

**Project Manual**

**Volume 2 - Field Sampling  
& QA/QC Plan**

**PENNSYLVANIA COASTAL ZONE MANAGEMENT PROGRAM**

**WATER QUALITY MONITORING STUDY  
FOR THE LAKE ERIE WATERSHED**

**SEPTEMBER 1996**

**Project: 2758-001**

**CZM Project No.: CZ1:94.06PE**

**A REPORT OF THE PENNSYLVANIA DEPARTMENT OF ENVIRONMENTAL PROTECTION  
TO THE NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION  
PURSUANT TO NOAA AWARD NO. - NA47OZ0248**



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**MALCOLM  
PIRNIE**

**ENVIRONMENTAL ENGINEERS, SCIENTISTS & PLANNERS**

**MALCOLM  
PIRNIE**

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**FIELD SAMPLING AND  
QUALITY ASSURANCE/QUALITY CONTROL PLAN  
WATER QUALITY MONITORING STUDY  
FOR THE LAKE ERIE WATERSHED**

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## **1.0 INTRODUCTION**

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The Erie County Department of Planning (ECDP), in conjunction with the Pennsylvania Department of Environmental Resources Division of Coastal Programs (DCP) and the Erie County Health Department (ECHD) retained Malcolm Pirnie to conduct a water quality survey of three Erie County subwatersheds. The project will be coordinated by the County while technical support and review activities will be performed by the DCP and ECHD. Project financing is through a federal Coastal Zone Management (CZM) grant program.

The purpose of this plan is to identify the quality control and assurance steps for sampling, field activities and laboratory analytical controls required to establish a water quality baseline for the Lake Erie Watershed. The activities included in this plan focus on the Elk Creek, Walnut Creek, and Twelvemile Creek subwatersheds, which together make up about 44.5 percent of the entire watershed area.

The Lake Erie Watershed covers 330 square miles; has 14 large subwatersheds and more than 500 individual drainage areas; and encompasses all or portions of 25 Erie County, Pennsylvania, municipalities, including the 10 coastal municipalities.

The Coastal Zone Act Reauthorization Amendments, Section 6217, require that states with coastal programs develop a Coastal Nonpoint Source Control Program (CNPCP). Water quality information for watersheds within the federally assigned CNPCP management areas is needed to help quantify the effects of nonpoint source pollutants on coastal water, identify particular parameters of concern, and establish appropriate baseline conditions for future effectiveness monitoring of management measure implementation.

### **1.1 DATA QUALITY OBJECTIVE**

---

The data quality objective is to collect representative samples and analyze them using methods that will produce accurate, precise values to be used to characterize the stations. The data will further be assessed to evaluate flow characteristics and potential pollutant loadings. As sampling activities progress, the objective will be to reduce the analytical parameter list and concentrate on those parameters that have the greatest potential to affect pollutant loading to Lake Erie.

## **2.0 SAMPLING**

Malcolm Pirnie will subcontract laboratory analytical and sample collection activities to Church Laboratories, Inc., located in Fairview, Pennsylvania. Church is a certified full service laboratory that also provides sample collection services. Field and analytical data will be recorded by laboratory personnel on a form similar to the one that will be transmitted throughout the project from Church Laboratories to Malcolm Pirnie for review and report preparation.

Presented on Figures 2-1 and 2-2 are maps showing approximate water quality sampling station locations. Malcolm Pirnie will inspect each subwatershed for precise sampling locations that are near the discharge of each creek, upstream of any influences of Lake Erie.

Malcolm Pirnie personnel will be present during the first dry weather sample collection task to identify the sample collection locations for the subcontractor.

The subcontractor will notify Mr. Joseph Vogel of the Erie County Department of Health (ECDOH) at (814) 451-6700 of pending sampling events. The ECDOH may elect to split samples during dry or wet weather sampling events.

### **2.1 DRY WEATHER SAMPLING**

---

Dry weather sampling activities will commence following sample location siting. A minimum of 48 to 72 hours of antecedent dry weather is required prior to collection of dry weather samples.

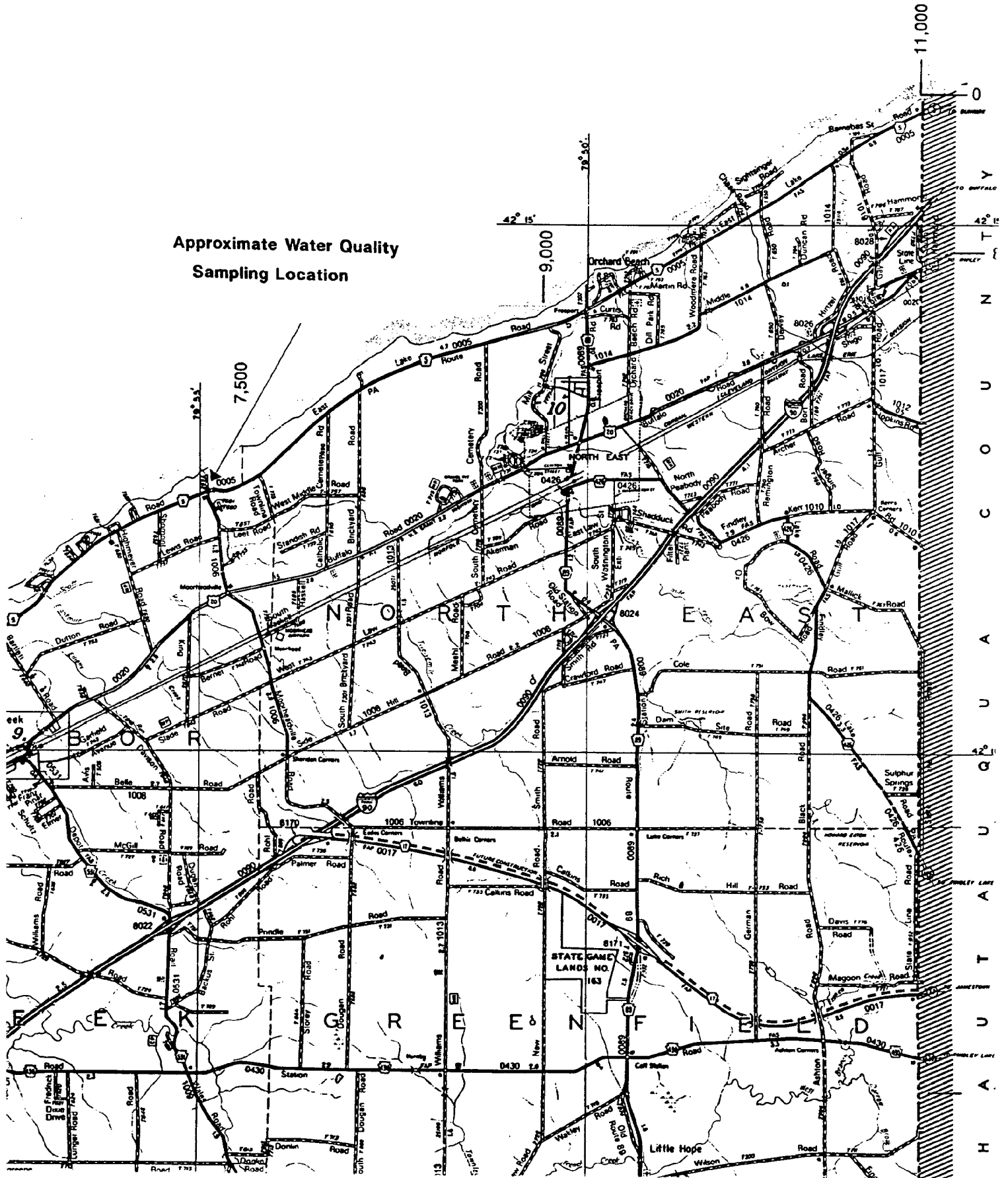
### **2.2 WET WEATHER SAMPLING**

---

Wet weather sampling activities will commence following a number of conditions. A minimum of 48 to 72 hours of antecedent dry weather conditions will proceed wet weather sampling activities. Malcolm Pirnie will estimate the travel time of each subwatershed in an effort to determine proper wet weather sampling protocols. By evaluating the travel time of each stream, we will attempt to collect samples in a timely fashion that captures any "first flush" effects of a precipitation event. Rainfall intensity and

FIGURE 2-1

Approximate Water Quality  
Sampling Location



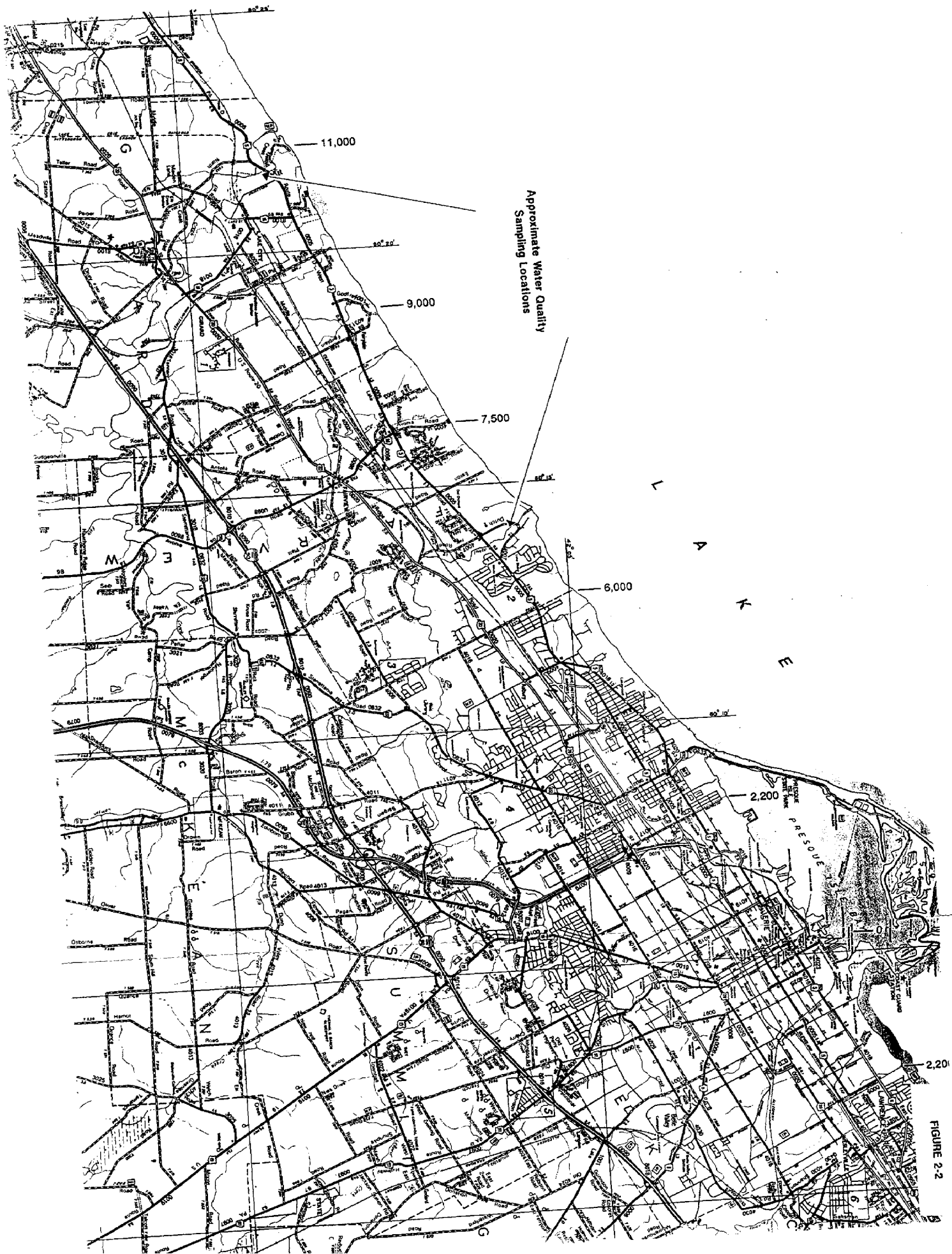


FIGURE 2-2



duration, time of travel and estimated flows will all factor into the decision to initiate wet weather sampling. We will review the developed wet weather protocol with the sampling crew prior to the first wet weather sampling event.

### **2.3 DEPTH AND VELOCITY MEASUREMENTS**

---

Procedures for collection of depth and velocity measurements will be developed following the initial site visit to select the sample site. Based on an evaluation of the sample collection location, the number of depth and velocity measurements that are required during each "round" of sampling will be determined. Depth and velocity measurement procedures and techniques will be reviewed with the sampling crew prior to the collection of the first sampling event.

### **2.4 INITIAL SAMPLING**

---

Table 2-1 illustrates the overall sampling program approach. Initially, one dry weather sampling event will be performed where all three monitoring locations will be sampled. The depth of flow at each sampling location for each stream will be recorded when the grab sample is collected. We estimate that the time to collect the first round of samples from each stream will approach two hours. This procedure will be completed three times, collecting an equal volume of sample each time. These three sets of grab samples collected at each stream station will be composited by the analytical laboratory and tested for the complete parameter list (see Table 2-2). This will serve as baseline or background data for the study. Listed in Table 2-3 are the approved U. S. Environmental Protection Agency (USEPA) methods and detection limits that the laboratory will use when analyzing inorganic parameters.

In addition, one wet weather sampling event will be performed at the three monitoring locations for the full list of parameters. Sample collection will be conducted as described above during the storm events.

<b>TABLE 2-1</b>	
<b>WATER QUALITY MONITORING STUDY FOR THE LAKE ERIE WATERSHED</b>	
<b><i>SAMPLING APPROACH</i></b>	
<b>Initial Monitoring (Spring and Summer Season):</b>	
1 Event (dry)	6-hour composite - Full list of parameters
1 Event (wet)	6-hour composite - Full list of parameters
<b>Intermediate Reduced Parameter Sampling (Spring and Summer Season):</b>	
1 Event (dry)	6-hour composite - Initial parameters-of-interest
3 Events (wet)	6-hour composite - Initial parameters-of-interest
<b>Reduced Parameter Sampling (Fall Season):</b>	
4 Events (wet)	6-hour composite - Final parameters-of-interest

**TABLE 2-2**

**WATER QUALITY MONITORING STUDY FOR THE LAKE ERIE WATERSHED**

**ANALYTICAL PARAMETERS**

PADER Chapter 16 Test Parameters	PADER Chapter 93 Test Parameters
<p>Antimony Arsenic Beryllium</p> <p>Cadmium Chromium Total Chromium VI</p> <p>Copper Lead Mercury</p> <p>Nickel Selenium Silver</p> <p>Thallium Zinc Cyanide (free)</p> <p><b>Pesticides:</b> Aldrin alpha-BHC beta-BHC gamma-BHC (Lindane)</p> <p>delta-BHC alpha-Chlordane gamma-Chlordane</p> <p>4,4'-DDT 4,4'-DDE 4,4'-DDD</p> <p>Dieldrin alpha-Endosulfan</p> <p>beta-Endosulfan Endosulfan Sulfate Endrin</p> <p>Endrin Aldehyde Heptachlor Heptachlor Epoxide Toxaphene</p>	<p>Aluminum Alkalinity Ammonia Nitrogen</p> <p>Bacteria/Fecal Coliform Hardness Iron</p> <p>Manganese Nitrite - Nitrogen Nitrate - Nitrogen</p> <p>Chloride Oil and Grease CBOD<sub>5</sub></p> <p>Total Suspended Solids Phosphorus COD</p> <p><b>Field Measurements:</b> Dissolved Oxygen pH Temperature Conductivity</p>

<p align="center"><b>TABLE 2-3</b></p> <p align="center"><b>WATER QUALITY MONITORING STUDY FOR THE LAKE ERIE WATERSHED</b></p> <p align="center"><i>Approved USEPA Analytical Methods and Detection Limits for Inorganics</i></p>		
<b>Parameter</b>	<b>Analytical Method</b>	<b>Method Detection Limit mg/l</b>
Aluminum	202.1	0.1
Antimony	204.2	0.003
Arsenic	206.2	0.001
Beryllium	210.1	0.005
Cadmium	213.2	0.0001
Chromium	218.1	0.05
Chromium, hexavalent	218.4	0.01
Copper	220.2	0.001
Iron	236.1	0.03
Lead	239.1/239.2	0.1/0.001
Manganese	243.1	0.01
Mercury	245.1	0.0002
Nickel	249.1	0.04
Selenium	270.2	0.002
Silver	272.2	0.0002
Thallium	279.1/279.2	0.1/0.001
Zinc	289.1	0.005

## **2.5 INITIAL SELECTION OF PARAMETERS-OF-INTEREST**

---

At the conclusion of the sampling and analysis of the dry weather and wet weather events, a meeting will be scheduled with ECDP and DCP. At this meeting the concentrations of parameters from the dry weather and wet weather events will be evaluated with respect to:

- Presence above detection limits.
- Historical presence above detection limits.

Based on these criteria, the full parameter list may be reduced for subsequent sampling efforts. Each of the sampling locations will be evaluated individually which may result in different parameter-of-interest lists.

## **2.6 INTERMEDIATE REDUCED PARAMETER SAMPLING**

---

Once an initial parameters-of-interest list has been agreed upon by ECDP and DCP for each sampling location, a second set of events will be sampled. Samples will be collected for one dry weather event and three wet weather events in the same manner as described in Section 2.4. The samples will be analyzed for the initial parameters-of-interest lists.

## **2.7 FINAL SELECTION OF PARAMETERS-OF-INTEREST**

---

Once the data from the second dry weather and three wet weather sampling events have been reviewed for adequacy in meeting the data quality objectives of the sampling program, the concentrations of those parameters detected will be compared and evaluated with respect to:

- Frequency of presence above detection limits.
- Existing water quality standards.
- Potential pollutant loading to Lake Erie.

Based upon these criteria, the initial parameter list may be further reduced for future sampling efforts. The objective is to both reduce sampling costs and to concentrate on those parameters which have the greatest potential to influence the evaluation of

pollutant loadings to Lake Erie. It should be noted that the parameter list again will be reviewed individually for each sampling point and that each point may not have the same recommended list of final parameters-of-interest.

## **2.8 REDUCED PARAMETER SAMPLING**

---

Once a final parameter-of-interest list has been established for each sampling point, an additional four wet weather sampling events will be performed at all three sampling locations. The samples will be analyzed for the final list of parameters-of-interest.

## **3.0 SAMPLING AND SAMPLE CUSTODY PROCEDURES**

### **3.1 GENERAL SAMPLING PLAN**

---

This sampling plan addresses the procedures to be used to obtain representative stream samples from Elk Creek, Walnut Creek, and Twelve Mile Creek, descriptions of sampling equipment and containers to be used. Appropriate sampling procedures will be utilized to collect representative samples. A description of the technique, the rationale, and the criteria to be employed for selection of sampling locations and the frequency of sampling is described. Specific sampling procedures to be used (USEPA), will be referenced. For non-standard or modified sampling methods, detailed procedures with appropriate references will be required.

#### **3.1.1 Sampling Methods**

All persons involved with the sampling program will participate in a review of sampling procedures to be conducted by Malcolm Pirnie and will be technically competent and familiar with the procedures employed. They will be familiar with all aspects of this QA/QC Plan as well as the data quality objective of this program.

### **3.2 SAMPLE CONTAINERS AND PREPARATION**

---

#### **3.2.1 General**

Sample containers shall be made of materials that will not contaminate the sample. See Appendix A for acceptable containers.

#### **3.2.2 Bacteriological Samples**

Plastic bottles (at least 125 ml capacity), caps, and their liners must withstand sterilization temperatures and impart no toxic or bacteriostatic compounds to the sample.

Clean containers with a phosphate-free laboratory detergent and hot water, then rinse repeatedly with hot water followed by at least three rinses with laboratory deionized water.

Sterilize containers in an autoclave at a minimum of 121°C, 15 psi for at least 30 minutes. Loosen screw caps slightly to avoid rupture of container.

If the sample to be collected contains residual chlorine, add sodium thiosulfate in an amount to provide a concentration of about 100 mg/l in the sample. Omit this addition if thiosulfate interferes with subsequent examination.

### **3.3 SAMPLE ACQUISITION - GENERAL**

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**3.3.1** See Appendix A for container types for each parameter or group of parameters.

**3.3.2** Label samples with information listed in Section 3.6. For each ten or multiple of ten samples collected in a set, one sample shall be collected in duplicate.

**3.3.3** A field log book will be kept for all sampling and will include the applicable items listed in Section 3.7.

**3.3.4** Additional sampling instructions specific for acquisition of liquids are contained in subsequent Section (3.4).

### **3.4 ACQUISITION OF LIQUID SAMPLES**

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#### **3.4.1 For General Chemical/Physical Analyses**

**Grab Samples:** Before taking the samples, rinse the sample container at least three times by filling it to about one-fourth capacity with water to be sampled.

It is important to obtain the most representative sample possible. If a stream is sampled avoid disturbing the sediment at the site by approaching the site from downstream.

Analytical parameters where composite sampling is not suitable, such as fecal coliform and oil and grease, will be collected during the second round of grab sampling activities, initially. If during the sampling program it becomes apparent that collection of these samples is more advantageous to be completed during Rounds 1 or 3, we will notify the ECDP of this change via letter.



**Composite Samples:** Composite samples may be made by combining individual grab samples taken at frequent intervals.

Composite samples are not suited for samples to be analyzed for dissolved gases, pH, oil and grease, bacteria, temperature or other parameters with holding periods less than the composite cycle or that cannot be agitated or poured from one container to another.

### **3.5 CHAIN-OF-CUSTODY**

---

To establish the documentation necessary to trace sample possession from the time of collection, a Chain-of-Custody Record (Figure 3-1) must be completed and accompany each sample or sample set.

The form is signed by the sample collector and by any individual who has custody of the samples until they are delivered to Church Laboratory, Inc. The Laboratory Supervisor (or his representative) acknowledges receipt of the samples at the laboratory by initialing the Chain-of-Custody Record.

### **3.6 SAMPLE LABELS**

---

Sample labels are located on the face of each container and are to include the following information as applicable:

- Collector's initials.
- Location.
- Date sampled.
- Time sampled.
- Church Laboratory, Inc. I.D. Number (when received in laboratory).
- Required analysis.
- Field information.

### **3.7 RECORD KEEPING PROCEDURES**

---

The following information shall be recorded by the sampling crew at the time of sampling:

- Unique sample designation, location, sketch.
- Name of sampler.



**CHURCH** laboratory, inc.

(814) 474-2044

7397 CHESTNUT STREET • P.O. BOX 83  
FAIRVIEW, PA. 16415

**Mailing Address:**

Name: \_\_\_\_\_

Address: \_\_\_\_\_

City: \_\_\_\_\_ ST \_\_\_\_\_ ZIP \_\_\_\_\_

Attn: \_\_\_\_\_

**CHAIN OF CUSTODY RECORD**

Sample name &/or Description	Date Sampled	Time Sampled	Sample Matrix	No. of Containers	Notes:

**SAMPLED BY:**  
 Print Name: \_\_\_\_\_  
 Signature: \_\_\_\_\_  
 Date: \_\_\_\_\_

**RECEIVED BY:**  
 Print Name: \_\_\_\_\_  
 Signature: \_\_\_\_\_  
 Date: \_\_\_\_\_

**RELINQUISHED BY:**  
 Print Name: \_\_\_\_\_  
 Signature: \_\_\_\_\_  
 Date: \_\_\_\_\_

**RECEIVED FOR LABORATORY BY:**  
 Print Name: \_\_\_\_\_  
 Signature: \_\_\_\_\_  
 Date: \_\_\_\_\_

Comments: \_\_\_\_\_

No of Samples: \_\_\_\_\_ PO Number: \_\_\_\_\_ Lot No: \_\_\_\_\_ Lab ID No: \_\_\_\_\_

Client Authorization: \_\_\_\_\_ Date: \_\_\_\_\_

- Weather.
- Method of collection.
- Time and date of sampling.
- Field measurements and calibration.
- Observations and remarks.

Malcolm Pirnie has developed and included a typical form to be used during each sample event (Form 001). All data sheets will be forwarded to Malcolm Pirnie for recordkeeping.

### **3.8 SAMPLE PRESERVATION**

---

Samples to be analyzed for any parameter listed in Table 3-1 must be preserved according to instruction given in that procedure.

A container of the same type used in sampling must be filled with deionized water, and the same preservative used in the actual samples is added to the deionized water and labeled field blank. The field blank is analyzed along with the samples to determine if there is any contamination attributable to the sampling process. Field blanks will be analyzed at a rate of approximately one per twenty samples.

### **3.9 SAMPLE HOLDING**

---

Properly preserved samples may be held up to the holding times listed in Table 3-1. Regardless, samples should be analyzed as soon as possible to ensure the minimum loss or gain of the parameter of interest. Whenever an analysis has exceeded its holding time, it must be noted on the final report.

### **3.10 SAMPLE LOG-IN AND ANALYTICAL SPECIFICATIONS**

---

The Laboratory Supervisor (or his designate) acknowledges receipt of samples on the Chain-of-Custody Record. Next the samples are assigned a Church Laboratory Identification Number. This number is logged in a bound book. The Church Laboratory sample number is placed on the sample bottle and the appropriate color coded work sheet is completed and placed in the pending work file box.



COUNTY OF ERIE

**WATER QUALITY MONITORING**  
**FOR LAKE ERIE WATERSHED STUDY**

**FIELD LOG SHEET**

LOCATION:	
DATE:	
SAMPLERS NAME:	
WEATHER CONDITIONS:	

	<i>ROUND 1</i>	<i>ROUND 2</i>	<i>ROUND 3</i>
TIME			
pH			
DO			
CONDUCTIVITY			
TEMP			
<b>DEPTH MEASUREMENTS</b>			
St 1			
St 2			
St 3			
St 4			
St 5			
<b>VELOCITY MEASUREMENTS</b>			
St 1			
St 2			
St 3			
St 4			
St 5			

<b>OTHER SITE OBSERVATIONS</b>

**TABLE 3-1**  
**WATER QUALITY MONITORING STUDY FOR THE LAKE ERIE WATERSHED**  
**CONTAINERS, PRESERVATIVES AND HOLDING TIMES\***  
**WATER SAMPLES**

Parameter	Container	Preservative	Holding Time	Analytical Method	Method Reference
Pesticides	One (1) 1-liter amber glass bottle, Teflon-lined lid.	Cool to 4°C	Extract within 5 days and analyze within 40 days of collection	508	1
Total Metals	One (1) 1-liter polyethylene bottle	HNO <sub>3</sub> to pH <2	28 days mercury, 6 months others	200 series	2
Hexavalent Chromium	500 ml polyethylene bottle	Cool to 4°C	24 hours	218.4	2
Total Suspended Solids	100 ml polyethylene bottle or glass	Cool to 4°C	7 days	160.2	2
Alkalinity	500 ml plastic or glass	Cool to 4°C	14 days	310.1 or 2	2
Chloride	100 ml plastic or glass	None required	28 days	325.2 or 3	2
Ammonia-Nitrogen	500 ml plastic or glass	Cool to 4°C H <sub>2</sub> SO <sub>4</sub> to pH <2	14 days	350.1 or 2	2
Nitrate-Nitrite	100 ml plastic or glass	Cool to 4°C H <sub>2</sub> SO <sub>4</sub> to pH <2	14 days	353.2 or 3	2
Oil and Grease	One (1) 1-liter amber glass bottle	Cool to 4°C H <sub>2</sub> SO <sub>4</sub> to pH <2	24 hours	413.1	2
CBOD <sub>5</sub>	500 ml plastic or glass	Cool to 4°C	24 hours	507	3
Total Phosphorus	500 ml plastic or glass	Cool to 4°C H <sub>2</sub> SO <sub>4</sub> to pH <2	28 days	365.4	2
Phenols	500 ml glass	Cool to 4°C H <sub>2</sub> SO <sub>4</sub> to pH <2	28 days	420.2	2

**TABLE 3-1**  
**WATER QUALITY MONITORING STUDY FOR THE LAKE ERIE WATERSHED**  
**CONTAINERS, PRESERVATIVES AND HOLDING TIMES\***  
**WATER SAMPLES**

Parameter	Container	Preservative	Holding Time	Analytical Method	Method Reference
Cyanide, Free	500 ml plastic or glass	Cool to 4°C NaOH to pH > 12	14 days	00719A	5
Bacteria, Fecal Coliform	125 ml sterilized plastic or glass	Cool to 4°C Add $NA_2S_2O_3$	6 hours	**	4
Hardness	500 ml plastic or glass	Cool to 4C	24 hours	130.2	2

**Notes:**  
 \* The laboratory shall achieve a Method Detection Limit which meets those limits established in PADER, Title 25, Chapters 93 and 16 for the particular methodology listed in this table.  
 \*\* No specific numerical method available.

**Method Reference:**  
 1. USEPA, 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act", Friday, October 26, 1984.  
 2. USEPA, 600/4-79-020, "Methods for Chemical Analysis of Water and Wastes", revised March 1984.  
 3. AWWA-WPCF, "Standard Methods for the Examination of Water and Wastewater, 16th Edition, 1985."  
 4. USEPA, "Microbiological Methods for Monitoring the Environment", December 1978.  
 5. DER Method.

### **3.11 SAMPLE AND DATA MOVEMENT IN THE LABORATORY**

---

#### **3.11.1 Sample Storage and Movement**

When refrigeration is necessary, samples are stored at 4°C until analysis is performed. Otherwise they are stored in a designated area as specified by the Laboratory Supervisor. The Laboratory Supervisor or his designate will provide individual instruction which specifies the parameters to be analyzed for the sample(s). As these parameters are completed the analyst places the results on the appropriate work sheet.

Samples should be kept until holding times are exceeded or until client gives approval to discard samples.

#### **3.11.2 Data Movement**

During analysis a parameter specific worksheet must be completed. This worksheet must contain the following:

- Church Laboratory I.D. Number.
- Sampling date.
- Type of sample.
- Quality control data per client specifications.
- Parameter name.
- Results and analysis.
- Procedure number (when applicable).
- Dilution factors (when applicable).
- Sample weight (when applicable).
- Blank results (when applicable).

When analysis of a sample or set of samples is complete the Laboratory Supervisor or his designate will review the worksheet. Any mistakes will be reviewed with the analyst and corrected. The worksheet is then submitted to the secretary for transfer to the client report form. This form is then reviewed and signed by the Laboratory Supervisor.

## 4.0 ANALYTICAL PROCEDURES

### 4.1 ANALYTICAL METHODS/PROCEDURES

---

Analytical methods used shall be USEPA-approved standard methods wherever practical. All inorganic parameters listed in Chapter 16 and all Chapter 93 parameters shall be analyzed according to methodology contained in either:

- USEPA, 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act", Friday, October 26, 1984.
- USEPA, 600/4-79-020, "Methods for Chemical Analysis of Water and Wastes", revised March 1984.
- AWWA-WPCF, "Standard Methods for the Examination of Water and Wastewater, 16th Edition, 1985.
- USEPA, "Microbiological Methods for Monitoring the Environment", December 1978.
- DER Method.

Where alternate standard methods are available, the most cost-effective method shall be used provided it satisfies project requirements for precision, accuracy, specificity, sensitivity, and is approved by ECHD and DCP.

Malcolm Pirnie has received a copy of the Commonwealth of Pennsylvania certification for Church Laboratory, Inc. This document (Attachment A) indicates that the laboratory utilizes appropriate analytical instrumentation, methodologies, procedures and calculations that conform to standard laboratory practices. We expect that the laboratory analytical instrumentation and methodology accuracy are verified through proper matrix spikes, method blanks and duplicates as appropriate for proper QA/QC checks and data validation. We anticipate that detailed information pertaining to these practices will be available upon request.



**MALCOLM  
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**ATTACHMENT A**

**CHURCH LABORATORIES, INC.  
COMMONWEALTH OF PENNSYLVANIA CERTIFICATION**

# DEPARTMENT OF ENVIRONMENTAL RESOURCES

OFFICE OF MANAGEMENT AND TECHNICAL SERVICES

BUREAU OF LABORATORIES

## COMMONWEALTH OF PENNSYLVANIA

Certifies that

CHURCH LABORATORY INC  
7397 CHESTNUT STREET PO BOX 83  
FAIRVIEW, PA 16415  
I. D. # 25-070

having duly met the requirements of  
Chapter 109, Subchapter H, Safe Drinking Water Rules and Regulations  
issued under the Pennsylvania Safe Drinking Water Act of May 1, 1984  
(P.L. 206, No. 43), (35 P.S. 55 721, 1-721.17)  
is hereby approved as a

### Certified Drinking Water Laboratory

To perform the following analyses:

Microbiology

Inorganic


Trace Metals (Groups 1-3), Nitrate/Nitrite, Fluoride, Sulfate, Cyanide, Corrosivity

Organic

Total Trihalomethanes, Volatile Organic Compounds (Groups 1-2), Pesticides (Group 1), Synthetic Organic  
Chemicals (Groups 1&3), PCB

Expiration Date: 1/1/96

Certificate not transferable  
Surrender upon revocation  
To be conspicuously displayed at the Laboratory

  
Floyd Kefford, Bureau Director  
Bureau of Laboratories

**APPENDIX A**  
**SAMPLE PRESERVATION**

## APPENDIX A

## SAMPLE PRESERVATION

Once collected, a sample must be analyzed immediately or stored in a container with a preservative to maintain the integrity of the sample. This chapter provides guidance on preservation methods, holding times, storage condition and container materials.

Complete preservation of samples, either domestic sewage, industrial wastes, or natural waters, is a practical impossibility. Regardless of the nature of the sample, complete stability for every constituent can never be achieved. At best, preservation techniques can only retard the chemical and biological change that take place in a sample after the sample is removed from the parent source. To maintain the integrity of the sample, appropriate selection of containers, pretreatment of containers if necessary and the holding times form the integral part of the sample preservation program.

## 1.1 METHODS OF PRESERVATION

Methods of preservation are relatively limited and are intended generally to: 1) retard biological action; 2) retard hydrolysis of chemical compounds and complexes; and 3) reduce volatility of constituents.

Preservation methods are generally limited to chemical addition, pH control, refrigeration, and freezing. Combinations of these methods are often used for the preservation of the sample.

1.1.1 Chemical Addition

The most convenient preservative is a chemical which can be added to a sample bottle prior to sampling. When the sample is added, the preservative disperses immediately, stabilizing the parameter(s) of concern for long periods of time. When the preservative added interferes with other parameters being measured, additional samples for those parameters must be collected. For example, concentrated nitric acid added for the preservation of some of the metals would interfere with BOD, so an additional sample must be collected for BOD.

1.1.1.1 pH Control

pH control to preserve the sample is dependent upon chemical addition. As an example, to keep metal ions in a dissolved state concentrated nitric acid is added to lower the pH to less than 2.

\*Taken from US EPA, 1982. Handbook for Sampling and Sample Preservation of Water and Wastewater (EPA-600/4-82-029).

#### 1.1.2 Freezing

Freezing has been the subject of many preservation studies. It is felt by some that freezing would be a method for increasing the holding time and allowing collection of a single sample for all analysis. However, the residue solids components (filterable and nonfilterable) of the sample change with freezing and thawing. Therefore, return to equilibrium and then high speed homogenization is necessary before any analyses can be run. This method may be acceptable for certain analysis but not as a general preservation method.

#### 1.1.3 Refrigeration

Refrigeration or icing has also been studied with various results. This is a common method used in field work and has no detrimental effect on sample composition. Although it does not maintain integrity for all parameters it does not interfere with any analytical methods.

#### 1.1.4 Preservation Guidelines

For NPDES samples, the permit holder must use specific preservatives if the sample cannot be analyzed immediately after collection. If preserved, the analyses must be conducted within a specified time frame. Guidance submitted for approval to the 304h committee, US EPA, is shown in Table 1.1. Because approval and subsequent publication in the Federal Register has not taken place as of publication of the handbook, the reader is urged to keep abreast of existing NPDES regulations and changes through Federal Register publications. In addition, some parameter holding times differ for drinking water samples, for example, microbiological and nitrate parameters.

Table 1.2 provides additional references and furnishes data on preservation methods, storage and holding times for different parameters found in various literature sources. However, for a specific application of the data, reference to the original publication should be made.

#### 1.1.5 Alternative Preservation Methods

Alternative preservation methods with different preservatives or storage conditions can be used if its effectiveness can be demonstrated by supporting data through preservation studies. Such preservation studies must specify:

1. Type of water/wastewater used as a sample in the experiment
2. Type of containers used
3. Pretreatment of the container and the glassware used
4. Preservation methods used
5. Specific temperatures or temperature range used

6. Duration of storage
7. Stored in light or darkness
8. Quality Control samples - spikes, duplicates.
9. Blanks - controls
10. Number of samples analyzed and results
11. Statistical analysis, precision and accuracy

## 1.2 CONTAINERS

A variety of factors affect the choice of containers and cap material. These include resistance to breakage, size, weight, interference with constituents, cost and availability. There are also various procedures for cleaning and preparing bottles depending upon the analyses to be performed on the sample.

### 1.2.1 Container Material

The two major types of container materials are plastic and glass.

Glass	Plastic
1. Kimax or Pyrex brand - Borosilicate	1. Conventional Polyethylene
2. Vycor - generally lab ware	2. Linear polyethylene
3. Ray - Sorbor Low-actinic generally lab ware	3. Polypropylene
4. Corex - generally lab ware	4. Polycarbonate
	5. Rigid polyvinyl chloride
	6. Teflon

All these materials have various advantages and disadvantages. Kimax or Pyrex brand borosilicate glass is inert to most materials and is recommended where glass containers are used. Conventional polyethylene is to be used when plastic is acceptable because of reasonable cost and less absorption of metal ions. The specific situation will determine the use of glass or plastic. However, use glass containers for pesticides, oil and grease, and other organics. Table 1.3 summarizes the advantages and disadvantages of these materials.

### 1.2.2 Container Caps

There are two major types of plastic used in containers caps: Polyethylene and bakelite with liners. Polyethylene caps are recommended for ease of cleaning unless oil and grease analyses are to be performed. Caps with Teflon lines should be used for pesticides and oil and grease samples. Silicone rubber material should be avoided for Trace Metals because in zinc contaminations. There are three liner types available and the advantages/disadvantages are listed in Table 1.4.

### 1.2.3 Container Structure

Use a wide mouth container in most instances. This structure will permit easy filling and sample removal. It is also easily clean,

quickly dried, and can be stored inverted. Use a narrow neck bottle when interaction with the cap liner or outside environment is to be minimized. Use a solvent cleaned glass container for pesticide sample collection.

#### 1.2.4 Disposable Containers

Use disposable containers when the cost of cleaning is high. These containers should be precleaned and sterile. The most commonly used disposable container of this type is the molded polyethylene cubitainer shipped nested and sterile to the buyer. However since their cubic shape and flexible sides make them almost impossible to clean thoroughly, use these containers only once.

#### 1.2.5 Container Washing

The following procedure should be followed to wash containers and caps for inorganic and general parameters:

1. Wash containers and caps with a non-phosphate detergent and scrub strongly with a brush (if possible wash liners and caps separately).
2. Rinse with tap water, the deionized water.
3. Invert to drain and dry.
4. Visually inspect for any contamination prior to storage.
5. If the container requires additional cleaning, rinse with a chromic acid solution (35 ml saturated sodium dichromate solution in 1 liter of sulfuric acid - this solution can be reused). Then rinse with tap water and deionized water and dry as indicated above.

#### 1.2.6 Container preparation

For certain parameters, a special cleaning procedure is needed to avoid adsorption or contamination due to interaction with container walls. These procedures are outlined below:

1. **Metals:** If metals are to be analyzed, rinse the container with a solution of one part nitric acid to four parts water, then with distilled water. If phosphorus is to be analyzed, rinse the container with a solution of one part hydrochloric acid to one part water, followed by distilled water. Treat the caps similarly.
2. **Organics:** If oil and grease or pesticides are to be analyzed, rinse the sample container with methylene chloride, followed by acetone. For pesticide analysis, use pesticide grade hexane or acetone. The container should have been previously cleaned with chromic acid solution as

described in Section 17.2.5. Treat the container caps similarly.

3. Sterilization: For microbiological analyses, sterilize the container and its stopper/cap by autoclaving at 121°C for 15 minutes or by dry heat at 180°C for two hours. Heat-sensitive plastic bottles may be sterilized with ethylene oxide at low temperatures. Wrap bottles in kraft paper or cover with aluminum foil before sterilization to protect against contamination. An acceptable alternative for emergency or field use is sterilization of containers by boiling in water for 15 minutes.

### 1.3 HOLDING TIME

Holding time is the time interval between collection and analysis. In general, the shorter the time that elapses between collection of a sample and its analysis, the more reliable will be the analytical results.

It is impossible to state exactly how much time may be allowed to elapse between collection of a sample and its analysis; this depends on the character of the sample, particular analysis to be made, and the conditions of storage.

For NPDES purposes, in accordance with Federal Register, part 136 follow the recommendations given in Table 1.1 and keep abreast of revised holding times that will be published in the Federal Register.

For information purposes, however, data relating to holding times for general and inorganic parameters was collected from various literature sources and is tabulated in Table 1.2.

### 1.4 SAMPLE VOLUME

The volume of sample collected should be sufficient to perform all the required analyses plus an additional amount to provide for and quality control needs, split samples or repeat examination. Although the volume of sample required depends on the analyses to be performed, the amount required for a fairly complete analysis is normally about eight liters, (about two gallons). The laboratory receiving the sample should be consulted for any specific volume requirements. Individual portions of a composite sample should be a least 100 ml in order to minimize sampler solids bias. Depending on the sampling frequency and sample volume, the total composited sample should be a minimum of 8 liters (about 2 gallons). Refer to EPA's Methods for Chemical Analyses of Water and Wastes 1979, EPA 600/4-79-020, for the sample volumes required for specific types of pollutant analyses.



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