sheets for the number of sites being sampled.

Waders or footwear that can get wet. Don't sample barefoot!

Rubber gloves if sampling below a wastewater treatment plant or in waters suspected to be polluted.

Towel and a dry, warm change of clothes.

Clip board and pencil (ink runs if the sheet gets wet)

First Aid kit

Let someone know where you are going and when you expect to return.

3) Preparing At the Sample Site:

Park in a safe location! Do not block traffic!

Confirm the site location. Refer to your site directions to confirm that you have the right location.

Check river conditions. Be aware of your own physical limitations and the difficulty collecting water at certain locations under certain conditions. If a sample site is too difficult under any conditions, let the volunteer coordinator know. High flows can turn even the most placid water into a raging torrent. Don't attempt to collect a sample if you feel the least bit of risk. Avoid dangerous situations.

Carefully make your way to the river or to your site in a boat. Watch for steep banks and poison ivy.

If sampling from a bridge, be wary of passing traffic! Don't lean over bridge rails while sampling unless you are firmly anchored to the ground or bridge structure with good hand and foot holds.

4) Filling out field sheet and the label on the sample container

A copy of the MassWWP River Sampling field sheet and instructions are provided at the end of this section for your use. Record weather conditions and other observations on the field sheets using the codes at the bottom of the sheet. Record any other observations or comments.

If the sample container is labelled, fill in the requested information such as date, time, site #, and your name or initials.

5) Collecting the Sample

The Massachusetts Department of Environmental Protection's Standard Operating Procedures recommend that samples be collected in the following order:

Bacteria (coliform)
Dissolved Oxygen
pH and Temperature
Chemical
Nutrient
Metal

If you are sampling several or all of these, sample in this order.

There are two basic methods for collecting stream water samples: center stream and stream bank collection. When feasible and safe, center stream as opposed to stream bank collection is recommended by MassWWP. Steps to center stream sampling are provided in the protocols for dissolved oxygen, pH and alkalinity, and fecal coliform. Of course, to use the center stream method in deep water, the monitoring site must be at a bridge or the monitor must have a boat.

If site conditions dictate that you must sample from a bridge or road crossing, be sure to take the sample on the upstream side of the structure and follow these guidelines:

1) Use a polyethylene bucket and attach a rope if sampling from a bridge.
2) Rinse bucket 3 times with stream water.
3) Let the bucket drift downstream toward you to fill it gradually with stream water.
4) Slowly and gently raise the bucket out of the stream up to the bridge - don't jostle the bucket, as this will add oxygen to the sample!
5) Fill your sample bottles gradually with the stream water from the bucket, allowing as little air as possible into the bottle.
6) Cap the bottle.

When sampling center stream in waders or from a boat, the monitor should:

1) Wade into the stream disturbing as little sediment as possible.
2) Stand so that you are facing upstream (the opposite direction the stream is flowing).
3) Rinse the bottle two to three times with river water.
4) Collect sample according to the specific requirements outlined in the protocols section of this *Manual*.
5) Cap the bottle.

Complete your field sheet AT THE SITE. If you don't complete the worksheet at the time of sampling, your observations and data will not be as accurate.

6) Returning Field Sheet and Sample to Lab for Analysis

After the sample is collected, check to make sure it has been properly labelled, then store it for transport to the lab. Samples for some tests must be iced while others must simply be kept out of the light. Refer to the protocols in this *Manual* for more information on preservation techniques required for specific tests.

MassWWP RIVER SAMPLING FORM

Site:_____ Stream Name:_____
Name of Monitor:_____

Date:_____ Time:_____ Collector ID:_____
Site ID:_____

WEATHER
Current Air Temperature:_____C

Current Weather (write number from list below):_____
1:clear 2:part. cloudy 3:overcast 4:fog/haze 5:drizzle
6:light rain 7:mod. rain 8:heavy rain 9:snow or sleet 10:other_____

PHYSICAL
Water Temperature:_____C

Water Color (write number from list below):_____
1:muddy (brown) 2:silty (gray) 3:green 4:tea 5:cloudy 6:clear 7:other_____

Water Odor (write number from list below):_____
1:rotten egg 2:chlorine 3:musky 4:gas or oil 5:none 6:other_____

Observed Use (write number(s) from list below):_____
1:swimming 2:fishing 3:boating 4:skating 5:other_____

If known: Stage: _____ feet

If known: Discharge:_____cfs If at gaging station, identify station:_____

If stage not known, estimate water level (write number from list below):_____
1: very low 2:low 3:medium 4:high 5:very high

COMMENTS
Note any observed changes in stream or bank character since last test, and other comments.

SAMPLE PRESERVATION: none____ iced & kept in dark____

MassWWP River Sampling Instructions
Filling out Field Sheets

Use a separate sheet for each site sampled. Use pencil or waterproof pen.

Obtain collector ID and site ID's from coordinator.

Enter both the **site #** and the **field replicate # on your bottle**. For example, if you filled 2 DO bottles from site DR01, then you would have bottle numbers DR01 #1 and DR01 #2.

Weather:
Measure air temperature upon arrival at your site.

Physical:
Observed Use: If you see any recreational or other activity on the river, it's helpful to write it down. Observations of this type can help answer the question "who cares?" when you present data to an audience.

Stage: Stage is the level of water above the river bottom. Read it from a permanent staff gage and record in feet. If USGS elevations are used, please convert to a corresponding stage. If no device for recording stage is present, estimate the water level as described on field sheet.

Comments: Eroded banks, vegetation gone, obstructions in stream channel, increased sediment; anything different or noteworthy.

Sample preservation: This helps us track the sample from the stream to the point of analysis. Please indicate if you refrigerated a sample in the dark for storage for later analysis. DO NOT FREEZE SAMPLES.

Quality Control with MassWWP: An Overview

At present, MassWWP operates a QC program for dissolved oxygen, pH, and alkalinity laboratory tests.

Quality Control tests are conducted for 2 main reasons:

to document the accuracy of your program's sampling results.
to catch and correct errors **before** you analyze the field samples that volunteers have collected.

Errors can be due to mistakes in field technique, lab technique, improper or dirty equipment and supplies, or for other reasons. Most of the QC assistance provided by MassWWP targets laboratory procedures. However, your use of replicate samples is a form of QC, helping you to detect and minimize errors occurring in the field. See Part One, section IV, "The Importance of Quality Data" for tips on field QC, as well as Part Two, section IV, "Quality Control On Your Own: An Overview."

The DO, pH, and alkalinity QC program works as described below. **To assure the highest degree of quality control in your program, please follow this script religiously.**

Prior to each sampling date, MassWWP will mail each group's **lab analyst** a set of bottles containing standard solutions ("standards") of chemicals that can be analyzed (with minor procedural differences) as if they were actual field samples. The DO or pH and alkalinity values each standard represent are unknown to your lab analyst, in order to eliminate any bias in the procedure. Standards should arrive 2 - 5 days prior to your regular sampling date. **If your standards are arriving late, please contact us so that we can remedy the situation.**

Refrigerate these standards upon receipt. However, before running the QC test, take them out and let them warm to room temperature.

Perform a QC test on the standards, following procedures described in the appropriate QC sections of this manual. **Do this at least 2 days prior to the field sampling date.**

Call MassWWP with the results you obtain. We are available at 413-545-5531 Monday through Friday, to provide you with the true values. If any discrepancy exists between your results and MassWWP's, we'll discuss it with you and take corrective action as necessary. Such action might include a recommendation for a change in technique, mailing out replacement reagents, etc.

On the day your field samples are analyzed:

1) Perform a QC test on the standards before you analyze your field samples.

2) Record the result on the lab data sheet.

3) Analyze your field samples.

4) If you are analyzing 50 or more field samples at a time, you must perform a second QC test on the standards after you've analyzed your field samples. If you are analyzing 40 or less field samples at a time, MassWWP recommends, but does not require, that you peform a second QC test.

5) Record this second result on the lab data sheet.

Quality Control On Your Own: An Overview

In addition to participating in the MassWWP QC program, each volunteer water quality monitoring group would be well served by a written QA/QC plan of its own. This document spells out your sampling and analysis regimes in detail and serves as a reference for volunteers as well as a testament to the quality of your data for users. Please see Part One, section IV of this *Manual* for a description of QA/QC procedures. However, the following general guidelines will help minimize variation among volunteers when collecting and analyzing samples:

QC During Field Sample Collection

It is important to collect samples properly. A sample is a small selection of the actual material it represents. For example, for fecal coliform analysis, the sample type, location, and timing must consider the entire population to accurately reflect the "real world." Therefore it is imperative that all samplers be familiar with, and adhere to, procedures, recommendations and safety guidelines for the collection and analysis of water quality samples. Improperly collected samples cannot be analyzed, and thus, negate considerable effort and cost expended in their collection.

Always sample at the same site and spot, marking the site with colored tape if necessary.
Center stream sampling sites should ideally be at least three inches deep, free from debris and surface scum.
When sampling from a bridge, always sample on the upstream side.
Keep fingers out of buckets and bottles and caps.
When calibrating meters, pour some of the calibrating buffer or reagent into a clean beaker and calibrate. Do not immerse probe directly in buffer and/or reagent bottles as you may contaminate these solutions.
Label all bottles with assigned site number, date, time.
Once collected, samples should be kept cool and dark. This is to slow down biological activity that could alter results.
When icing samples, put 5 inches or less of ice at bottom of cooler - don't fill cooler to top, as meltwater could enter the bottle and contaminate your sample.

QC During Sample Analysis if working with local lab or WWTP

The Massachusetts Department of Environmental Protection recommends analyzing replicate samples at 10% of the sites, for example, at one site in ten. If you sample fewer than ten sites, try to keep close to this average over the course of the season. For instance, if you sample eight sites, then one replicate per sample day is in order. If you sample five sites, take one replicate every two months. However, if you can and wish to, more frequent replicates will improve your QC documentation. Call MassWWP for more advice.

IV. In the Field/In the Lab: MassWWP Recommended Procedures for Sample Collection and Analysis of Dissolved Oxygen, Temperature, pH and Alkalinity, and Fecal Coliform

For each indicator, we have first described the field sample collection procedure, including sample transport requirements ("In the Field"). We suggest that you photocopy and laminate these instructions so that they can be used by volunteer teams in the field for reference purposes. A checklist of field equipment you'll need follows. Next comes the lab analysis section ("In the Lab"), beginning with the MassWWP QC procedure for each parameter. Remember, you need to run the QC standards a few days prior as well as just before field sample analysis. Step-by-step procedures for lab analysis of your field samples follows. Equipment checklists for QC and lab analysis are provided. Total equipment lists and sources of equipment and supplies for each indicator appear in Appendix A.

Use of these protocols is intended to accompany MassWWP training sessions. Appendix E contains a matrix of parameters that groups might wish to sample in addition to the basic set described in full in this Manual. For advice on what tests best suit your needs, be sure to contact MassWWP.

A. In the Field: Dissolved Oxygen

Collecting the Sample:

ALWAYS TAKE TEMPERATURE AT SAME TIME YOU COLLECT DO SAMPLE -for calculating % saturation later. Immerse thermometer four to six inches below the water surface for at least thirty seconds to allow it to equilibrate. Read the thermometer immediately after removing it from the water.

1) Use a 300 ml BOD sample bottle. The water sample must be collected in such a way that you can stopper the bottle while it is still submerged. That means that you must be able to reach into the water with both arms. For DO samples, an extension pole is not feasible. The water must be deeper than the sample bottle and free of surface scum and debris.

2) Carefully wade into the stream, avoid stirring up bottom sediments. Stand so that you are facing one of the banks. If you are collecting from a bridge, make sure you are on the upstream side. If you are in a canoe, have your partner steady it and face one of the banks.

3) Collect the sample so that you are not standing or floating upstream of the bottle. Remove the stopper of the BOD bottle. Point BOD bottle downstream and slowly lower it into the water until the lip is just submerged. Allow the water to fill the bottle very gradually, avoiding any turbulence or air bubbles (this will add oxygen to the sample and skew your results). Submerge completely and allow to overflow to ensure that air bubbles are not trapped in the sample or gently tap the bottle to allow bubbles to escape.

4) Holding the bottle vertically, remove it from the river, leaving water around the cap at the flared mouth of the bottle. Cap the bottle by dropping the stopper directly into the bottle neck from 1/4 inch above. Check to make sure there are no air bubbles or space left at the top. If there are, you need to start over. Take your eyedropper and fill it with water from the stream. Go to the stream bank for step 5.

5) If there are no air bubbles present in the bottle, **"fix" the sample** immediately as described below:

a) Remove the stopper and add the contents of one Manganous Sulfate Powder Pillow (#1) and one Alkaline Iodide-Azide Powder Pillow (#2) to the 300 ml sample, using scissors or clippers to open packages. HINT: You may need to "roll" the pillow gently between your fingers to ensure delivery of all the powdered reagent into the sample bottle. Residual reagent powder around bottle neck can be washed into the bottle by swirling bottle gently.

b) Immediately insert the stopper so air is not trapped in the bottle. Holding the stopper in place, invert the bottle several times to dissolve the powder. An orange-brown flocculent precipitate will form if oxygen is present.

c) Allow sample to sit undisturbed and wait until the flocculent in the solution has settled to the bottom half of the bottle. Again invert the stoppered bottle several times and wait until the flocculent has settled. This insures complete reaction of the sample and reagents. HINT: Don't be afraid to invert vigorously several times for proper mixing and dissolution of reagents.

d) Remove the stopper and the contents of pillow #3 (Sulfamic Acid). Immediately insert the stopper so air is not trapped and invert several times to mix. The floc will dissolve and leave a yellow color if oxygen is present. HINT: If you have trouble avoiding introducing an air bubble in the sample at this step,

put a marble in the sample after adding pillow 3.

The oxygen in the sample is now "fixed" and ready to be analyzed in the lab.

6) Cap the bottle and seal by pouring a small amount of water into the flared lip area with the eyedropper of river water you collected in step 4.

7) Fill out the field sheet completely. Write the site # on the bottle, if it was not already done for you.

Troubleshooting:

Air bubbles may get trapped in the bottle under the glass stopper. This is most likely to happen after pillows # 1 and 2 have been added and the bottle has been inverted. Inverting the bottle may spill any water residing in the neck of the bottle.

TO FIX THIS: Ideally, learn how to drop the stopper from 1/4 inch above the bottle directly into the neck. This will form an airless seal. An alternative is to use an eyedropper filled with stream water from your site. After adding Reagent # 3 (sulfamic acid), dribble a bit of water into the bottle. This has the added advantage of rinsing into the solution any particles clinging to the bottle neck.

Transporting the Sample:

Store the bottle upright in your cooler. **The sample must be analyzed in the lab within 8 hours!**

Tip: Some groups maintain a complete extra set of bottles, so volunteers can collect next month's bottles as they drop off their samples at the lab. If you follow this procedure, make sure your bottles are kept in Zip-loc bags and boxed, or in some other clean and secure container.

CHECKLIST: Dissolved Oxygen

Field equipment:

___ Thermometer

___ 300 ml BOD bottle (1 per sample, or 2 per site, if taking duplicate samples)

___ Manganous Sulfate Powder Pillows (Pillow # 1) (1 per sample)

___ Alkaline Iodide-Azide Powder Pillows (Pillow # 2) (1 per sample)

___ Sulfamic Acid Powder Pillows (Pillow # 3) (1 per sample)

___ Fingernail clippers or scissors for cutting powder pillows

___ Eye dropper for topping off BOD bottle, if necessary

___ Field Sheet & pencil

___ Cooler or other transport container

___ Rubber gloves

___ Safety goggles

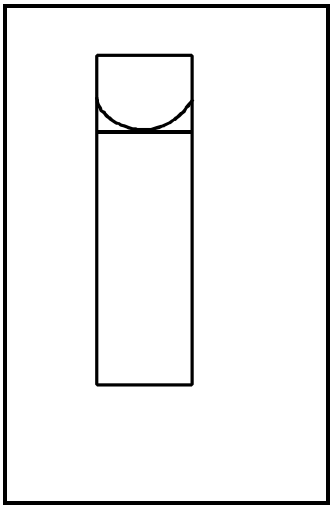
In The Lab: Dissolved Oxygen QC

Quality Control Procedure #1 - using QC test standard received from MassWWP:

1) Remove QC standard from refrigerator, warm to room temperature before testing.

2) Rinse out a 500 milliliter graduated cylinder by pouring a few mls of the test standard into it, swirling it around the cylinder, then pouring it down the drain.

3) Carefully measure exactly 300 mls of the test standard into the 500 ml graduated cylinder. When you measure a liquid quantity in a cylindrical container, a "meniscus", (a shallow U shape) forms on the liquid's surface. The bottom of the U should rest on the 300 ml line.



4) Pour the standard into a 300 ml DO bottle.

5) Slowly empty the contents of a **alkaline iodide-azide** powder pillow (Pillow # 2) into the bottle. (You don't use powder pillow # 1 in this QC test). Cap bottle so there is no air bubble, then invert several times. Let the solution settle, then invert several times again.

6) Empty the contents of a **sulfamic acid** powder pillow (Pillow # 3) into the bottle. Swirl this around until the reagent is dissolved. The solution should turn yellow.

7) Measure 100 mls of this "fixed" solution in a graduated cylinder. Transfer to a 250 ml erlenmeyer flask or beaker.

This fixed sample is now ready to titrate. Since this is a 100 ml sample, use the 0.2 N sodium thiosulfate cartridge (see Table 2).

In the Lab: Dissolved Oxygen Titration

Note: Run a QC test using test standards supplied by MassWWP before you process your field samples; please refer to the QC procedures on page....

1) Insert a clean delivery tube into the titration cartridge.

2) Attach the cartridge to the titrator body.

3) Over a sink, hold the titrator with the cartridge pointing straight up so any bubbles will drift to the top of the cartridge. Turn the delivery knob to eject air and a few drops of titrant - until there are no more bubbles present in the delivery tube or the cartridge. Reset the digit counter to 0.

4) Use the graduated cylinder to measure the correct volume of "fixed" field sample from the 300 ml BOD bottle according to Table 2 above.

5) Transfer the sample into a 250 ml erlenmeyer flask or 250 ml beaker. Place the flask on a white surface because you will need to observe a color change.

6) Place the delivery tube tip into the solution and swirl gently the flask (or use a magnetic stirrer) while turning the delivery knob. Continue titrating until your sample turns a pale yellow color. If the sample abruptly turns clear, you've gone past the endpoint and selected the wrong sodium thiosulfate or sample size. Re-titrate using a larger sample volume or lower strength sodium thiosulfate.

7) Add a few drops of Starch Indicator Solution and swirl to mix. This will turn your field sample dark blue.

8) Continue to titrate and swirl your sample until it turns clear. Record the digits required. If you are unsure that the color change from blue to clear was complete, deliver another few digits, one at a time. If no further color change is noted, use the first recorded number as your value. Otherwise, use the last digit at which a color change was noted.

9) Calculate mg/l of DO: DO = Digits Required x 0.02

10) Record your result on the data sheet.

11) Refer to the DO / temperature Table # 3 to see how close your result is to the theoretical value. Remember, your results can indicate dissolved oxygen values greater than 100%. If there's a problem, call MassWWP.

In the Lab: Dissolved Oxygen Troubleshooting.

1) Some brown particles may remain when the sample is ready for titration. This can cause variable results because the chemicals in the sample are now unevenly concentrated.

TO AVOID THIS: Carefully observe the BOD bottle after adding all three reagents. If particles are visible, or if there is a deposit on the bottom of the bottle, try shaking the bottle to dissolve any remaining solid matter. If this doesn't work, use a plastic, teflon, stainless steel or glass stirring rod or spatula to stir up the bottom sediments. This should allow the acid in the solution to fully dissolve the particles. You are then ready to titrate.

NOTE: Make sure you rinse the stirring rod well after trying this, to avoid corrosion of your utensil.

2) If your results seem wildly inaccurate, check to see you are using the correct Sodium Thiosulfate cartridge. Some folks have been known to use a sulfuric acid cartridge by mistake (that cartridge is used for pH and alkalinity analysis).

3) If you have titrated a quality control sample from the standard solution received from MassWWP and your value seems very high (remember, DO almost never goes above 14 mg/l in natural settings), it may be because you added powder pillow #1 to the standard before titrating. This QC test only uses pillows # 2 and # 3.

3b) Advance the plunger manually or with the delivery knob until titrant is forced out of the delivery tip and the delivery tube is filled with solution. Do this as you would a hypodermic syringe, with the delivery tip nearly straight up to remove all bubbles.

4) Sometimes an old cartridge can give an inaccurate reading, particularly if it has been left uncapped and allowed to evaporate somewhat. If you suspect the cartridge, try using a new one.

Checklist: Dissolved Oxygen

Laboratory Equipment For field sample and QC standard analysis:

___ Hach Digital Titrator

___ Hach Sodium Thiosulfate (0.2 N) Titration Cartridge (with clean delivery tube):

___ Starch Indicator Solution

___ Drop dispenser (for starch solution)

___ Fixed Water Samples in 300 ml BOD Bottles

___ Graduated Cylinder, 250 ml

___ Erlenmeyer Flask, 250 ml

___ Magnetic stirrer and stirring bar (optional)

___ Lab Sheet

___ Safety goggles and gloves

Additional Equipment For Quality Control tests.

___ 500 ml graduated cylinder

___ 500 ml beaker

In the Lab: Dissolved Oxygen Tabulation and Clean-Up

Figuring Percent Saturation of Dissolved Oxygen

When the pressure of oxygen in the air is the same as it is in the water, a water body is said to be at **saturation**, or 100% saturated. The dissolved oxygen (in mg/l) of water at saturation changes with temperature: the higher the temperature, the less oxygen water holds. Massachusetts Surface Water Quality Standards express minimum criteria for dissolved oxygen in both mg/l and % saturation (see Appendix C for details). To calculate % saturation of the sample, you divide the measured dissolved oxygen content of your sample by the maximum oxygen content possible at the temperature of your sample. The maximum oxygen content of water at various temperatures is given in Table 3 below.

For example, if you measured a DO concentration of 5 mg/l at 20 °C (river temperature) you would divide 5 mg/l by 9.08, the maximum concentration at 20 degrees C. The percent saturation would be 55%.

Your DO Measurement
Max. DO Concentration at Your Measured Temperature = ____% Saturation

Table 3. Maximum Dissolved Oxygen Concentration

Temp(C)	DO(mg/l)	Temp(C)	DO(mg/l)	Temp(C)	DO(mg/l)
0	14.6	18	9.45	36	6.82
1	14.19	19	9.26	37	6.71
2	13.81	20	9.07	38	6.61
3	13.44	21	8.9	39	6.51
4	13.09	22	8.72	40	6.41
5	12.75	23	8.56	41	6.31
6	12.43	24	8.4	42	6.22
7	12.12	25	8.24	43	6.13
8	11.83	26	8.09	44	6.04
9	11.55	27	7.95	45	5.95
10	11.27	28	7.81		
11	11.01	29	7.67		
12	10.76	30	7.54		
13	10.52	31	7.41		
14	10.29	32	7.28		

15	10.07	33	7.16		
16	9.85	34	7.05		
17	9.65	35	6.93		

CALCULATIONS

Data management:
1) Please fill out all forms completely.
2) Make a copy of your completed data sheets.
3) Mail the **copy** to MassWWP at Blaisdell House, UMass, Amherst MA 01003 - within 1 week of the test date, please.
4) Keep the original data sheet in an accessible file: a manila folder or 3 ring binder is a good idea.

Lab Cleanup for QC and sample analysis:
1) Wash glassware with distilled or deionized water. Periodically clean with a good lab detergent such as Alconox.
2) Remove the delivery tube from the cartridge. Rinse well, including inside of delivery tube.
3) Cap the sodium thiosulfate cartridge. **This is important - the solution will evaporate otherwise.**
4) Label the cartridge and store **out of the reach of children.**
5) Store reagents (powder pillows) in a cool place.

Prepare for next month's sample date:
1) Check to see how many data sheets you have for next month's sampling. If not enough for all samplers, make copies.
2) Check supply of bottles, reagents, cartridges. Order immediately if you don't have enough to get through next month.
3) **Mail the empty QC standard bottles back to MassWWP.**

4) Check the important dates on your calendar for next month:
Date on which you send a reminder note or phone call to volunteers.
Date you call lab to remind them to keep it open for you.
Date you will conduct a QC test (preferably 2 - 5 days prior to field sample date).
Date you bring bottles and data sheets to lab for volunteers to pick up.

Suggestions for the technical advisor:

It's a good idea for the technical advisor to make and copy a checklist of things the volunteer coordinator, field samplers and lab personnel should do each month with blank spots to fill in specific dates.

The checklist will vary for each group, depending on how a program is organized. Some examples of reminders a group might use:
2 weeks before test: Send a reminder note or phone call to volunteers.
2 - 4 days before test: run a QC test to check you equipment.
2 days before test: Call lab to remind them to keep it open for you.
Day before test: bring bottles and data sheets to lab for volunteers to pick up.
Morning of test: Place cooler w/ice at lab for volunteers to put samples in.

Remember, the more organized you are, the more free time you'll have.

To calculate the amount of equipment and supplies you will need for a season:

Digital titrators. Hach digital titrators are used to measure both dissolved oxygen and alkalinity. Many groups organize teams who collect samples from several sites, then bring samples to a lab where all samples are titrated with a single titrator. This system can work for up to 10 or more sites per titrator, but as it takes

5 to 10 minutes to run a sample, the purchase and use of additional titrators might be worth your while, in order to preserve the sanity of the lab analyst.

BOD Bottles: In addition to your regular sampling sites, we suggest taking one extra sample (a replicate sample) for every ten sites, or 10% of your sites, for quality control. Also, add one bottle for every 4 - 5 sites to account for breakage. Some groups like to have an extra set of bottles on hand for each site, so volunteer samplers can pick up their bottles for next month's sampling at the same time they drop off their field samples.

Reagents (or powder pillows): You'll need one pillow each of reagents #1,2, and 3 for each sample you take - or 2 of each per site, if you're doing duplicates. In addition, figure on several for QC sampling each month. QC sampling uses only pillows # 2 and 3, so you will need more of these. Figure at least 3 extra per program per month for practice tests, or perhaps more if you encounter a problem or wish to experiment with additional sites or investigate unscheduled pollution events, train new folks, etc. Always have at least a 2 month supply on hand.

Sodium thiosulfate cartridges: These are supposed to provide enough chemicals to titrate approximately 100 samples. However, if your waters are high in dissolved oxygen, you'll use the cartridges up faster. It's good to always have 2 on hand, in case one goes bad from being left with a loose cap or from some other accident. Keep refrigerated, and replace after each season.

Starch Indicator Solution: A pint or so of the "warehouse variety" should last a season. These contain preservatives, but you should still keep it refrigerated. If you make your own from potato starch, watch out for mold or other signs of spoilage.

MassWWP River Sampling

Lab sheet instructions

General instructions:

Date: Enter date samples were analyzed.

Temp.: For the "external" temperature / DO QC test. Enter the temperature of the water immediately before you analyze it.

Bottle #: Enter both the **site #** and the **field replicate #**. For example, if you filled 2 BOD bottles from site DR01, then you would have bottle #s DR01 #1 and DR01 #2. Make sure this # matches the site # on the field sheet!

Replicate #: On the lab sheets, replicate # indicates how many times you've run a test. For instance, if you tested DO QC bottle # 930793 three different times, enter replicate # 1, #2, or #3 for each test, respectively. Or, ran 2 analyses from DO bottle DR01 #1, enter replicate # 1 and #2, respectively.

QA/QC I.D.: Enter the bottle number, as written on the QC sample bottle sent by MassWWP.

Sheet #1: DO QC documentation.

Expected DO: Read the table and enter this value **after** you perform this QC test.

MASSACHUSETTS WATER WATCH PARTNERSHIP
RIVER SAMPLING

Laboratory Data Sheet # 1

DISSOLVED OXYGEN QUALITY CONTROL DOCUMENTATION

To Be Completed By Lab Analyst

Date: _____ River: _____ Technician: _____

Quality Control - external with MassWWP sample
Run #1: Conduct **before** testing field samples.

QA/QC I.D. (Bottle #)	digits of titrant	Measured D.O. mg/l

Quality Control - external with MassWWP sample
Run #2: Conduct **after** testing field samples.

QA/QC I.D. (Bottle #)	digits of titrant	Measured D.O. mg/l

MASSACHUSETTS WATER WATCH PARTNERSHIP
RIVER SAMPLING

Laboratory Data Sheet #2

DISSOLVED OXYGEN FIELD SAMPLE ANALYSIS

To Be Completed By Lab Technician

Date: _____ River: _____ Technician: _____

Field Samples

Sample I.D. (Bottle #)	Replicate No.	digits of titrant	Measured D.O. mg/l

Dissolved oxygen (milligrams per liter) = digits of titrant x .02

In the Field: pH

Collecting a pH Sample:

1) Take sample from mid-stream, if possible. If not, get as far out from shore as is safe. Collect sample so that you are not standing or floating upstream of the bottle.

2) Hold thermometer four to six inches under water for at least 30 seconds. Record temperature.

3) Uncap Nalgene bottle, rinse three times with river water and dip completely under water, filling to overflowing.

4) Cap bottle while it is still underwater, in order to eliminate any air from the sample bottle.

Transporting the Sample to lab:

1) Keep in a cool dark place such as a cooler.

2) Deliver to lab within 6 hours.

CHECKLIST

Field equipment for pH and alkalinity:

___ Thermometer

___ Nalgene bottle (at least 250 ml, preferably 500 ml)

___ Field sheet and pencil

___ Cooler

In the Lab: pH and Alkalinity QC

Please review the section on pH meter care and maintenance. Check your pH meter out thoroughly each month before you proceed with analysis. Use of a pH meter accurately requires calibration with known pH buffers before each use (see section IVB for equipment care). These buffers have a limited shelf life. It is a good idea to warm up both you and the pH electrode with a trial titration before you begin QA/QC or field sample analysis.

Quality control for pH and alkalinity consists of normal pH measurement and titration of a standard provided by MassWWP and sent to you prior to field collection. The procedures for analyzing QC standards provided by MassWWP and of field samples you collect are exactly the same.

Remember, the general QC program requires that you:

Always standardize your pH meter using the pH 4 and 7 buffers prior to any analysis of QC standards or field samples. Prior to measuring alkalinity, it is a good idea to check your titrator before inserting the sulfuric acid cartridge to see if the counter works properly. Some have been known to skip a digit at the ten or hundred place.

Run a QC test 2 - 5 days prior to testing your field samples. Record your results.

Call MassWWP with the results of this test. Resolve any problems encountered.

Run a QC test on the standards immediately before and immediately after you analyze your field samples. Record your results.

Several days prior to sampling, you will receive a QC standard from MassWWP. Follow the procedures described for pH and alkalinity measurement. Phone MassWWP with the results at 413-545-5532 from nine to five Monday through Friday. If there is a significant discrepancy between what we expect and what you measured, we will work with you to troubleshoot the problem so that you are confident of quality analysis for the field samples.

On the day that you analyze your field samples, analyze your QC standard again. If you are analyzing more than five samples at a time, you should run a QC standard before and after field sample analysis. If you are analyzing less than five samples, you may run the QC standard before and after, but are required to run a standard only prior to field sample analysis. These results should be reported on the pH & alkalinity lab data sheet.

In the Lab: pH Measurement

Follow the same steps for analyzing both the field samples and QC standards:

1) Remove QC standard or field sample from refrigerator, bring to room temperature before testing (about an hour). **Keep bottle capped while it is warming up, to avoid sample/standard coming into contact with air.**

2) Measure **100 ml** of the sample/standard in a 150 ml or larger graduated cylinder. Pour into a 150 ml or larger beaker. Recap QC bottle.

3) Rinse your pH electrode in deionized or distilled water, then place the pH electrode in the test sample/standard. **pH should be analyzed within 5 minutes of uncapping the sample/standard bottle.**

4) The sample/standard should be stirred very gently, preferably with a magnetic stirrer. **Careful not to break the glass pH electrode!**

5) Watch for the meter reading to become stable. (This may take up to 3 minutes).

6) When stable, but not in excess of 5 minutes, record the sample pH to the nearest 0.01 pH unit.

7) Record pH value on the lab data sheet. Keep the pH electrode immersed in the sample/standard as you continue with the alkalinity procedure.

IF the pH of your sample/standard is ABOVE 4.5, proceed directly to the lab procedure for alkalinity on page 68.

IF the pH of your sample/standard is BELOW 4.5, proceed to the next page for additional steps required for the lab procedure for alkalinity.

IF the pH of your sample/standard is BELOW 4.5:

1) Make a note of the initial pH value on your data sheet.

2) Enter "0" in the 4.5 column of the data sheet.

3) Titrate as described in steps 1-12 on page 68 until the pH is 0.3 units below the initial pH value.

4) Enter the digits of titrant used in the 4.2 column of the data sheet.

5) Write down the pH reading where you stopped (as an accuracy check).

6) Calculate alkalinity using Method 2.

In the Lab: Alkalinity Titration

Titrations go better if the delivery tip is positioned under the surface of the solution being titrated. For one or two samples, the titrator can be held in the hand. However, it is easier to mount the titrator on a ring stand using a clamp. Try to keep the titrator in a vertical position (delivery tube down) throughout all titrations; putting the titrator horizontally on the bench between titrations may introduce bubbles in the tip.

1) **Put on your safety goggles!**

2) Attach a sulfuric acid cartridge to the Hach Digital Titrator. Attach a clean delivery tube to the cartridge.

3) Advance the plunger manually or with the delivery knob until titrant is forced out of the delivery tip and the delivery tube is filled with solution. Do this as you would a hypodermic syringe, with the delivery tip nearly straight up to remove all bubbles.

4) Check for leaks where the tip connects to the cartridge.

5) Rinse the tip **gently** with distilled water or sample and dry with a Kimwipe; this is important because the titrant is concentrated and even a small amount left on the tube can affect your results. Do not flush titrant out of the tip.

6) Reset the digital titrator counter to zero and you are ready to titrate.

7) Holding the titrator vertically, immerse the delivery tip into the sample, and begin adding titrant. Titrate until the pH is lowered to 4.5.

8) Record the number of digits of titrant it takes to get to 4.5 pH.

9) Continue titrating, **without** resetting the counter, until you get to 4.2 pH. Keep an eye on the digital counter to make sure it does not accidentally skip digits.

10) Record the number of digits shown on the counter.

11) After completing a titration and recording the digits of titrant used, rinse the delivery tip with distilled water. **This is easily forgotten when busy.**

12) RESET THE COUNTER before titrating the next sample.

13) Calculate Alkalinity using the formulas provided on page ...

If you make a mistake and overshoot the initial 4.5 pH mark:
1) Record the pH value you reached and the number of digits required to get there.

2) Continue titrating as above, until you reach a pH value 0.3 units below the value you reached above.

3) Record the second pH value and the number of digits. Calculate alkalinity as shown in Method 1..

CHECKLIST

pH and Alkalinity Laboratory Equipment

___ SAFETY GOGGLES.

___ Rubber gloves.

___ Wash bottle.

___ 150 ml or larger graduated cylinder.

___ 150 ml or larger beaker.

___ pH meter in good working order.

___ Hach Digital Titrator, with clean delivery tube.

___ Sulfuric acid cartridge, .16N.

___ Distilled or deionized water to clean.

___ Lab data sheets.

Optional, but preferred:

___ Magnetic stirrer, with stir bar.

___ Ring stand and clamp to hold titrator with.

___ Kimwipes

In the Lab: pH and Alkalinity Tabulation and Clean-Up

Calculating alkalinity (ANC) in mg/l CaCO3

If initial pH was above 4.5, use Method 1:

Alkalinity = (2A - B) x 0.1.
where:
A = digits used to pH 4.5.
B = digits used to pH 4.2 (INCLUDING digits to get to 4.5).

Example: It took 100 digits to lower pH to 4.5, another 25 to lower to 4.2.
A = 100. B = 125.
Alkalinity = (2x100 - 125) x 0.1 = 7.5 mg/l CaCO3.

The volume of sample you analyze affects this calculation. You should always titrate 100 mls of sample or standard solution. Should the need arise to titrate 50 mls, use equation (2A - B) x .02; if titrating 200 mls, use equation (2A - B) x 0.05.

If initial pH was below 4.5, use Method 2:

Alkalinity = (2A - B) x 0.1.
where:
A = 0
B = the endpoint # of digits.

Example:
Initial pH is 4.3. The sample required 22 digits to lower the pH to 4.0.
A = 0. B = 22.
Alkalinity = (0 - 22) x 0.1 = - 2.2 mg / l.

Although the negative alkalinity value may not seem to make much sense, it is an extremely important measurement for assessment of acidification. Negative alkalinity values indicate that not only has all the buffering capacity of the water been exhausted, but the water now has an excess of strong acids present which further depress the pH.

CALCULATIONS

Data management:
1) Please fill out all forms completely.
2) Make a copy of your completed data sheets.
3) Mail the **copy** to MassWWP at Blaisdell House, UMass, Amherst MA 01003 - within 1 week of the test date, please.
4) Keep the original data sheet in an accessible file: a manila folder or 3 ring binder is a good idea.

Lab Cleanup:
1) Wash glassware with distilled or deionized water. Periodically clean with a lab detergent such as Alconox. Use a scrub brush if there is dirt in the bottle.
2) Wash Nalgene bottles and caps in the same manner. fill them with distilled water to store.
3) Remove the delivery tube from the cartridge. Rinse well, including inside of delivery tube.
4) Cap the sulfuric acid cartridge. **This is important - the solution will evaporate otherwise.**
5) Label cartridge and store in refrigerator, out of the reach of children.

Prepare for next month's sample date:
1) Check to see how many forms you have for next month's sampling. If not enough for all samplers, make copies.

2) Check supply of bottles, reagents, cartridges. Order immediately if you don't have enough to get through next month.

3) **Mail the QC standard bottles back to MassWWP.**

4) Check the important dates on your calendar for next month: for instance:
Date on which you send a reminder note or phone call to volunteers.
Date you call lab to remind them to keep it open for you.
Date you will conduct a QC test (preferably 2 - 5 days prior to sample date).
Date you bring bottles and data sheets to lab for volunteers to pick up.

To calculate the equipment and supplies you'd need for a season:

Digital titrators. Hach digital titrators are used to measure both dissolved oxygen and alkalinity. Many groups organize teams who collect samples from several sites, then bring samples to a lab where all samples are titrated with a single titrator. This system can work for up to 10 or more sites per titrator, but as it takes 5 to 10 minutes to run a sample, the purchase and use of additional titrators might be worth your while, in order to preserve the sanity of the lab analyst.

Nalgene Bottles. In addition to your regular sampling sites, we recommend taking one extra sample (a replicate sample) for every ten sites, or 10% of your sites. Some groups like to have a second set of bottles on hand for each site, so volunteer samplers can pick up their bottles for next month's sampling at the same time they drop off their field samples.

Sulfuric Acid Cartridges. Average alkalinity values for Massachusetts waters are 18 mg/l. At this value, you are likely to get about 50 tests per cartridge. If your river has higher alkalinity, you'll use up the cartridges faster. More acidic waters will use less of the titrant. Figure the number of sites and number of sample dates you're doing. Triple or quadruple that amount, to account for replicates, QC tests, and other special events. That will give a rough idea of how many cartridges you'll need. It's a good idea to have 2 on hand, in case one goes bad. Keep refrigerated and replace after each season.

pH meter. In most cases, we recommend you try to obtain use of a reliable pH meter, rather than purchasing your own. pH meters work best when used frequently, rather than once or twice a month. Many colleges, wastewater treatment plants, environmental consulting firms, and some high schools and businesses have meters they might let you use. Feel free to call MassWWP to discuss this if you have questions.

pH electrodes. If you purchase a meter, electrodes will come with it. They will require careful maintenance if you expect them to last more than 1 year. Refer to section IVB on care of your pH meter.

MassWWP River Sampling
Lab sheet instructions

General instructions:

Date: Enter date samples were analyzed.

Temp.: For the "external" temperature / DO QC test. Enter the temperature of the water immediately before you analyze it.

Bottle #: Enter both the **site #** and the **field replicate #**. For example, if you filled 2 BOD bottles from site DR01, then you would have bottle #s DR01 #1 and DR01 #2. Make sure this # matches the site # on the field sheet!

Replicate #: On the lab sheets, replicate # indicates how many times you've run a test. For instance, if you tested DO QC bottle # 930793 three different times, enter replicate # 1, #2, or #3 for each test, respectively. Or, ran 2 analyses from DO bottle DR01 #1, enter replicate # 1 and #2, respectively.

QA/QC I.D.: Enter the bottle number, as written on the QC sample bottle sent by MassWWP.

Sheets #3 and #4: pH and ANC.

Volume Titrated: How many mls of water did you titrate? Usually 100 ml.

Digits: Enter the number of digits of sulfuric acid it took to reach pH 4.5 and 4.2. Remember that the 4.2 reading INCLUDES the number of digits it took to get to pH 4.5, so it will always be higher than the first reading.

Alkalinity: You may enter the results of the calculation, giving the ANC in mg/l CaCO3. However, our computer will calculate this for you, so it's not necessary.

MASSACHUSETTS WATER WATCH PARTNERSHIP
RIVER SAMPLING

Laboratory Data Sheet # 3

pH AND ALKALINITY QUALITY CONTROL DOCUMENTATION

To Be Completed By Lab Technician

Date: _____ River: _____ Technician: _____

Quality Control - external, sample from MassWWP

Run #1: To be conducted **before** analysis of field samples

QA/QC No. (Bottle #)	pH	Volume Titrated (V)	digits to pH 4.5 (A)	digits to pH 4.2 (B)	Alkalinity (mg/l)*

Quality Control - external, sample from MassWWP

Run #2: To be conducted **after** analysis of field samples

QA/QC No. (Bottle #)	pH	Volume Titrated (V)	digits to pH 4.5 (A)	digits to pH 4.2 (B)	Alkalinity (mg/l)*

MASSACHUSETTS WATER WATCH PARTNERSHIP
RIVER SAMPLING

Laboratory Data Sheet # 4

pH AND ALKALINITY FIELD SAMPLE ANALYSIS

To Be Completed By Lab Technician

Date: _____ River: _____ Technician: _____

Sample Analysis

Sample I.D. (Bottle #)	Replicate#	pH	Volume Titrated (V)	digits to pH 4.5 (A)	digits to pH 4.2 (B)	Alkalinity (mg/l)

Alkalinity = (2A - B) x 0.1

In the Field: Fecal Coliform Bacteria

Sampling waters for fecal coliforms involves four basic steps:

1) Preparation - approximately 2 hours
2) Sample collection - approximately 15 minutes per site.
3) Filtration and Incubation - approximately 5 minutes per sample (not including the 24-hour incubation period)
4) Tabulation and Cleanup - approximately 2 hours

1) Preparing sample containers: Factory-sealed, pre-sterilized, disposable Whirl-pak bags need no preparation. Bottles should have tape over the cap or some seal marking it to indicate that they have been sterilized. Check to be sure that the seal has not been removed. Re-used sample containers (and all glassware used in this procedure) must be rinsed and sterilized at 121°C for 15 minutes using an autoclave.

2) Collecting the sample: Sample away from the riverbank in the main current. In any case, avoid sampling stagnant water! The outside curve of the river is often a good place to sample since the main current tends to hug this bank. In shallow stretches, wade into the center current carefully to collect the sample. If wading is not possible, tape your sample bottle to an extension pole or use a boat. Reach out from shore or boat as far as safely possible. A boat will be required for deep sites. Try to maneuver the boat into the center of the main current to collect the water sample.

> Samples for bacteria must be analyzed within 6 hours ofcollection. After collecting samples, keep them on ice and bring them to the lab or drop-off point as soon as possible.

For Screw-cap Sample Bottles:

> 1. Remove the cap from the bottle just before sampling. Don't touch the inside of the bottle or the cap. If you accidentally touch the inside of the bottle, it is contaminated and you must use another one!
>
> 2. *Wading*: try to disturb as little bottom sediment as possible. In any case, be careful not to collect water that has sediment from bottom disturbance. Stand facing upstream. Collect the water sample on your upstream side.
> *Boat*: Carefully reach over the side and collect the water sample on the upstream side of the boat.
>
> 3. Hold the bottle near its base and, with mouth pointing down, plunge it below the water surface. If you are using an extension pole, remove the cap, turn the bottle upside down and plunge it into the water, facing upstream. Collect a water sample 8 to 12 inches beneath the surface or mid-way between the surface and bottom if shallow.
>
> 4. Turn the bottle underwater into the current and away from you. In slow-moving river reaches, push the bottle underneath the surface and away from you in an upstream direction.

5. Leave a one inch air space in the bottle. Do not fill bottle completely (so that the sample can be shaken just prior to analysis). Recap the bottle carefully - remember, don't touch the inside!

6. Fill in the bottle # and/or site # on the appropriate field sheet. This Is Important! It's the only way the lab coordinator will know which bottle goes with which site.

7. Place the sample in the iced cooler. Bring all samples to the lab for analysis within **six hours** of sampling. Late or warm samples tend to yield highly inaccurate results.

For Whirl-pak Bags:

1. Tear off the top of the bag along the perforation above the wire tab just prior to sampling. Avoid touching the inside of the bag! If you accidentally touch the inside of the bag, use another one!

2. *Wading*: Try to disturb as little bottom sediment as possible. In any case, be careful not to collect water that contains bottom sediment. Stand facing upstream. Collect the water sample on your upstream side.
Boat: Carefully reach over the side and collect the water sample on the upstream side of the boat.

3. Hold two white pull tabs in each hand and lower the bag into water on your upstream side with the opening facing upstream. Open the bag mid-way between the surface and the bottom by pulling the white pull tabs. The bag should begin to fill with water. You may need to"scoop" water into the bag by pushing it upstream and away from you. Fill the bag no more than 3/4 full!

4. Bring the bag out of water. Pour off excess water. Pull on the wire tabs to close the bag. Continue holding the wire tabs and flip the bag over at least 4-5 times quickly to seal the bag. Don't squeeze the air out of the top. Fold the ends of the wire tabs together at the top of the bag, being careful not to puncture the bag. Twist them together forming a loop. Label the bag with the site number, date, and time and put the sample on ice in a cooler.

5. Fill in the bag and/or site# on the appropriate field sheet. This Is Important! It's the only way the lab coordinator will know which bottle goes with which site.

6. Place the sample in the cooler. Bring all samples to the lab for analysis within **six hours**.

Remember to label the bag with Site #, date, and time!

In the Lab: Fecal Coliform Bacteria

Preparation for Lab Analysis

1) Wash and sterilize labware: pipets, sample bottles, filter funnels (wrapped in kraft paper or foil), dilution bottles, tweezers. Wash labware with non-phosphate detergent, rinse well with tap water and final rinse with distilled or deionized water. Autoclave at 121°C for 15 minutes. If using pressure cooker type autoclave pay close attention to temperature/pressure gauge. Prepare and sterilize buffered water if needed (see Step 6 below).

2) Clean and disinfect work area.

3) Set out pipets, petri plates, membrane filters, absorbent pads, filter funnels, buffered water, dilution bottles, graduated cylinder, marking pen, gas burner, tweezers, filtration unit, vacuum pump, hot plates with 1000 mL beakers full of sterile water.

4) Turn water bath on and set to 44.5°C (± 0.2°C) prior to beginning sample run. Allow 2 hours for water temperature to stabilize. After the bath reaches 44.5°C check frequently to assure that the temperature fluctuation does not exceed ± 0.2°.

5) Prepare M-FC nutrient media (follow directions on bottle) Do not reuse media after it is more than 96 hours old. To make rosolic acid solution to mix with FC medium:

a.Weigh out 0.1 gram of rosolic acid on weighing paper and put into a 10 mL test tube.
b.With a 10 mL volumetric pipet add 10 mL of 0.2N NaOH to test tube.
c.Cover with parafilm and shake until dissolved.
d.Keep in refrigerator until ready to use with M-FC media (solution is good until it turns muddy - approx. 96 hours).

6) Prepare Buffered Rinse Water:
Using the pre-measured potassium dihydrogen phosphate and magnesium choride powder pillows, follow the manufacturer's directions to prepare an appropriate volume, about 20 ml per sample, of sterile buffered rinse water. This is used to wash down the sides of the filter funnel during filtration.

Filtration and Incubation

1) Place absorbent pads in petri dishes and saturate with M-FC media. Pour off any excess after the pad has soaked for several minutes.

2) Dip tweezers in ethanol and flame in burner. Allow tweezers to cool before touching membrane filter.

3) Remove membrane filter from sterile wrapping with tweezers. If you accidentally touch the membrane filter with your hand, discard it and start over with a new one.

4) Place filter on filter holder and put funnel over filter. If filter melts from heat of tweezers or if a piece breaks or it cracks, replace with another filter.

5) The first sample run should be a "negative" (distilled or buffered rinse water). The second should be a "positive" (a water sample known to contain bacteria). See step 12. For the first field water sample, shake sample bag vigorously for 10 seconds, remove cap, and pour 50 milliliters of sample into filter funnel.

6) Turn vacuum on. When all the liquid has been sucked through the filter, wash down the sides of the filter with sterile buffer water and vacuum through.

7) Flame tweezers and remove filter from holder. Be careful to clamp just the edge of the filter with tweezers. Grab filter with tweezers no more than 1/8 inch from filter edge - do not to touch the surface area of the filter that may have bacteria trapped on it.

8) Remove lid of a petri plate and place membrane filter on absorbent pad. Make sure the filter is perfectly flat and that there are no air pockets between membrane filter and absorbent pad.

9) Replace lid and mark the plate with the site or container number.

10) Place filter funnel and base in a pan or beaker of boiling water for a few minutes to sterilize. Be sure to allow the funnel and base to cool before using. A good procedure is to have two or three funnels and bases that you can rotate through the boiling water.

11) Repeat above procedure for 50mL and 1 mL of each sample.

12) To help assure that sterile conditions have been maintained, run *negative* and *positive* control plates at the beginning, after every ten samples, and at the end:

A negative control plate will help detect any cross-contamination that may occur from sample to sample, or any contaminants that have been introduced externally. Filter about 50 ml of the buffered rinse water instead of a water sample. If any bacteria show up on this plate after incubation, contamination has occurred and the results of samples filtered after this will be invalid. Mark the first negative control plate as -1, the second as -2, etc. Mark these as the site number on your lab sheet. This will enable you to keep track of when these were run.

It is also necessary to run a positive control plate to assure that if bacteria are present they are being detected. Perform the same filtration procedure as for a sample but use water that is

known to contain fresh fecal matter. Influent to a wastewater treatment plant works well or deydrated bacteria may be obtained from the EPA. It is only necessary to use a small amount of this water - 1 ml or so. Again, use the -1, -2, etc. marking procedure described above to document when these plates were run.

13) Transfer the plates to Whirl-Pak bags and seal.

14) Place each sealed Whirl-pak, with the plates enclosed, in a larger Whirl-pak and seal. Immerse in water bath set at 44.5°C (± 0.2°) for 24 hours (± 2 hours). Whirl paks are sterile plastic bags that have an opening which is sealed by folding over the opening and securing it with twist ties that are attached to the mouth of the bag. It is very important that the bags are sealed properly to avoid leakage while the petri plates incubate in the water bath. Leakage will negate the test results and all your work will be lost.

To properly seal the whirl-pak: fold over the twist tie opening of the bag at least three times. It is very important that each fold be wrinkle free. Then fold over each end of the twist tie toward the middle of the folds to clamp the folds together. There should be a slight amount of air trapped in the bag. Give the bag a gentle squeeze between the palms of your hands to test the seal. If you notice air leakage re-seal the bag. It is this air pressure that keeps water from seeping in the bag.

15) Record the mL's filtered and the time the incubation was begun for each sample.

16) Wash sample bottles and other apparatus used for processing samples so that it may be sterilized in the autoclave for the next run.

In the Lab: Fecal Coliform Tabulation and Clean-Up

The Massachusetts Surface Water Quality Standards express swimming and shellfishing criteria as the number of fecal coliform colonies per 100 milliters of water. To figure out the number of colonies in your samples, follow these steps:

1) Remove petri plates from whirl paks. For each sample, select the membrane filter with the number of colonies within the acceptable range and count membranes with ideally 20-60 blue stained colonies. If not familiar with the blue color that is characteristic of fecal coliform colonies, have someone who is experienced check your results, i.e., save the petri plates in the refrigerator and have someone confirm your results. Calculate the final value using the formula:

Example:

2) Record the 65 in the "filter count" column on the lab sheet. Record the final value in the "fecal coliforms per 100 mL" column on the lab sheet. as "650". Note: If the total of all of the colonies on the plate is over 200, the colonies are too numerous to count (TNTC) and no actual count is made (see Example 3A. below to calculate results).

3) If the counts on the filters for all of the aliquots for a sample are not within the ideal range of 20 -60, use the following calculation methods (from Irma Simon, ME DEP, 1990). Examples are given based on 50 mL and 10 mL aliquots filtered for each sample.

A. If both counts are > 60: e.g. 130 (for 10 mL) and TNTC (for 50 mL), then:

Example:

Record the result on the lab sheet preceded by an "E" for estimated: "E800".

B. If both counts are < 20: e.g. 2 (for 10 mL) and 15 (for 50 mL):

Example:

Record the result on the lab sheet as "30"

C. If counts are both > 60 and < 20; e.g. 15 (for 10 mL) and 350 (for 50 mL):

Example:

Record the result on the lab sheet as "150"

4) Place petri plates back in whirl-paks and sterilize in autoclave. If time allows, wash and sterilize labware for next sampling run

CALCULATIONS:.

MASSACHUSETTS WATER WATCH PARTNERSHIP
RIVER SAMPLING

Laboratory Data Sheet # 5

BACTERIA SAMPLE ANALYSIS

To Be Completed By Lab Technician

Date: _____ River: _____ Technician: _____

Method: _____ Membrane Filter _____ MPN

Bacteria Type: ___ **Fecal Coliform** ___ **Total Coliform** ___ **E. coli**

___ **Other** (Specify): _____

Sample I.D. (Bottle #)	Replicate No.	Dilution Factor	# Colonies	Colonies / 100 ml

MassWWP River Sampling
Lab sheet instructions

General instructions:

Date: Enter date samples were analyzed.

Temp.: For the "external" temperature / DO QC test. Enter the temperature of the water immediately before you analyze it.

Bottle #: Enter both the site # and the field replicate #. For example, if you filled 2 BOD bottles from site DR01, then you would have bottle #s DR01 #1 and DR01 #2. Make sure this # matches the site # on the field sheet!

Replicate #: On the lab sheets, replicate # indicates how many times you've run a test. For instance, if you tested DO QC bottle # 930793 three different times, enter replicate # 1, #2, or #3 for each test, respectively. Or, ran 2 analyses from DO bottle DR01 #1, enter replicate # 1 and #2, respectively.

QA/QC I.D.: Enter the bottle number, as written on the QC sample bottle sent by MassWWP.

Sheet #5: Bacteria.

Method: MassWWP has provided a protocol for the membrane filter technique. If you are working with a local WWTP, indicate whether they are using the Most Probable Number technique.

Bacteria Type: Enter the type you are testing.

Dilution Factor: Enter amount of SAMPLE (before dilution) that is filtered in this test. For example, if 10 ml were filtered straight onto the filter, enter 10 ml. If 1 ml of sample were diluted in 100 ml of distilled water, and you then filtered 10 ml of that dilution, enter .1 ml.

Colonies: Enter the NUMBER OF COLONIES YOU ACTUALLY COUNTED.

IV.B. Equipment Calibration and Care

Care of your pH meter

General electrode care and handling procedures are very important in your lab because pH measurements will only be as good as the condition of your electrode(s). For greater accuracy in your measurements and longer electrode life, there are a few areas of electrode care with which you should be familiar.

Storage

Glass combination or separate pH and reference electrodes should be kept wet. The reference electrode requires a free-flowing junction, so be sure to maintain the reference filling solution at a level significantly above the storage or sample solution level at all times. This will provide a positive head pressure, which forces the filling solution out through the junction rather than the storage solution into the probe.

For long-term dry storage, the sleeve or plug should cover the filling hole to reduce any flow of filling solution. During calibration or short-term storage in pH 4 buffer, this sleeve or plug must be slid away or removed to allow flow of the reference solution into the sample.

To obtain a faster electrode response, the glass electrode should be stored in a slightly acidic solution. In the protective cap for the glass electrode, put a drop or two of pH 4 buffer and put the cap on the electrode, carefully. Distilled water extracts ions from the bulb causing a slower response; pH 7 buffer over a long time period ages the electrode slightly.

If using a separate reference electrode, the best solution would be to place the reference electrode in its own filling solution but this can be messy. Providing KCl to both sides of the junction keeps it flowing freer. To reduce the salt crust of saturated solution, an approximately 0.1 M KCl solution may be used, but for storage only. Experience indicates that simply covering the filling hole with the protective sleeve and storing dry suffices in most instances as long as the soaking procedure is followed.

For combination electrodes, store the electrode in a combined solution of approximately 0.1 M KCL in pH 4 buffer.

If the reference electrode is to be stored for more than four months, it should be emptied of liquid and stored dry in a sleeve. During the sampling season, keep it immersed in pH 4 buffer.

One day or more prior to analysis, soak both electrodes in fresh pH 4 buffer. During analysis, place the electrodes in the same buffer and store them in the buffer when not in use.

Reference Electrode Filling Solution

Read the instructions that came with your electrodes carefully. When filling electrodes or replacing the solution, use whatever solution is called for in the instructions. When in doubt, call MassWWP and we will advise you. Be sure to ascertain which filling solution is correct for your electrode(s) and double check that your filling solution matches these requirements.

NOTE: Due to their unique micropore junction, it is recommended that permanently filled or Gel electrodes be stored hanging dry.

Preliminary Electrode Response Testing

If your electrode exhibits slow response, poor span between two buffer values or undue sensitivity to movement of the electrode, rejuvenation may be necessary to improve performance.

Response varies with the electrode and the solution it is in. Generally working electrodes reach 0.05 pH units of the final reading in buffer within 10 seconds. A stable reading (less than 0.01 pH units per minute change) should be reached in fresh water samples within a minute or two. If you have to wait too long (5 minutes or more) then the pH itself may change due to the contact of the water sample with air.

Electrodes may also require adjusting the slope to values significantly different from 100% for two point calibration. Perform the following test if in doubt:

Set your meter to 100% slope and room temperature, then standardize as usual with pH 7 buffer. Without moving the slope dial, read a pH 4 buffer. It should read between 3.85 and 4.15; set the slope to read pH 4, the slope should be 95% to 105%.

If your electrode exhibits either of the above problems or is sensitive to movement, rejuvenation is in order.

Glass Electrode Rejuvenation

To treat the bulb of the pH electrode:

We can provide 2 bottles of acid and base (0.1N). **BE CAREFUL WHEN HANDLING THESE SOLUTIONS - USE RUBBER GLOVES AND WEAR PROTECTIVE EYEWEAR. IF YOU GET ANY ON YOU RINSE IT OFF WITH LOTS OF WATER.** To treat, simply dip the bulb into the acid and immediately into the base. Repeat this several times. Then rinse the electrode under tap water and let sit in pH 4 buffer for 1/2 hour. Rinse the electrodes and restandardize as you normally do with pH 7 and pH 4 buffers. You may need to do this several times a year.

Another treatment is to gently wash the pH bulb with a tissue soaked in methanol. Rinse with water and soak in pH 4 buffer.

To treat the reference electrode:

Replace the 4M KCl solution in the reference electrode and get rid of crystals that may have formed. If there are lots of crystals, then shake out the solution and put deionized pure water into the filling hole and soak the electrode tip in hot tap water for 15 minutes or so until the crystals have dissolved. Then shake all the liquid out of the filling hole in the reference electrode and refill with fresh 4 M KCl. Let the electrode sit at room temperature for 1/2 hour before use. Frequently add more 4M KCl solution to the reference electrode since it will continually leak out and evaporate. The solution in the electrode should be within 1/2 inch of the filling hole. The hole should be open when reading pH but close it when you are through for the day or else the solution will evaporate and new crystals will form. If you still have problems with slow response, try rubbing the tip on your blue jeans or on very fine (600 grit) sandpaper.

Final Test For Linearity

Standardize the meter as described below. Rinse the electrodes and your sample cup with pure deionized water. Then titrate 100.0 ml of deionized water with your 0.16N acid as follows: Make sure your digital titrator is working and reset to zero. Add 10 digits of acid, record digits and pH, increase acid to 20 digits, record pH; repeat until you have added 100 digits of acid and stop. Send the results to us and we will send you a report. If you want to see the results yourself, try plotting the hydrogen ion concentration ($H = 10^{(-pH)}$) vs. digits and see if the line is straight.

Movement Sensitivity

If your meter gives wild readings and is sensitive to your touch, it may not be properly grounded. Try using a three prong power plug or attach a wire from the meter to a cold water pipe. Sometimes a problem of fluctuating readings or consistently wrong readings can be solved by disconnecting and reconnecting the electrode connectors several times. Apparently an oxide layer can sometimes cause these symptoms.

CALIBRATION

The pH meter should be standardized (calibrated) prior to sample analyses and after every 25 sample analyses. Buffers should be at room temperature ($68^{o}F$). Remove the electrodes from the pH 4 buffer solution where they have been soaking for at least one day. Rinse with deionized water. Insert the electrodes in pH 7.00 buffer and adjust the calibration dial until exactly pH 7.00 shows on the meter. Remove the electrodes and rinse with deionized water. Place the electrodes in pH 4.01 buffer and adjust the slope until the meter shows pH 4.01. Rinse with deionized water. Test the pH 7 buffer again. If necessary, repeat the calibration.

A note on buffers

The accuracy of your pH measurement is in direct relation to the accuracy of the standard buffer solution used to calibrate your pH meter. In order to maintain a reasonable degree of accuracy when making a pH measurement, a number of precautions concerning the care and use of buffers should be observed. These include:

Do not use buffers after their expiration date. Mold growth, CO_2 absorption and contamination cause changes in the buffer pH.
Do not use buffers which have mold growth floating in the buffer.

Always cap the buffer container when storing to prevent contamination and reduce CO_2 pickup.

pH buffer values change with temperature. It is best to test buffers at room temperature. In any case, record the temperature of your buffer solution. Refer to the chart below (interpolating the expected value if your buffer temperature is between the temperatures listed) before standardizing the meter.

Do not pour used buffer back into the bottle.

Buffer Values at Various Temperatures

Temperature C	Temperature F	pH 4.0	pH 7.0
0	32	4.003	7.119
5	41	3.998	7.086
10	50	3.996	7.058
15	59	3.996	7.035
20	68	3.999	7.015
25	77	4.004	7.000
30	86	4.011	6.988

Calibrating your thermometers

The following protocol is used by the Chesapeake Bay Citizen Monitoring Program to calibrate new field thermometers before they are distributed to volunteers. The field thermometers, which read to 0.5°C are purchased from a scientific supply house. MassWWP thermometers read to 0.1°C.

The Chesapeake Bay Citizen Monitoring Program uses a non-certified precision thermometer, available for about $30.00, for the calibration procedure. If a greater degree of accuracy is required, you may wish to check your precision thermometer against a certified thermometer. Certified thermometers are very expensive, but you may be able to find an agency or university lab that will let you bring your thermometer in and check it against their certified thermometer.

Maintenance checks on the calibrated thermometers are performed during one of the two annual QC sessions that are held for volunteers. At the session, all the volunteers' thermometers are put into a water bath at the same time and checked to ensure that they all read within 0.1 to 0.2 degree Celsius of the precision thermometer.

Equipment needed

Precision-grade thermometer that reads in increments of 0.1 degree Celsius; insulated cooler; wide-mouthed jar, such as a one-quart mayonnaise jar; string or twine; ice.

Procedure

The day before you will be calibrating the thermometers, fill the insulated cooler with tap water. Suspend the precision thermometer in the water by tying it with a string to a cabinet door or other stable object above the cooler. Allow the water to equilibrate overnight.

The following day, use string to loosely tie together the field thermometers that you want to calibrate. Calibrate no more than ten thermometers at a time.

Step One: Room-temperature bath calibration

Suspend the thermometers in the water in the cooler. Let stand for fifteen minutes, then read and record the value for all the thermometers, including the precision thermometer.

Let stand another fifteen minutes, then take a second reading on all thermometers.

Step Two: Ice-bath calibration

Prepare an ice bath in the wide-mouth jar. Make sure the ice to water ratio is such that the jar is packed with ice at the bottom.

Suspend precision and field thermometers in the bath. Let stand fifteen minutes, then take and record readings.

Let stand another fifteen minutes, adding more ice if floating above the bottom of the jar, then take second readings.

Analysis of results

The thermometers should read to within 0.1 degree of the precision thermometer. Any thermometer outside of this range should not be used.

Appendix D: Further Reading

American Public Health Association. 1992. Standard Methods for the Examination of Water and Wastewater. 18th ed. American Public Health Association, 1015 15th Street, NW, Washington, DC 20005.

Hach Company, Water Analysis Handbook, 1989.

Izaak Walton League of America. 1990. A Citizen's Guide to Clean Water. 1401 Wilson Blvd, Level D, Arlington, VA 22209.

Keith, L.H. 1990. Principles of Environmental Analysis. *Analytical Chemistry* 55:2210-2218

Massachusetts Department of Environmental Protection, 1990 Massachusetts Surface Water Quality Standards. Technical Services Branch, North Grafton, Massachusetts.

Plafkin, James L., et. al. 1989. Rapid Bioassessment Protocols for Use in Streams and Rivers: Benthic Macroinvertebrates and Fish. Report # EPA/444/4-89-001. U.S. EPA, Washington, DC.

River Watch Network. 1993. Benthic Macroinvertebrate Monitoring Manual.

Riverways Programs, Massachusetts Department of Fisheries, Wildlife and Environmental Law Enforcement, Shoreline Survey: A Stream Team..., 1992; Adopt-A-Stream Workbook: How to Protect..., 1993; A Citizen's Guide to the NPDES Process: How to Protect Your Local River or Stream, 1993; Physical Habitat Survey, in process.

U.S. Environmental Protection Agency Region I. 1992. Guidance for Quality Assurance Project Plans for Environmental Monitoring Projects (abridged form dated January 21).

U.S. Environmental Protection Agency. 1990. Volunteer Water Monitoring: A Guide for State Managers. EPA 440/90010. US EPA (WH-553), 401 M Street, SW, Washington, DC 20460.

U.S. Environmental Protection Agency, Office of Water. 1994. National Directory of Volunteer Environmental Monitoring Programs, Fourth Edition. EPA 841-B-94-001. US EPA (4503F), 401 M Street, SW, Washington, DC 20460.

The Volunteer Monitor. 1990+. Eleanor Ely, editor, 1318 Masonic Avenue, San Francisco, CA 94117.