Environmental Technology Verification Protocol

Drinking Water Systems Center

PROTOCOL FOR EQUIPMENT VERIFICATION TESTING FOR REMOVAL OF SYNTHETIC ORGANIC CHEMICAL CONTAMINANTS

Prepared by

NSF

NSF International

Under a Cooperative Agreement with

EPA U.S. Environmental Protection Agency

ETV ETV ETV

EPA/NSF ETV
PROTOCOL FOR EQUIPMENT VERIFICATION TESTING
FOR THE REMOVAL OF SYNTHETIC ORGANIC
CHEMICAL CONTAMINANTS

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Drinking Water Systems
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Environmental Technology Verification Program

U.S. ENVIRONMENTAL PROTECTION AGENCY

Throughout its history, the United States Environmental Protection Agency (EPA) has evaluated technologies to determine their effectiveness in preventing, controlling, and cleaning up pollution. EPA is now expanding these efforts by instituting a new program, the Environmental Technology Verification Program---or ETV---to verify the performance of a larger universe of innovative technical solutions to problems that threaten human health or the environment. ETV was created to accelerate the entrance of new environmental technologies into the domestic and international marketplace. It supplies technology buyers and developers, consulting engineers, states, and EPA regions with high quality data on the performance of new technologies. This encourages more rapid availability of approaches to better protect the environment.

ETV Drinking Water Systems Center
Concern about drinking water safety has accelerated in recent years due to much publicized outbreaks of waterborne disease and information linking ingestion of arsenic to cancer incidence. The EPA is authorized through the Safe Drinking Water Act (SDWA) to set numerical contaminant standards and treatment and monitoring requirements that will ensure the safety of public water supplies. However, small communities are often poorly equipped to comply with all of the requirements; less costly package treatment technologies may offer a solution. These package plants can be designed to deal with specific problems of a particular community; additionally, they may be installed on site more efficiently--- requiring less start-up capital and time than traditionally constructed water treatment plants. The opportunity for the sales of such systems in other countries is also substantial.

The EPA has partnered with NSF International (NSF) to verify performance of small drinking water systems that serve small communities. It is expected that both the domestic and international markets for such systems are substantial. The EPA and NSF have formed an oversight stakeholders group composed of buyers, sellers, and states (issuers of permits), to assist in formulating consensus testing protocols. A goal of verification testing is to enhance and facilitate the acceptance of small drinking water treatment equipment by state drinking water regulatory officials and consulting engineers while reducing the need for testing of equipment at each location where the equipment use is contemplated. NSF will meet this goal by working with equipment manufacturers and other agencies in planning and conducting equipment verification testing, evaluating data generated by such testing, and managing and disseminating information. The manufacturer is expected to secure the appropriate resources to support its part of the equipment verification process, including provision of equipment and technical support.

The verification process established by the EPA and NSF is intended to serve as a template for conducting water treatment verification tests that will generate high quality data for verification of equipment performance. The verification process can help in moving small drinking water equipment into routine use more quickly. The verification of an equipment's performance involves five sequential steps:

     1. Development of a Product Specific Test Plan (PSTP);
     2. Execution of verification testing;

3. Data reduction, analysis, and reporting;
4. Performance and cost factor (labor, chemicals, energy) verification; and
5. Report preparation and information transfer.

This verification testing program is being conducted by NSF with participation of manufacturers, under the sponsorship of the EPA Office of Research and Development (ORD), National Risk Management Research Laboratory (NRMRL), Water Supply and Water Resources Division (WSWRD) - Cincinnati, Ohio. NSF's role is to provide technical and administrative leadership and support in conducting the testing. It is important to note that verification of the equipment does not mean that the equipment is "certified" by NSF or EPA. Rather, it recognizes that the performance of the equipment has been determined and verified by these organizations.

Partnerships
The EPA and NSF cooperatively organized and developed the ETV Drinking Water Systems (DWS) Center to meet community and commercial needs. NSF and the Association of State Drinking Water Administrators (ASDWA) have an understanding to assist each other in promoting and communicating the benefits and results of the project.

NSF INTERNATIONAL

Mission Statement
NSF, an independent, non-governmental organization, is dedicated to being the leading global provider of public health and safety-based risk management solutions while representing the interest of all stakeholders.

NSF Purpose and Organization
NSF is an independent not-for-profit organization. For more than 52 years, NSF has been in the business of developing consensus standards that promote and protect public health and the environment and providing testing and certification services to ensure manufacturers and users alike that products meet those standards. Today, millions of products bear the NSF Name, Logo and/or Mark, symbols upon which the public can rely for assurance that equipment and products meet strict public health and performance criteria and standards.

Limitations of use of NSF Documents
This protocol is subject to revision; contact NSF to confirm this revision is current. The testing against this protocol does not constitute an NSF Certification of the product tested.

ORGANIZATION AND INTENDED USE OF PROTOCOL AND TEST PLANS

NSF encourages the user of this protocol to also read and understand the policies related to the verification and testing of drinking water treatment systems and equipment.

The first chapter of this document describes the protocol required in all studies verifying the performance of equipment or systems removing synthetic organic chemical contaminants (SOCs). The remaining chapters, or Technology Specific Test Plans (TSTPs), describe the additional requirements for equipment and systems using specific technologies to attain the goals and objectives of the protocol: the removal of (SOCs).

Prior to the verification testing of drinking water treatment systems, plants, and/or equipment, the equipment manufacturer and/or supplier must select an NSF-qualified Field Testing Organization (FTO). This designated FTO must write a PSTP to define the testing plan specific to the product. The equipment manufacturer and/or supplier will need this protocol and the TSTP(s) contained herein and possibly other ETV protocols and TSTPs to develop the PSTP, depending on the treatment technologies used in the unit processes or treatment train of the equipment or system. More than one protocol and/or TSTP may be necessary to address the equipment's capabilities in the treatment of drinking water.

Testing shall be conducted by an NSF-qualified FTO that is selected by the manufacturer. Water quality analytical work to be completed as a part of a TSTP shall be contracted with a laboratory that is certified, accredited or approved by a state, a third-party organization (i.e., NSF), or the EPA. For information on a listing of NSF-qualified FTOs, contact NSF.

ACKNOWLEDGMENTS

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CHAPTER 1

EPA/NSF ETV
PROTOCOL FOR EQUIPMENT VERIFICATION TESTING
FOR THE REMOVAL OF
SYNTHETIC ORGANIC CHEMICAL CONTAMINANTS

REQUIREMENTS FOR ALL STUDIES

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1.0 INTRODUCTION

This document is the protocol that will be used for verification testing of equipment designed to achieve removal of synthetic organic chemical contaminants (SOCs). This protocol may be applicable to various types of water treatment equipment capable of removing SOCs. Equipment testing may be undertaken to verify performance of drinking water treatment systems employing processes that may include but are not limited to coagulation/clarification, oxidation or mixed oxidation processes, adsorption, granular activated carbon biological filtration, encapsulation, and/or membrane processes for removal of SOCs. The specific SOC to be targeted for removal during verification testing shall be clearly identified in the Product Specific Test Plan (PSTP) prior to the initiation of testing by the Field Testing Organization (FTO). The PSTP may include more than one Technology Specific Test Plan (TSTP); however, the FTO must adhere to the specific minimum requirements of each protocol in developing a PSTP.

The testing of new technologies and materials that are unfamiliar to NSF International (NSF) and/or the Environmental Protection Agency (EPA) will not be discouraged. It is recommended that resins or membranes or any other material or chemical in the equipment conform to NSF /American National Standards Institute (NSF/ANSI) Standard 60 and 61.

The final submission of the PSTP shall:

- Include the information requested in this protocol;
- Conform to the format identified herein; and
- Conform to the specific Environmental Technology Verification (ETV) TSTP(s) related to the manufacturer's statement(s) of performance capabilities that are to be verified.

This protocol document is presented in two fonts. The non-italicized font provides the rationale for the requirements and background information that the FTO may find useful in preparation of the PSTP. *The italicized text indicates specific protocol deliverables that are required of the FTO or the manufacturer and that must be incorporated in the PSTP.*

The following glossary terms are presented here for subsequent reference in this protocol:

- Distribution System - A system of conduits by which a primary water supply is conveyed to consumers, typically by a network of pipelines.

- EPA - The United States Environmental Protection Agency, its staff or authorized representatives.

- Equipment - Testing equipment for use in the verification test, which may be defined as either a package plant or modular system.

- Field Testing Organization (FTO) - An organization qualified to conduct studies and testing of drinking water treatment systems in accordance with protocols and test plans. The role of the

FTO is to ensure preparation of an acceptable PSTP; to enter into contracts with NSF, as discussed herein; arrange for or conduct the skilled operation of a system during the intense periods of testing during the study, and to perform the tasks required by the protocol.

- Manufacturer - A business that assembles and/or sells package plant equipment and/or modular systems. The role of the manufacturer is to provide the package plant and/or modular system and technical support during the verification test. The manufacturer is also responsible for providing assistance to the third party FTO during operation and monitoring of the package plant or modular system during the verification test.

- Modular System - A packaged functional assembly of components for use in a drinking water treatment system or packaged plant that provides a limited form of treatment of the feedwater(s) and which is discharged to another packaged plant or the final step of treatment to the distribution system.

- NSF - NSF International, its staff, or other authorized representatives.

- Package Plant - A complete water treatment system including all components from the connection to the raw water(s) intake through discharge to the distribution system.

- Plant Operator - The person working for a small water system who is responsible for operating water treatment equipment to produce treated drinking water. This person may also collect samples, record data and attend to the daily operations of equipment throughout the testing periods.

- Product Specific Test Plan (PSTP) - A written document of procedures for on-site/in-line testing, sample collection, preservation, and shipment and other on-site activities described in the EPA/NSF ETV protocol(s) and TSTP(s) that apply to a specific make and model of a package plant/modular system.

- Protocol - A written document that clearly states the objectives, goals and scope of the study as well as the TSTP(s) for the conduct of the study. The protocol shall be used for reference during manufacturer participation in verification testing.

- Report - A written document that includes data, test results, findings, and any pertinent information collected in accordance with a protocol, analytical methods, procedures etc., in the assessment of a product whether such information is in preliminary, draft or final form.

- Technology Specific Test Plan (TSTP) - A written document that describes the procedures for conducting a test or study for the application of water treatment technology. At a minimum, the TSTP will include detailed instructions for sample and data collection, sample handling and sample preservation, precision, accuracy, reproducibility goals, and quality assurance/quality control (QA/QC) requirements.

- Testing Laboratory - An organization certified by a third- party independent organization, Federal agency, or a pertinent state regulatory authority to perform the testing of drinking water samples. The role of the testing laboratory in the verification testing of equipment is to analyze the water samples in accordance with the methods and meet the pertinent QA/QC requirements described in the protocol, TSTP, and PSTP.

- Verification - To establish the evidence on the range of performance of equipment and/or device under specific conditions following a predetermined protocol(s) and TSTP(s).

- Verification Statement - A written document that summarizes a final report reviewed and approved by NSF on behalf of the EPA or directly by the EPA.

- Water System - The water system that operates water treatment equipment to provide treated water to its customers.

1.1   Objectives

The specific objectives of verification testing may be different for each system, depending upon the statement of performance objectives of the specific equipment to be tested. The objectives developed by each manufacturer will be defined and described in detail in the PSTP developed for each piece of equipment. The manufacturer's performance objectives are used to establish data quality objectives (DQOs) to develop the experimental design of the verification test. The broader the performance objectives, the more comprehensive the PSTP must be to achieve the DQOs. The objectives of equipment verification testing may include but are not limited to the following:

- Generation of field data appropriate for verifying the performance of the equipment;
- Generation of operation and maintenance (O&M) information to assist users and potential operators of equipment; and
- Evaluation of new advances in equipment and equipment design.

An important aspect in the development of verification testing is to describe the procedures that will be used to verify the statement of performance objectives made for water treatment equipment. A PSTP document shall incorporate the QA/QC elements needed to provide data of appropriate quality sufficient to reach a defensible position regarding the equipment performance. Although verification testing conducted at a single site may not represent every environmental situation, which may be acceptable for the equipment tested, it will provide data of sufficient quality to make a judgment about the application of the equipment under conditions similar to those encountered in the verification testing.

It is important to note that verification of the equipment does not mean that the equipment is "certified" by NSF or EPA. Rather, it recognizes that the performance of the equipment has been determined and verified by these organizations.

1.2 Scope

This protocol outlines the verification process for equipment designed to remove SOCs. This protocol can be used in conjunction with a number of different TSTPs for drinking water treatment systems designed to achieve removal of SOCs. This protocol is not an NSF or third-party consensus standard and it does not endorse the equipment or technologies described herein.

An overview of the verification process and the elements of the PSTP to be developed by the FTO are described in this protocol. Specifically, the PSTP shall define the following elements of the verification test:

- Roles and responsibilities of verification testing participants;
- Procedures governing verification testing activities such as equipment operation and process monitoring; sample collection, preservation, and analysis; and data collection and interpretation;
- Experimental design of the field operations procedures. The field operations procedures will identify recommended equipment maintenance and cleaning methods;
- QA/QC procedures for conducting the verification test and for assessing the quality of the data generated from the verification test; and
- Health and safety measures relating to biohazard (if present), electrical, mechanical and other safety codes.

Content of PSTP:

The structure of the PSTP must conform to the outline below: The required components of the Document will be described in greater detail in the sections below.

- *TITLE PAGE*
- *FOREWORD*
- *TABLE OF CONTENTS - The Table of Contents for the PSTP should include the headings provided in this document although they may be modified as appropriate for a particular type of equipment to be tested.*
- *LIST OF DEFINITIONS - A list of key terms used in the PSTP should be provided*
- *EXECUTIVE SUMMARY - The Executive Summary describes the contents of the PSTP (not to exceed two pages). A general description of the equipment and the statement of performance objectives which will be verified during testing as well as the testing locations, a schedule, and a list of participants.*
- *ABBREVIATIONS AND ACRONYMS - A list of the abbreviations and acronyms used in the PSTP should be provided.*
- *EQUIPMENT VERIFICATION TESTING RESPONSIBILITIES (described in the sections below)*
- *EQUIPMENT CAPABILITIES AND DESCRIPTION (described in the sections below)*
- *EXPERIMENTAL DESIGN (described in the sections below*
- *FIELD OPERATIONS PROCEDURES (described in the sections below)*
- *QUALITY ASSURANCE PROJECT PLAN (described in the sections below)*

- *DATA MANAGEMENT AND ANALYSIS (described in the sections below)*
- *SAFETY PLAN (described in the sections below)*

2.0   EQUIPMENT VERIFICATION TESTING RESPONSIBILITIES

2.1   Verification Testing Organization and Participants

The required content of the PSTP and the responsibilities of participants are listed at the end of each section. In the development of a PSTP, a manufacturer and its designated FTO shall provide a table including:

- The name, affiliation, and mailing address of each participant;
- A point of contact;
- Description of participant's role;
- Telephone and fax numbers; and
- E-mail address.

2.2   Organization

The organizational structure for the verification testing showing lines of communications shall be provided by the FTO in its application on behalf of the manufacturer.

2.3   Verification Testing Site Name and Location

This section discusses background information on the verification testing site(s), with emphasis on the quality of the feedwater, which in some cases may be the source water at the site. The PSTP must provide the site names and locations at which the equipment will be tested. In most cases, the equipment will be demonstrated at more than one site. Depending upon the verification testing requirements stipulated in the TSTP employed, testing of the equipment may be required under different conditions of feedwater quality (or source water quality) that allow evaluation of system performance over a range of seasonal climate and weather conditions.

2.4   Site Characteristics

The PSTP shall include an area location map showing access from major streets and highways and a site layout drawing with equipment footprints and dimensions. The drawing should indicate the location of existing facilities, the source of the feedwater, and where the treated water will be discharged and the waste streams disposed. The PSTP shall also indicate if any facilities other than the equipment would be required to perform the test such as additional trailers or temporary structures for sample collection and preparation, electrical power, concrete pads, drainage, easements, etc. The location of SOC waste treatment, disposal and discharge facility or method of removal shall be clearly identified in the site plan. The PSTP must include a description of the test site. This shall include a description of where the equipment will be located. If the feedwater to the equipment is the source water for an existing water treatment plant, describe:

- The raw water intake;
- The opportunity to obtain raw water without the addition of any chemicals; and
- The operational pattern of raw water pumping at the full-scale facility (is it continuous or intermittent?).

The source water characteristics shall be described and documented. The PSTP shall also describe facilities to be used for handling the treated water and wastes (i.e., residuals) produced during the verification test. The PSTP will state whether the required water flows and waste flows produced are dealt with in an acceptable way, and whether any water pollution discharge permits are needed.

2.5 Responsibilities

The PSTP shall identify the organizations involved in the testing and describes the primary responsibilities of each organization. Multiple manufacturers testing for removal of SOCs may be conducted concurrently. The responsibilities of the manufacturer will vary depending on the type of verification testing. However, at a minimum, the manufacturer shall be responsible for:

- Providing the equipment to be evaluated during verification testing. The equipment must be in complete working order at delivery to the test site;
- Providing logistical and technical support, as required; and
- Providing equipment that explicitly meets all requirements of the Occupational Safety and Health Administration (OSHA), National Electrical Manufacturers Association (NEMA), Underwriters Laboratory Inc. (UL), NSF, and other appropriate agencies to ensure operator safety during verification testing.

The FTO shall be responsible for:

- Preparation of the PSTP;
- Providing needed logistical support, establishing a communication network, and scheduling and coordinating the activities of all verification testing participants;
- Ensuring that locations selected as test sites have feedwater quality consistent with the objectives of the verification testing (the manufacturer may recommend a site(s) for verification testing.);
- Managing, evaluating, interpreting, and reporting on data generated by the verification testing; and
- Evaluating and reporting on the performance of the technologies applied to achieve removal of SOCs.

Content of PSTP Regarding Verification Testing Responsibilities:

The FTO shall be responsible for including the following elements in the PSTP:

- *Definition of the roles and responsibilities of appropriate verification testing participants;*

- *A table, which includes the name, affiliation, and mailing address of each participant, a point-of-contact, their role, telephone and fax numbers, and e-mail address;*
- *Organization of operational and analytical support;*
- *List of the site name(s) and location(s); and*
- *Description of the test site(s), the site characteristics and identification of where the equipment will be located.*

The manufacturer shall be responsible for:

- *Provision of complete, field-ready equipment for verification testing;*
- *Provision of logistical, and technical support, as required;*
- *Provision of assistance to the qualified FTO during operation and monitoring of the equipment during the verification testing;*
- *Reviewing the PSTP; and*
- *Reviewing the verification report.*

3.0   EQUIPMENT CAPABILITIES AND DESCRIPTION

3.1   Equipment Capabilities

The manufacturer and its designated FTO must identify in a statement of performance objectives the specific performance criteria to be verified and the specific operational conditions under which the verification testing shall be performed. In conjunction with a statement of performance objectives, the FTO shall state the pertinent detection limits for the specific analytical method. Statements should be made regarding the applications of the equipment, the known limitations of he equipment and under what conditions the equipment is likely to fail or underperform. The statement of performance objectives must be specified and verifiable by a statistical analysis of the data. Examples of two different types of statements of performance objectives that may be verified in this testing are:

1. "This system is capable of achieving 98% removal of the SOC chlordane 60-day operation period at a flux of 15 gpm/sf (75% recovery; temperature between 20 and 25°C) in feedwaters with chlordane concentrations less than 0.1 mg/L and total dissolved solids (TDS) concentrations less than 500 mg/L."

2. "This system is capable of producing a product water with a chlordane concentration less than 2 μg/L during a 60-day operation period at a flux of 15 gpm/sf (75% recovery; temperature between 20 and 25°C) in feedwaters with chlordane concentrations less than 0.1 mg/L and TDS concentrations less than 500 mg/L."

An example of a statement of performance objectives that would not be acceptable is presented below:

"This system will achieve removal of SOCs in accordance with the Safe Drinking Water Act (SDWA) on a consistent and dependable basis."

The statement of performance objectives shall identify the water quality objectives to be achieved by the equipment and evaluated in the verification testing. For each statement of performance objectives proposed by the FTO and the manufacturer in the PSTP, the following information shall be provided:

- Applications of the equipment;
- Known limitations of the equipment;
- Advantages it provides over existing equipment;
- Percent removal of the targeted SOC;
- Rate of treated water production (i.e., flux);
- Product water recovery;
- Feed stream water quality regarding pertinent water quality parameters;
- Temperature;
- Concentration of targeted SOC; and
- Other pertinent water quality and operational conditions.

During verification testing, the FTO must demonstrate that the equipment is operating at a steady-state prior to collection of data to be used in verification of the statement of performance objectives. The following equation shall be used to determine percent removal of the SOC investigated:

$$Percent\ SOC\ Removal = \left[1 - \frac{Finished\ Water\ SOC\ Concentration}{Feed\ Water\ SOC\ Concentration}\right] * 100\%$$

The FTO, on behalf of the manufacturer, shall be responsible for identification of which SOC shall be monitored and recorded for testing under the statement of performance objectives in the PSTP. The analysis of SOCs in the feedwater, treated water and wastewater streams shall be performed by a state-certified, third-party accredited or EPA-accredited laboratory using an approved *Standard Method*.

The statement of performance objectives prepared by the FTO (in collaboration with the manufacturer) shall also indicate the range of water quality under which the equipment can be challenged while successfully treating the feedwater. Statements of performance objectives that are not too easily met may not be of interest to the potential user, while performance objectives that are overstated may not be achievable. If a manufacturer relies on integrated physio-chemical processes for SOC removal, the statement of performance objectives must include the overall water treatment system SOC removal performance. The statement of performance objectives forms the basis of the entire verification test and must be chosen appropriately. Therefore, the design of the PSTP should include a sufficient range of feedwater quality to permit verification of the statement of performance objectives.

It should be noted that many of the drinking water treatment systems participating in verifying SOC removal might be capable of achieving multiple water treatment objectives. Although this protocol and the associated TSTPs are oriented towards removal of SOCs from feedwaters, the manufacturer may want to look at the treatment system's removal capabilities for additional water quality parameters.

3.2 Equipment Description

Description of the equipment for verification testing shall be included in the PSTP. Data plates shall be permanent and securely attached to each production unit. The data plate shall be easy to read in English or the language of the intended user, located on the equipment where it is readily accessible, and contain at least the following information:

- Equipment Name;
- Model Number;
- Manufacturer's name and address;
- Electrical requirements - volts, amps, hertz and phase;
- Equipment size and weight;
- Shipping requirements and special handling precautions;
- Equipment maintenance requirements;
- Serial Number;
- Warning and Caution statements in legible and easily discernible print size; and
- Capacity or output rate (if applicable).

In addition, the manufacturer must provide the equipment with all OSHA required safety devices (if applicable).

Content of PSTP Regarding Equipment Capabilities and Description:

The PSTP shall include the following elements:

- *Description of the equipment to be demonstrated including photographs from several perspectives;*
- *Brief introduction and discussion of the engineering and scientific concepts on which the SOC removal capabilities of the water treatment equipment are based;*
- *Description of the treatment equipment and each process included as a component in the modular system including all relevant schematics of treatment and pretreatment systems;*
- *Brief description of the physical construction/components of the equipment, including the general environment requirements and limitations, required consumables; weight, transportability, ruggedness, power and other pertinent information needed, etc.;*
- *Statement of typical rates of consumption of chemicals, a description of the physical and chemical nature of wastes, and the rates of waste generation (concentrates, residues, waste products, required regeneration frequencies; materials replacement frequencies; etc.);*
- *Definition of the performance range of the equipment;*
- *Identification of any special licensing requirements associated with the operation of the equipment;*
- *Description of the applications of the equipment and the removal capabilities of the treatment system relative to existing equipment. Comparisons shall be provided in such areas as: treatment capabilities, requirements for chemicals and materials, power, labor*

requirements, suitability for process monitoring and operation from remote locations, ability to be managed by part-time operators; and

- *Discussion of the known limitations of the equipment. The following operational details shall be included: the range of feedwater quality suitable for treatment with the equipment, the upper limits for concentrations of contaminants that can be removed to concentrations below a certain level, level of operator skill required to successfully use the equipment.*

4.0 EXPERIMENTAL DESIGN

This section discusses the objectives of the verification testing, factors that must be considered to meet the performance objectives, and the statistical analysis and other means that the FTO will use to evaluate the results of the verification testing.

4.1 Objectives

The objectives of verification testing are to evaluate equipment in the following areas:

- Performance relative to the manufacturer's stated range of SOC removal objectives and equipment operation;
- The impacts of variations in feedwater quality (such as dissolved organic carbon (DOC), temperature, turbidity, microbial concentration, pH, alkalinity, etc.) on equipment performance;
- The logistical, human, and economic resources necessary to operate the equipment; and
- The reliability, ruggedness, cost factors, range of usefulness, and ease of operation.

The manufacturer shall be responsible for selection of those treatment challenges listed in the TSTPs that are most appropriate for their equipment. For example, if equipment were only intended for removal of SOCs, there would be no need to conduct testing to evaluate the removal of hardness ions or metal ion species. However, it should be noted that many of the drinking water treatment systems participating in verifying SOC removal might be capable of achieving multiple water treatment objectives. The verification test may for example be undertaken to demonstrate equipment removal capabilities for a wide number of constituents. In addition, the FTO and the manufacturer may wish to construct the PSTP so that verification testing may also demonstrate the treatment system's removal capabilities and treatment operations for additional water quality parameters. The incorporation of additional treatment objectives may also necessitate attention to the other applicable protocol and TSTPs in the development of the PSTP.

4.2 Equipment Characteristics

This section discusses equipment characteristics or factors that will be considered in the design and implementation of verification testing. These factors include:

- Ease of operation;

- Degree of operator attention required;
- Response of equipment and treatment process to changes in feedwater quality;
- Electrical requirements;
- System reliability features including redundancy of components;
- Feed flow requirements;
- Discharge requirements;
- Spatial requirements of the equipment (footprint);
- Unit processes included in treatment train;
- Chemicals needed;
- Chemical hazards associated with equipment operation; and
- Response of treatment process to intermittent operation.

Verification testing procedures shall simulate routine conditions as much as possible and in most cases testing may be done in the field. Under such circumstances, simulation of field conditions would not be necessary.

4.2.1 Qualitative Factors

Some factors, while important, are difficult or impractical to quantify. These are considered qualitative factors. Important factors that cannot easily be quantified are the modular nature of the equipment, ease of operation, the safety of the equipment, the portability of equipment, and the logistical requirements necessary for using it.

Typical qualitative factors to be discussed are listed below, and others may be added. The PSTP shall discuss those factors that are appropriate to the test equipment that may include:

- Reliability or susceptibility to environmental conditions:
- Equipment safety:
- Effect of operator experience on results; and
- Effect of operator's technical knowledge on system performance and robustness of operation.

4.2.2 Quantitative Factors

Many factors of the equipment characteristics can be quantified by various means during verification testing. Some can be measured while others cannot be controlled. Typical quantitative factors to be discussed are listed below, and others may be added. The PSTP shall discuss those factors that are appropriate to the test equipment that may include:

- Power and consumable supply (such as chemical and materials) requirements;
- Productivity and performance of equipment;
- Monitoring requirements for pressure, flow, and temperature;
- Cost factors of operation, expendables and waste disposal;
- Hydrodynamics of system;

- Chemical equivalents of process streams;
- Safety features of equipment;
- Length of operating cycle; and
- Daily labor hours required for O&M.

These quantitative factors will be used as an initial benchmark to assess equipment performance.

4.3 Water Quality Considerations

The primary treatment goal of the equipment employed in verification testing through this protocol is to achieve removal of SOCs found in feedwaters (or raw waters) such that finished waters are of acceptable water quality. The objectives of verification testing may also be to assure production of water with palatable, healthful and consistent water quality. The experimental design and statement of performance objectives in the PSTPs shall be developed so the relevant questions about water treatment equipment capabilities can be answered.

Manufacturers should carefully consider the capabilities and limitations of their equipment and have their statement of performance objectives sufficiently challenge their equipment. The FTO on behalf of the manufacturer should adopt an experimental approach to verification testing that would provide a broad market for their products, while recognizing the limitations of the equipment. The FTO should not adopt a verification experimental approach to removal of SOCs that would be beyond the capabilities of the equipment. A wide range of contaminants or water quality problems that can be addressed by water treatment equipment varies, and some treatment equipment can address a broader range of problems than other types. Manufacturers shall use TSTPs as the basis for the development of the experimental plan in each specific PSTP.

4.3.1 Feedwater Quality

One of the key aspects related to demonstration of equipment performance in verification testing is the range of feedwater quality that can be treated successfully, resulting in treated water quality that meets water quality goals or regulatory requirements. The manufacturer and FTO should consider the influence of feedwater quality on the quality of treated waters produced by the equipment, such that product waters meet the designated water quality goals stated in the PSTP. As the range of feedwater quality that can be treated by the equipment becomes broader, the potential applications for treatment equipment with verified performance capabilities might also increase.

The FTO shall provide a list of SOCs in the PSTP that may be pertinent in equipment performance for removal of SOCs. Characteristics of feedwater quality that may be important for treatment equipment intended to remove SOCs should be identified in the applicable PSTP.

One of the questions often asked by regulatory officials in approval of water treatment equipment is: "Has it been shown to work on the water where it is proposed to be used?" By

covering a large range of water qualities, verification testing is more likely to provide an affirmative answer to that question.

4.3.2   Treated Water Quality

Production of treated water of a high quality, having no trace of SOC shall be the primary goal of the water treatment systems included in verification testing. If an FTO states that water treatment equipment can be used to treat water to meet specified regulatory requirements for removal of SOCs, verification testing must provide data that support such a statement of performance objectives, as appropriate.

The FTO, on behalf of the manufacturer, shall be responsible for identification of the specific SOCs that shall be monitored during verification testing. A state-certified, third-party accredited or EPA accredited laboratory shall perform water quality analysis for the specific SOCs identified in water samples provided by the FTO. This issue shall be discussed further in Section 5.2.

In addition, the FTO may wish to make a statement about performance objectives of the equipment for removal of other contaminants that are not directly related to SOC removal. For example, some water treatment equipment can be used to meet aesthetic goals. Removal goals for some of these parameters may also be presented in the PSTP as additional statements of performance objectives.

4.4   Synthetic Organic Chemical Contaminants Testing

Because of the numerous varieties of SOCs, analytical procedures must be approved or proven techniques. Many methods for SOC analysis are outlined in Standard or EPA Methods and shall be employed in verification testing and evaluation of SOCs. Should an approved method be non-existent for an individual SOC, then a proposed method may be allowed after at least three labs have successfully demonstrated the method to achieve a standard degree of uncertainty in analysis. The manufacturer would be required to document and submit details of analytical procedures used to measure the specific SOC.

Frequency of sampling and SOC analysis shall be specified by the individual TSTPs used for the verification test and shall also be stipulated in the PSTP.

4.5   Recording Data

For all SOC experiments targeted towards removal of SOCs, water quality data on feedwater, finished water, and wastewater should be maintained at a minimum on the identified SOCs and other water quality parameters identified by the FTO. The specific water quality parameters to be monitored and with what frequency shall be stipulated in the TSTP(s) employed for development of the PSTP prior to initiation of the verification test. At a minimum, the following conditions shall also be maintained for each experiment:

- Water type (raw water, pretreated feedwater, product water, waste water);
- Experimental run (e.g., 1st run, 2nd run, 3rd run, etc.);
- Type of chemical addition, dose and chemical combination, where applicable (e.g., alum, cationic polymer, anionic polymer, ozone, monochloramine, scale inhibitor, etc.);
- Rate of flow through system, volume waste production as percent finished water flow, cumulative flow through system in terms of bed volumes (BV) (where applicable);
- Transmembrane pressure, membrane flux and element recovery (for membrane processes where applicable);
- Chemical cleaning frequency or regeneration frequency (where applicable); and
- Voltage requirements, current draw and power consumption at specific operating conditions.

4.6   Recording Statistical Uncertainty

For the analytical data obtained during verification testing, 95% confidence intervals shall be calculated by the FTO for water quality parameters in which eight or more samples are collected. The FTO shall ensure in the PSTP that sufficient water quality data and operational data are collected to allow estimation of statistical uncertainty for critical parameters. The specific TSTP(s) that may be employed with the protocol stipulate only a minimum frequency for monitoring of SOCs. The FTO shall therefore ensure that sufficient water quality and operational data is collected during verification testing for the statistical analysis described herein. The specific TSTP(s) shall specify which water quality parameters shall be subjected to the requirements of confidence interval calculation. The specific TSTP(s) shall specify which water quality parameters shall be subjected to the requirements of confidence interval calculation. DQOs and the vendor's performance objectives shall be used to assess which water quality parameters are critical and thus require confidence interval statistics. As the name implies, a confidence interval describes a population range in which any individual population measurement may exist with a specified percent confidence. The following formula shall be employed for confidence interval calculation:

$$\text{Confidence Interval} = \overline{x} \pm t_{n-1,1-\frac{a}{2}}\left(\frac{S}{\sqrt{n}}\right)$$

where: $\overline{x}$ = sample mean;
S = sample standard deviation;
n = number of independent measurements included in the data set;
t = Student's t distribution value with n-1 degrees of freedom; and
α = significance level, defined for 95% confidence as: 1 - 0.95 = 0.05.

According to the 95% confidence interval approach, the α term is defined to have the value of 0.05, thus simplifying the equation for the 95% confidence interval in the following manner:

$$\text{95\% Confidence Interval} = \overline{x} \pm t_{n-1,0.975}\left(\frac{S}{\sqrt{n}}\right)$$

With input of the analytical results for pertinent water quality parameters into the 95% confidence interval equation, the output will appear as the sample mean value plus or minus the confidence term.

The results of this statistical calculation may also be presented as a range of values falling within the 95% confidence interval. For example, the results of the confidence interval calculation may provide the following information: 520 ± 38.4 mg/L, with a 95% confidence interval range described as (482, 558).

Calculation of confidence intervals shall not be required for equipment performance results (e.g., filter run length, cleaning efficiency, in-line turbidity or in-line particle counts, etc.) obtained during the equipment verification testing. However, as specified by the FTO, calculation of confidence intervals may be required for analytical parameters such as SOC and non-purgeable dissolved organic carbon (NPDOC). To provide sufficient analytical data for statistical analysis, the FTO shall collect three discrete water samples at one set of operational conditions for each of the specified water quality parameters during a designated testing period. The procedures and sampling requirements shall be provided in detail in the PSTP.

4.7 Verification Testing Schedule

Verification testing activities include equipment set-up, initial operation, verification operation, and sampling and analysis. Initial operations are to be conducted so that equipment can be tested to be sure it is functioning as intended. If feedwater (or source water) quality influences operation and performance of the equipment being tested, the initial operations period serves as the shakedown period for determining appropriate operating parameters. The schedule of testing may also be influenced by coordination requirements with a utility.

For water treatment equipment involving removal of SOCs, an initial period of bench-scale testing of feedwater followed by treatment equipment operation may be needed to determine the appropriate operational parameters for testing equipment. A number of operational parameters may require adjustment to achieve successful functioning of the process train. These parameters may include but are not limited to the following: process rates; feedwater pH; chemical dosages, chemical types (where appropriate) and other parameters that may result in successful functioning of the process train. Chemical type, chemical dosages, and other operations that result in successful functioning of the process should be included.

It is recommended under this protocol that a minimum of one 60-day test period of verification testing be conducted to allow testing over a period of time to collect representative data. The specific operating and water quality parameters shall be stipulated by the selected TSTP(s) under this protocol and shall be used in development of the experimental plan and the preparation of the PSTP.

Content of PSTP Regarding Experimental Design

The PSTP shall include the following elements:

- *Identification of the qualitative and quantitative factors of equipment operation to be addressed in the verification testing;*

- *Identification and discussion of the particular water treatment issues and SOC concentrations that the equipment is designed to address, how the equipment will solve the problem, and who would be the potential users of the equipment;*
- *Identification of the range of key water quality parameters, given in applicable TSTPs, which the equipment is intended to address and for which the equipment is applicable;*
- *Identification of the key parameters of treated water quality and analytical methods that will be used for evaluation of equipment performance during the removal of SOCs. Parameters of significance for treated water quality are listed in applicable TSTPs;*
- *Description of data recording protocol for equipment operation, feedwater quality parameters, and treated water quality parameters;*
- *Description of the confidence interval calculation procedure for selected water quality parameters; and*
- *Detailed outline of the verification testing schedule, with regard to annual testing periods that will cover an appropriate range of annual climatic conditions, (i.e., different temperature conditions, seasonal differences between rainy and dry conditions).*

5.0   FIELD OPERATIONS PROCEDURES

5.1   Equipment Operations and Design

The TSTP specifies procedures that shall be used to provide accurate documentation of both equipment performance and treated water quality. Careful adherence to these procedures will result in definition of verifiable performance of equipment. The specific reporting techniques, methods of statistical analysis and the QA/QC of reporting SOC removal data shall be stated explicitly by the FTO in the PSTP before initiation of the verification test. (Note that this protocol may be associated with a number of different TSTPs for different types of process equipment capable of achieving removal of SOCs).

The design aspects of water treatment process equipment often provide a basis for approval by state regulatory officials and can be used to ascertain if process equipment intended for larger or smaller flows involves the same operating parameters that were relevant to the verification testing. The field operations procedures and testing conditions provided by the FTO shall therefore be specified to demonstrate treatment capabilities over a broad range of operational conditions and feedwater qualities.

Initial operations of the SOC removal equipment will allow FTOs to refine the equipment operating procedures and to make operational adjustments as needed to successfully treat the feedwater. Information generated through this period of operation may be used to revise the PSTP, if necessary. A failure at this point in the verification test could indicate a lack of capability of the process equipment and verification testing might be cancelled. Specific design aspects to be included in the PSTP are provided in detail, in the Manufacturer Responsibilities section below.

5.2 Selection of Analytical Laboratory and Field Testing Organization

To assess the performance of the equipment, the quality of the treated water produced using the equipment shall be determined by analysis at a state-certified, third-party accredited or EPA-accredited analytical laboratory with proven experience in detection and measurement of SOCs. In all cases, current EPA *Standard Methods* procedures shall be used in analysis of specified water quality parameters. Because of the variability of acceptance of laboratories from state to state, use of analytical laboratories certified in a large number of states is recommended. Furthermore, the selected analytical laboratory must be certified by the state in which the verification testing is being performed. Analytical results from the laboratory are to be provided directly to the NSF to maintain data integrity.

For field testing operations, the manufacturer shall employ an NSF-qualified FTO; the list of qualified FTOs may include engineering consulting firms, universities, or other qualified scientific organizations with experience operating drinking water treatment equipment. If a particular SOC does not have an accepted standard method procedure, then an analytical testing plan describing the procedure shall be submitted to NSF for approval.

5.3 Communications, Documentation, Logistics, and Equipment

NSF shall communicate regularly with the verification testing participants to coordinate all field activities associated with the verification test and to resolve any logistical, technical, or QA/QC issues that may arise as the verification testing progresses. The successful implementation of the verification test will require detailed coordination and constant communication between all verification testing participants.

All field activities shall be thoroughly documented. Field documentation will include:

- Field logbooks;
- Photographs;
- Field data sheets; and
- Chain-of-custody forms.

The qualified FTO shall be responsible for maintaining all field documentation. The field logbook shall have at least the following requirements.

- Field notes shall be kept in a bound logbook;
- Each page shall be sequentially numbered and labeled with the project name and number;
- Field logbooks shall be used to record all water treatment equipment operating data;
- Completed pages shall be signed and dated by the individual responsible for the entries; and
- Errors shall have one line drawn through them and this line shall be initialed and dated.

All photographs shall be logged in the field logbook. These entries shall include the time, date, direction, subject of the photograph, and the identity of the photographer. Deviations from the approved final PSTP shall be thoroughly documented in the field logbook at the time of inspection and in the verification report.

Original field sheets and chain-of-custody forms shall accompany all samples shipped to the analytical laboratory. Copies of field sheets and chain-of-custody forms for all samples shall be provided at the time of the QA/QC inspection and included in the verification report.

As available, electronic data storage and retrieval capabilities shall be employed to maximize data collection and minimize labor hours required for monitoring. The guidelines for use of data-loggers, laptop computers, data acquisition systems etc., shall be detailed by the FTO in the PSTP.

5.4 Initial Operations

Initial operations will allow equipment manufacturers to refine their operating procedures and to make operational adjustments as needed to successfully treat the feedwater. Information generated through this period of operation may be used to revise the PSTP, if necessary. A failure at this point in the verification testing could indicate a lack of capability of the process equipment and the verification test might be canceled.

5.5 Equipment Operation and Water Quality Sampling for Verification Testing

All field activities shall conform to requirements provided in the PSTP that was developed and NSF-approved for the verification test being conducted. All sampling and sample analyses conducted during the verification test shall be performed according to the procedures detailed by the FTO in the PSTP. As necessary for verification analyses, state-certified, third-party or EPA-qualified laboratories are selected to perform analytical services using approved Standard or EPA Methods. If unanticipated or unusual situations are encountered that may alter the plans for equipment operation, water quality sampling, or data quality, the situation must be discussed with the NSF technical lead. Any deviations from the approved final PSTP shall be thoroughly documented.

During routine operation of water treatment equipment, the total number of hours during which the equipment is operated each day shall be documented. In addition, the number of hours each day during which the operator was working at the treatment plant performing tasks related to water treatment and the operation of the treatment equipment shall be documented. The qualified FTO, the water system, or the plant operator shall describe the tasks performed during equipment operation.

Content of PSTP Regarding Field Operations Procedures

The PSTP shall include the following elements:

- *A table summary of the proposed time schedule for operating and testing;*
- *Field operating procedures for the equipment and performance testing, based upon the TSTP, including:*
    - *listing of operating parameters,*
    - *ranges for feedwater quality, and*
    - *sampling and analysis strategy;*
- *Provision of all equipment needed for field work associated with this verification testing;*

- *Provision of a complete list of all equipment to be used in the verification testing. A table format is suggested;*
- *Provision of field operating procedures; and*
- *At a minimum, a table(s) showing all parameters to be analyzed, the analytical methods, the laboratory reporting limits or quantification limits, sample volume, bottle type, preservation method, and holding times.*

Manufacturer Responsibilities:

- *Provision of all equipment needed for field work associated with this verification testing;*
- *Provision of a complete list of all equipment to be used in the verification testing. A table format is suggested; and*
- *Provision of field operating procedures.*

6.0 QUALITY ASSURANCE PROJECT PLAN

Every PSTP for verification testing must include a Quality Assurance Project Plan (QAPP) that specifies procedures that shall be used to ensure data quality and integrity. Careful adherence to these procedures will ensure that data generated from verification testing will provide sound analytical results that can serve as the basis for performance verification.

6.1 Purpose and Scope

The purpose of this section is to outline steps that shall be taken by operators of the equipment and by the analytical laboratory to ensure that data resulting from verification testing is of known quality and that a sufficient number of critical measurements are taken.

6.2 Quality Assurance Responsibilities

The FTO project manager is responsible for coordinating the preparation of the QAPP for the verification test and for its approval by NSF. The FTO project manager, with oversight from NSF, shall also ensure that the QAPP is implemented during all verification testing activities.

The manufacturer and NSF must approve the entire PSTP including the QAPP before the verification test can proceed. NSF must review and either approve the QAPP or provide reasons for rejection of the QAPP. NSF should also provide suggestions on how to modify the QAPP to make it acceptable, provided that the FTO has made a good faith effort to develop an acceptable QAPP (i.e., the QAPP is 75 to 80% acceptable with only minor changes needed to produce an acceptable PSTP. NSF will not write QAPPs for manufacturers.).

A number of individuals may be responsible for monitoring equipment operating parameters and for sampling and analysis QA/QC throughout the verification testing. Primary responsibility for ensuring that both equipment operation and sampling and analysis activities comply with the QA/QC requirements of

the PSTP shall rest with the FTO. QA/QC activities for the equipment shall include those activities recommended by the manufacturer and those required by NSF to assure the verification testing will provide data of the necessary quality.

QA/QC activities for the state-certified or third-party or EPA-qualified analytical laboratory that analyzes samples sent off-site shall be the responsibility of that analytical laboratory's supervisor. If problems arise or any data appear unusual, they shall be thoroughly documented and corrective actions shall be implemented as specified in this section. The QA/QC measurements made by the off-site analytical laboratory are dependent on the analytical methods being used.

6.3   Data Quality Indicators

The data obtained during verification testing must be of sound quality for conclusions to be drawn on the equipment. For all measurement and monitoring activities conducted for equipment verification, NSF and the EPA require that data quality parameters be established based on the proposed end uses of the data. Data quality parameters include four indicators of data quality:

- Accuracy;
- Precision;
- Completeness;
- Representativeness; and
- Statistical Uncertainty.

Treatment results generated by the equipment and by the laboratory analyses must be verifiable for the purposes of the verification testing program to be fulfilled. High quality, well-documented analytical laboratory results are essential for meeting the purpose and objectives of verification testing. Therefore, the following indicators of data quality shall be closely evaluated to determine the performance of the equipment when measured against data generated by the analytical laboratory.

6.3.1   Accuracy

For water quality analyses, accuracy refers to the difference between a sample result and the reference or true value for the sample. Loss of accuracy can be caused by such processes as:

- Errors in standards preparation;
- Equipment calibrations;
- Loss of target analyte in the extraction process;
- Interferences; and
- Systematic or carryover contamination from one sample to the next.

In verification testing, accuracy will be ensured by:

- Maintaining consistent sample collection procedures, including sample locations;
- Timing of sample collection;

- Sampling procedures;
- Sample preservation;
- Sample packaging;
- Sample shipping; and
- Random spiking procedures for the specific inorganic constituents chosen for testing.

The FTO shall discuss the applicable ways of determining the accuracy of the chemical and microbiological sampling and analytical techniques in the PSTP.

For water quality analysis, accuracy is usually expressed as the percent recovery. Percent recovery is the amount recovered during analysis. In general percent recovery can be calculated by dividing the measured amount added by the amount actually added.

$$\text{Percent Recovery} = \left(\frac{\text{Measured}_{\text{Sample}+\text{Spike}} - \text{Measured}_{\text{Sample}}}{\text{Actual}_{\text{Spike}}} \right) 100\% = \left(\frac{\text{Measured}_{\text{Spike}}}{\text{Actual}_{\text{Spike}}} \right) 100\%$$

For equipment operating parameters, accuracy refers to the difference between the reported operating condition and the actual operating condition. For equipment operating data, accuracy entails collecting a sufficient quantity of data during operation to be able to detect a change in operations. For water flow, accuracy may be the difference between the reported flow indicated by a flow meter and the flow as actually measured on the basis of known volumes of water and carefully defined times (bucket and stopwatch technique) as practiced in hydraulics laboratories or water meter calibration shops. For mixing equipment, accuracy is the difference between an electronic readout for equipment rotations per minute (rpms) and the actual measurement based on counted revolutions and measured time. Accuracy of head loss measurement can be determined by using measuring tapes to check the calibration of piezometers for gravity filters or by checking the calibration of pressure gauges for pressure filters. Meters and gauges must be checked periodically for accuracy, and when proven to be dependable over time, the time interval between accuracy checks can be increased. In the PSTP, the FTO shall discuss the applicable ways of determining the accuracy of the operational conditions and procedures.

6.3.2 Precision

Precision refers to the degree of mutual agreement among individual measurements and provides an estimate of random error. The standard deviation and the relative percent deviation recorded from sample analyses may be reported as a means to quantify sample precision. Precision measures the repeatability of measurement. It is usually expressed as the percent relative standard deviation (percent RSD). In general percent RSD can be calculated by dividing the standard deviation by the average. The methods to be employed for use of deviation shall be described by the FTO in the PSTP.

$$\text{Percent RSD} = \left(\frac{\text{Standard Deviation}}{\text{Average}}\right)100\% = \left(\frac{\sqrt{\sum_{i=1}^{n}\dfrac{\left(y_i - \bar{y}\right)^2}{n-1}}}{\sum_{i=1}^{n}\dfrac{y_i}{n}}\right)100\%$$

y_i = sample measurement

n = number of samples

For acceptable analytical precision under the verification testing program, the percent RSD for drinking water samples must be less than 30%. If the data generated during the ETV test does not meet the DQOs defined in this QA/QC section, additional testing and sampling will be required. If the DQOs are still not met through additional testing and the collection of additional samples, then a retest will be required.

6.3.3 Completeness

Completeness refers to the amount of data collected from a measurement process compared to the amount that was expected to be obtained. Completeness refers to the proportion of valid, acceptable data generated using each method. This portion of the required data for the selected test plan will be reported at the conclusion of each testing period.

The completeness objective for data generated during verification testing is based on the number of samples collected and analyzed for each parameter and/or method. The test plans will likely require a large number of samples to be collected for key and most important parameters and/or methods. The following chart illustrates the completeness objectives for performance parameter and/or method based on the sample frequency:

Number of Samples Per Parameter and/or Method	Percent Completeness
0-10	80%
11-50	90%
>50	95%

Completeness is defined as follows for all measurements:

%C = (V/T) X 100

where: %C = percent completeness;
V = number of measurements judged valid; and
T = total number of measurements.

Additional testing and collection of additional sample will be required if the percent completeness objectives are not met. If the completeness objectives are still not met through the collection of additional samples, then a retest will be required.

The following are examples of instances that might cause a sample analysis to be incomplete:

- Instrument failure;
- Calibration requirement not being met; and
- Elevated analyte levels in the method blank.

6.3.4 Representativeness

Representativeness refers to the degree to which the data accurately and precisely represent the conditions or characteristics of the parameter represented by the data. In verification testing, representativeness will be ensured by maintaining consistent sample collection procedures, including:

- Sample locations;
- Timing of sample collection;
- Sampling procedures;
- Sample preservation;
- Sample packaging;
- Sample shipping;
- Sample equipment decontamination; and
- Blind spikes.

Using each method at its optimum capability to provide results that represent the most accurate and precise measurement that it is capable of achieving also will ensure representativeness. For equipment operating data, representativeness entails collecting a sufficient quantity of data during operation to be able to detect a change in operations.

6.3.5 Statistical Uncertainty

Statistical uncertainty of the water quality parameters analyzed shall be evaluated through calculation of the 95% confidence interval around the sample mean. Description of the confidence interval calculation is provided in Section 4.6 – Recording Statistical Uncertainty.

6.4 Quality Control Checks

This section describes the QC requirements that apply to both the treatment equipment and the on-site measurement of water quality parameters. It also contains a discussion of the corrective action to be taken if the QC parameters fall outside of the evaluation criteria.

The QC checks provide a means of measuring the quality of data produced. The FTO may not need to use all of the checks identified in this section. The selection of the appropriate QC checks depends on the following:

- Equipment;
- Experimental design; and
- Performance goals

The selection of QC checks will be based on discussions between the FTO and NSF. Some types of QC checks applicable to operating water treatment equipment were described in Section 6.3.

6.4.1 Quality Control for Equipment Operation

This section will explain the methods to be used to check on the accuracy of equipment operating parameters and the frequency with which these QC checks will be made. A key aspect of verification testing is to provide operating results that will be widely accepted by state regulatory officials. If the quality of the equipment operating data cannot be verified, then the water quality analytical results may be of no value. Because water cannot be treated if equipment is not operating within specification, obtaining valid equipment operating data is a prime concern for verification testing.

An example of the need for QC for equipment operations is an incident of rejection of test data because the treatment equipment had no flow meter to use for determining engineering and operating parameters related to flow.

6.4.2 Water Quality Data

After treatment equipment is operating within specifications and water is being treated, the results of the treatment are interpreted in terms of water quality. The quality of water sample analytical results is just as important as the quality of the equipment operating data. Therefore, the QAPP must emphasize the methods to be employed for sampling and analytical QA. Analytical methods for on-site and off-site monitoring are presented within each TSTP. If new methods are published and approved or current methods updated, the most current methods shall be used. The important aspects of sampling and analytical QA are given below:

6.4.2.1 Duplicate Samples. Duplicate samples shall be analyzed for selected water quality parameters at specified intervals to determine the precision of analysis. The procedure for determining samples to be analyzed in duplicate shall be provided in the PSTP with the required frequency of analysis and the approximate number. Duplicate samples must include field duplicates and laboratory duplicates. Field duplicates measure the precision of the overall sampling and analysis procedures. Laboratory duplicates measure the precision associated only with the lab procedures.

6.4.2.2   Method Blanks. Method blanks are used for selected water quality parameters to evaluate analytical method-induced contamination, which may cause false positive results.

6.4.2.3   Spiked Samples. The use of spiked samples will depend on the testing program, and the contaminants to be removed. If spiked samples are to be used, specify the procedure, frequency, acceptance criteria, and actions if criteria are not met.

6.4.2.4   Travel Blanks. Travel blanks for selected water quality parameters shall be provided to the analytical laboratory to evaluate travel-related contamination.

6.4.2.5   Performance Evaluation Samples for On-Site Water Quality Testing. Performance evaluation (PE) samples are samples of unknown concentration prepared by an independent performance evaluation lab and are provided as unknowns to an analyst to evaluate his or her analytical performance. Analysis of PE samples shall be conducted onsite by the FTO and by the offsite laboratory before testing is initiated. If recent PE reports from the laboratory are not available, PE samples shall be submitted by the FTO to the analytical laboratory. The control limits for the PE samples shall be used to evaluate the FTO's and analytical laboratory's method performance. One kind of PE sample that would be used for on-site QA in most studies performed under this protocol would be an SOC PE sample.

A PE sample comes with statistics that have been derived from the analysis of the sample by a number of laboratories using EPA-approved methods. These statistics include a true value of the PE sample, a mean of the laboratory results obtained from the analysis of the PE sample, and an acceptance range for sample values. The analytical laboratory is expected to provide results from the analysis of the PE samples that meet the performance capabilities of the verification testing.

6.5   Data Reduction, Validation, and Reporting

To maintain good data quality, specific procedures shall be followed during data reduction, validation, and reporting. These procedures are detailed below.

6.5.1   Data Reduction

Data reduction refers to the process of converting the raw results from the equipment into concentration or other data in a form to be used in the comparison. The procedures to be used will be equipment dependent. The purpose of this step is to provide data that will be used to verify the statement of performance objectives. These data shall be obtained from logbooks, instrument outputs, and computer outputs as appropriate.

6.5.2   Data Validation

The operator shall confirm the completeness of the appropriate data forms and the completeness and correctness of data acquisition and reduction. The field team supervisor or

another technical person shall review calculations and inspect laboratory logbooks and data sheets to confirm precision, accuracy and completeness. The individual operators and the laboratory supervisor shall examine calibration and QC data. Laboratory and project managers shall confirm that all instrument systems are in control and those QA objectives for precision, accuracy, completeness, and method detection limits have been met.

Analytical outlier data are defined as those QC data lying outside a specific QC objective window for precision and accuracy for a given analytical method. Should QC data be outside of control limits, the analytical laboratory or field team supervisor will investigate the cause of the problem. If the problem involves an analytical problem, the sample will be reanalyzed. If the problem can be attributed to the sample matrix, the result will be flagged with a data qualifier. This data qualifier will be included and explained in the final analytical report.

6.5.3   Data Reporting

The data reported during verification testing shall be explicitly defined by the FTO in the PSTP. At a minimum, the data tabulation shall list the results for feedwater and treated water quality analyses, the results of SOC removal analyses, and equipment operating data. All QC information such as calibrations, blanks and reference samples are to be included in an appendix. All raw analytical data shall also be reported in an appendix. All data shall be reported in hardcopy and electronically in a common spreadsheet or database format.

6.6   Calculation of Data Quality Indicators

The equations for any data quality indicator calculations employed shall be provided. These include: precision, relative percent deviation, standard deviation, accuracy, and completeness.

6.7   System Inspections

On-site system inspections for sampling activities, field operations, and laboratories shall be conducted as specified by the TSTP. These inspections will be performed by the verification entity to determine if the TSTP and PSTP are being implemented as intended. At a minimum, NSF shall conduct one inspection of the sampling activities, field operations program and laboratories during the verification test. Separate inspection reports will be completed after the inspections and provided to the participating parties.

6.8   Reports

6.8.1   Status Reports

The FTO shall prepare periodic reports for distribution to pertinent parties, e.g., manufacturer, EPA, and the community. These reports shall discuss project progress, problems and associated corrective actions, and future scheduled activities associated with the verification testing. When problems occur, the manufacturer and FTO project managers shall discuss them

and estimate the type and degree of impact, and describe the corrective actions taken to mitigate the impact and to prevent a recurrence of the problems. The frequency, format, and content of these reports shall be outlined in the PSTP.

6.8.2 Inspection Reports

Any QA inspections that take place in the field or at the analytical laboratory while the verification testing is being conducted shall be formally reported by the FTO to the verification entity and manufacturer.

6.9 Corrective Action

Each PSTP must incorporate a corrective action plan. This plan must include the predetermined acceptance limits, the corrective action to be initiated whenever such acceptance criteria are not met, and the names of the individuals responsible for implementation.

Routine corrective action may result from common monitoring activities, such as:

- Routine site performance evaluation audits and
- Routine technical systems audits.

Content of PSTP Regarding the QAPP

The PSTP shall include the following elements:

- *Description of methodology for measurement of accuracy;*
- *Description of methodology for measurement of precision;*
- *Description of the methodology for use of blanks, the materials used, the frequency, the criteria for acceptable method blanks and the actions if criteria are not met;*
- *Description of any specific procedures appropriate to the analysis of the PE samples;*
- *Outline of the procedure for determining samples to be analyzed in triplicate, the frequency and approximate number;*
- *Description of the procedures used to assure that the data are correct;*
- *Listing of techniques and/or equations used to quantify any necessary data quality indicator calculations in the analysis of water quality parameters. These include accuracy, precision, and completeness (e.g., relative percent deviation, standard deviation, and confidence interval calculation);*
- *Outline of the frequency, format, and content of reports in the PSTP; and*
- *Development of a corrective action plan in the PSTP.*

The FTO shall be responsible for the following:

- Provision of all QC information such as calibrations, blanks and reference samples in an appendix. All raw analytical data shall also be reported in an appendix;

- Provision of all data in hardcopy and electronic form in a common spreadsheet or database format.

7.0 DATA MANAGEMENT, ANALYSIS AND REPORTING

7.1 Data Management and Analysis

The responsibilities of the FTO for data management and analysis have been provided in the Responsibilities Summary Sheet, the Project Guidance Manual, and/or the Terms and Conditions cited earlier in this protocol. The manufacturer, FTO, and NSF each have distinct responsibilities for managing and analyzing verification testing data. The FTO is responsible for managing all the data and information generated during verification testing. The FTO will also be responsible for analyzing and reporting the data in the verification report. The manufacturer is responsible for furnishing those records generated by the equipment FTO. NSF will be responsible for verification of the data.

A variety of data will be generated during verification testing. Each piece of data or information identified for collection in the approved PSTP shall be provided in the report. The data management section of the PSTP shall describe what types of data and information needs to be collected and managed, and shall also describe how the data will be reported for evaluation.

The raw data and the validated data must be reported. These data shall be provided in hard copy and in electronic format. As with the data generated by the innovative equipment, the electronic copy of the laboratory data shall be provided in a spreadsheet and a data dictionary shall be provided. In addition to the sample results, all QA/QC summary forms must be provided.

Other items that must be provided include:

- Field notebooks;
- Photographs, slides and videotapes (copies); and
- Results from the use of other field analytical methods.

7.2 Report of Equipment Testing

The FTO shall prepare a draft report describing the verification testing that was carried out and the results of that testing. This report shall include the following topics:

- Introduction;
- Executive Summary;
- Description and Identification of Product Tested;
- Procedures and Methods Used in Testing;
- Results and Discussion (discussion of results should be kept at a minimum to a avoid conclusions and recommendations);
- References;
- Appendices;

- QA/QC Results; and
- Inspection Report.

Content of PSTP Regarding Data Management and Analysis, and Reporting

The PSTP shall include the following:

- *Description of what types of data and information needs to be collected and managed and*
- *Description of how the data will be reported.*

8.0   SAFETY AND MAINTENANCE CONSIDERATIONS

The safety procedures shall address safety considerations and include adherence to all local, state and Federal regulations relative to safety and operational hazards. The safety procedures shall address safety considerations, which relate to the health and safety of personnel required to work on the site of the test equipment and persons visiting the site. Many of these items will be covered by site inspections and construction and operating permits issued by responsible agencies. The safety procedures shall address safety considerations, including the following as applicable:

- Regulations covering the transport, storage, handling and disposal of hazardous chemicals including acids, caustic and oxidizing agents;
- Chemical hazards and biohazards;
- Conformance with the National Electric Code;
- Provision of and access to fire extinguishers;
- Provision of sanitary facilities;
- Regulations covering site security;
- Conformance to any building permit requirements, such as provision of handicap access or other health and safety requirements; and
- Ventilation of equipment or of trailers or buildings housing equipment, if gases generated by the equipment could present a safety hazard.

For additional information on pilot plant and laboratory safety, please refer to:

- Palluzi, R. P. Pilot Plant and Laboratory Safety. New York: McGraw-Hill, 1994.
- Fuscaldo, A. A., et al. Laboratory Safety, Theory and Practice. New York: Academic Press. 1980.

Content of PSTP Regarding Safety

The manufacturer shall be responsible for:

- *Provisions of required written material (such as Material Data Safety Sheets);*

- *Compliance with all safety requirements of local, state and Federal laws and regulators; and*
- *Provisions of maintenance information and troubleshooting guidelines and instructions relative to the equipment to be verified.*

The PSTP shall include the following:

- *Address safety considerations that are appropriate for the equipment being tested and for the chemicals employed in the verification test.*

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CHAPTER 2

EPA/NSF ETV
EQUIPMENT VERIFICATION TESTING PLAN
FOR THE REMOVAL OF SYNTHETIC ORGANIC CHEMICAL CONTAMINANTS
BY MEMBRANE FILTRATION PROCESSES

Prepared by:
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LIST OF ABBREVIATIONS

DIC	dissolved inorganic carbon
EPA	Environmental Protection Agency
PSTP	Product-Specific Test Plan
FTO	Field Testing Organization
GAC	granular activated carbon
HF	hollow fiber
HSD	homogeneous solution diffusion model
IMS	Integrated Membrane Systems
IOC	inorganic compounds
MCL	maximum contaminant level
MCLG	maximum contaminant level goal
MF	microfiltration
MFI	modified fouling index
MTC	mass transfer coefficient
MWCO	molecular weight cut-off
NF	nanofiltration
NPDES	National Pollutant Discharge Elimination System
O&M	operation and maintenance
PEG	polyethlene glycol
QA/QC	Quality Assurance/Quality Control
RO	reverse osmosis
SCADA	Supervisory Control and Data Acquisition
SDI	silt density index
SDWA	Safe Drinking Water Act
SOC	synthetic organic chemical
SW	surface water
TFC™	thin-film composite
TOC	total organic carbon
TDS	total dissolved solids
UF	ultrafiltration
WTP	water treatment plant

1.0   APPLICATION OF THIS EQUIPMENT VERIFICATION TESTING PLAN

This document is the ETV Testing Plan (Plan) for evaluation of membrane processes to be used within the structure provided by the "EPA/NSF ETV Protocol For Equipment Verification Testing For The Removal Of Synthetic Organic Chemical Contaminants: Requirements For All Studies". This Plan is to be used as a guide in the development of the Product-Specific Test Plan (PSTP) for testing of membrane process equipment to achieve removal of synthetic organic chemical contaminants (SOCs).

In order to participate in the equipment verification process for membrane processes, the equipment Manufacturer and their designated Field Testing Organization (FTO) shall employ the procedures and methods described in this test plan and in the referenced ETV Protocol Document as guidelines for the development of a PSTP. The FTO shall clearly specify in its PSTP the SOCs targeted for removal and sampling program that shall be followed during Verification Testing. The PSTP should generally follow the Verification Testing Tasks outlined herein, with changes and modifications made for adaptations to specific membrane equipment. At a minimum, the format of the procedures written for each Task in the PSTP should consist of the following sections:

- Introduction

- Objectives

- Work Plan

- Analytical Schedule

- Evaluation Criteria

The primary treatment goal of the equipment employed in this Verification Testing program is to remove SOCs present in water supplies. Therefore, experimental design of the PSTP shall be developed so that relevant performance specifications for membrane process related to SOC removal are addressed. The Manufacturer shall establish a Statement of Performance Objectives (Section 3.0 General Approach) that is based upon removal of target SOCs from feedwaters. The experimental design of the PSTP shall be developed to address the specific Statement of Performance Objectives established by the Manufacturer. Each PSTP shall include all of the included tasks, Tasks 1 to 9.

2.0   INTRODUCTION

Membrane processes are currently in use for a number of water treatment applications ranging from removal of inorganic constituents; total dissolved solids (TDS), total organic carbon (TOC), synthetic organic chemicals (SOCs), radionuclides and other constituents.

In order to establish appropriate operations conditions such as permeate flux, recovery, cross-flow velocity, the Manufacturer may be able to apply some experience with his equipment on a similar water source. This may not be the case for suppliers with new products. In this case, it is advisable to require a pre-test optimization period so that reasonable operating criteria can be established. This would aid in preventing the unintentional but unavoidable optimization during the Verification Testing. The need of

pre-test optimization should be carefully reviewed with NSF, the FTO and the Manufacturer early in the process.

Pretreatment processes ahead of RO systems are generally required to remove particulate material and to ensure provision of high quality water to the membrane systems. For example, RO membranes cannot generally be applied to treatment of surface waters without pretreatment of the feedwater to the membrane system. For surface water applications, appropriate pretreatment, primarily for removal of particulate and microbiological species, must be applied as specified by the Manufacturer. In the design of the PSTP, the Manufacturer shall stipulate which feedwater pretreatments are appropriate for application upstream of the RO membrane process. The stipulated feedwater pretreatment process(es) shall be employed for upstream of the membrane process at all times during the Equipment Verification Testing Program.

3.0   GENERAL APPROACH

Testing of equipment covered by this Verification Testing Plan will be conducted by an NSF-qualified FTO that is selected by the equipment Manufacturer. Analytical water quality work to be carried out as a part of this Verification Testing Plan will be contracted with a laboratory certified by a State or accredited by a third-party organization (i.e., NSF) or the EPA for the appropriate water quality parameters.

For this Verification Testing, the Manufacturer shall identify in a Statement of Performance Objectives the specific performance criteria to be verified and the specific operational conditions under which the Verification Testing shall be performed. The Statement of Performance Objectives must be specific and verifiable by a statistical analysis of the data. Statements should also be made regarding the applications of the equipment, the known limitations of the equipment and under what conditions the equipment is likely to fail or underperform. Two examples of Statements of Performance Objectives that may be verified in this testing are:

1.   This system is capable of achieving 98 percent removal of the SOC chlordane 60-day operation period at a flux of 15 gpm/sf (75 percent recovery; temperature between 20 and 25 °C) in feedwaters with chlordane concentrations less than 0.1 mg/L and total dissolved solids concentrations less than 500 mg/L.

2.   This system is capable of producing a product water with a chlordane concentration less than 2 mg/L during a 60-day operation period at a flux of 15 gpm/sf (75 percent recovery; temperature between 20 and 25 °C) in feedwaters with chlordane concentrations less than 0.1 mg/L and total dissolved solids concentrations less than 500 mg/L.

During Verification Testing, the FTO must demonstrate that the equipment is operating at a steady-state prior to collection of data to be used in verification of the Statement of Performance Objectives. For each Statement of Performance Objectives proposed by the FTO and the Manufacturer in the PSTP, the following information shall be provided:

- percent removal of the targeted SOCs;

- rate of treated water production (i.e., flux);

- recovery;

- feedwater quality regarding pertinent water quality parameters;

- temperature;

- concentration of target SOC; and

- other pertinent water quality and operational conditions.

This ETV Testing Plan is broken down into 9 tasks, as shown in the Section 6.0, Overview of Tasks. These Tasks shall be performed by any Manufacturer wanting the performance of their equipment verified under the ETV Program. The Manufacturer's designated FTO shall provide full detail of the procedures to be followed in each Task in the PSTP. The FTO shall specify the operational conditions to be verified during the Verification Testing Plan. All permeate flux values shall be reported in terms of temperature-corrected flux values, as either gallons per square foot per day (gfd) at 77 °F or liters per square meter per hour (L/(m^2-hr)) at 25 °C.

4.0   BACKGROUND

This section provides an overview of the literature review related to SOC regulations, health effects and contaminant removal by membrane processes and membrane system design. These items will assist in recognizing the vast number of SOC contaminants, identifying the ability to remove SOCs from water supplies using membrane processes, defining membrane systems and describing the mechanisms that will help in qualifying and quantifying the removal efficiency of the membrane process tested.

4.1   Regulatory and Health Effects

Since the passage of the Safe Drinking Water Act of 1974 (SDWA) requiring the establishment of recommended maximum contaminant levels (MCLs) for compounds that are deemed undesirable for consumption in public water supplies. Since that time there has been a growing awareness of the need for the control and removal of organic and inorganic contaminants from potable drinking water supplies. At the time of the passage of the SDWA of 1974, there were more than 12,000 chemical compounds known to be in commercial use. Many of these synthetic compounds are finding their way into potable water sources and ultimately into finished drinking water.

Within the past decade, several hundred specific organic chemicals have been identified in minute amounts in various drinking water supplies in the United States and abroad. Although at the present time the specific cause(s) of cancer are little understood, many of these commercially used organic compounds have been found to cause both acute and chronic adverse health effects in humans at various exposure levels. Therefore, in order to minimize risks to human health, the exposure levels to these compounds must be reduced to the lowest level possible that is both technologically and economically feasible.

The chronic health hazards associated with the presence of SOCs in drinking water have become a major concern of United States governmental agencies in more recent times. Consequently, contamination of potable water by SOCs is a significant national problem. Phase II and V of the SDWA have promulgated MCLs for 32 SOCs, of which 15 have been identified as carcinogenic. Appendix A lists the MCL, source of contamination and potential health effects for each regulated SOC. In addition, Appendix B lists the 46 SOCs proposed in the <u>Drinking Water Regulations and Health Advisories</u> and the <u>Federal Register</u> to be considered for regulation (USEPA 1996, 1997).

4.2   SOC Removal by Membrane Processes

This ETV Testing Plan is applicable to any pressure-driven membrane process used to achieve removal of SOCs. Furthermore, this testing plan is applicable to spiral-wound (SW) and hollow-fiber (HF) membrane configurations.

Membrane processes have been shown to be highly effective for the removal of SOCs. However, removal is a function of membrane mass transfer coefficients (MTCs), flux, recovery and feed concentration and will be expected to vary by membrane type. RO is also effective in producing a better overall quality of water.

Some advantages to the use of membrane processes for the removal of SOCs include:

- a small space requirement;
- removal of contaminant ions, dissolved solids, bacteria, and particles; and
- relative insensitivity to flow and TDS levels, and low effluent concentration.

Disadvantages include:

- higher capital and operating costs;
- higher level of pretreatment required;
- possible membrane fouling; and
- large reject streams.

Pressure-driven membrane processes are currently in use for a broad number of water treatment applications including the removal of pesticides and herbicides (i.e. SOCs), natural organic matter (NOM) which contributes to disinfection by-product formation, dissolved minerals, radionuclides and microbial contaminants such as *Giardia* and *Cryptosporidium*. Typically, higher pressure membrane applications such as nanofiltration (NF) and reverse osmosis (RO) are capable of removing SOCs, as well as ions contributing to hardness.

In contrast, low-pressure membrane processes, such as microfiltration (MF) and ultrafiltration (UF) are typically employed to provide a physical barrier for removal of microbial and particulate contaminants from drinking waters. However, the MF and UF membrane processes have not been shown to be effective for removal of SOCs unless another unit operation such as granular activated or powdered activated carbon is employed.

Suppliers of drinking water are subject to stringent government regulations for potable water quality regarding allowable pesticide and herbicide (i.e. SOCs) concentrations. In particular, European standards require less than 0.1 µg/L for any one particular pesticide or herbicide and no greater than 0.5 µg/L for total pesticides and herbicides in drinking water. Many investigators have shown that RO/NF are effective techniques for pesticide and herbicide removal (Duranceau 1992, Camp 1995, Takigawa et.al. 1995, and Kruithof et.al. 1995). However, specific mechanisms underlying SOC rejection are largely unknown. In the paragraphs to follow, results from published accounts of pesticide reduction and the inferences regarding suspected mechanisms for removal are presented.

It has been demonstrated that membrane processes are effective for SOC removal (Duranceau and Taylor 1992, and Hofman et.al. 1993). However the mechanisms for SOC removal are still under investigation and are a subject of research. Intensive research efforts have investigated the associated rejection mechanisms for various pesticides and herbicides. Included among these mechanisms are:

- size exclusion,
- steric hindrance (shape),
- electrostatic repulsion
- adsorption
- matrix effects

In general, uncharged pesticide and herbicide rejection by RO/NF has been observed to decrease with decreasing molecular size (i.e. molecular weight or molecular cross-sectional area) (Kruithof et.al 1995, Chen et.al 1997, and Berg and Gimbel 1997). Since molecular weight and molecular cross-sectional area are not always directly related, distinguishing between these two parameters is an important consideration for determination of a size exclusion rejection mechanism for uncharged SOCs (Berg and Gimbel 1997).

A study where NF treatability of a mixture of Elbe River (Germany) water and ground water with high sulfate and hardness content spiked with trace amounts of several SOCs ($C_{feed} \approx 1\mu g/L$) was conducted with both flat-sheet membrane films and spiral wound elements. Simazine, atrazine, terbutylazine, diuron, metazachlorine, TCA, and mecoprop composed the pesticide "cocktail" with which the surface water was spiked. Rejection of uncharged species terbutylazine, atrazine and simazine were reported to be in order of increasing size (Berg and Gimbel 1997). With the only difference between these species being the number of methyl groups, terbutylazine, with three methyl groups, was the highest rejected. Atrazine being the next largest in size was better rejected than simazine. Charged organic species were found to be significantly more rejected (predominately >85% for all membranes) by the negatively charged membranes than the polar SOCs despite substantial size differences. However, a combination of both electrostatic repulsion and size was suspected to influence rejection as demonstrated by higher rejection of the SOC mecoprop as compared to its smaller charged counterpart TCA. By adjusting the feed pH to 3, added insight was provided by analyzing the rejections of mecoprop in its dissociated and undissociated form. These results showed greater rejection for the dissociated form of mecoprop. The rejection of the undissociated form was less than in its dissociated form and was comparable to the

rejection of uncharged diuron, which suggested a removal mechanism for these non-polar species to be that of steric hindrance.

Additional flat-sheet testing has been performed to evaluate the effects of matrix conditions upon pesticide rejection as applied to different membrane polymers. Reported evaluations (Chen et.al. 1997) have demonstrated general pesticide rejection in order of highest to lowest by membrane film to be polyamide, amine, and cellulose acetate based polymers. This conclusion resulted from an overall assessment of pesticides commonly used in both the U.S and Europe and their rejection in separate distilled, inorganic, organic and inorganic-organic matrices. These pesticides included simazine, atrazine, cyanazine, bentazone, diuron, DNOC, pirimicarb, metamitron, metribuzin, MCPA, mecoprop, and vinchlozolin at feed concentrations of approximately 10 µg/L. These investigators also demonstrated that solvent properties, inorganic versus organic in particular, did not have a large influence upon SOC rejection. The order of pesticide rejection by matrix listed in order of increasing to decreasing rejection of pesticides was reported to be inorganics, organics, distilled water and combination of inorganic and organic. Among all four matrices, overall rejection varied by less than 10%. While the flat-sheet film tests were able to detect significant performance differences among cellulose acetate versus thin-film composite membranes, "finite differences (using similar types of membranes) were not detected using cell tests because of variations in membrane films due to manufacturing or analytical limitations."

SOC removal has also been the focus of attention for several Dutch Utilities. The PWN Water Supply Company of North Holland has studied cellulose acetate membrane polymers as applied to surface water for over 15 years (Camp 1995). Joint research between PWN and KIWA has shown thin-film composite (TFC) membranes to have better rejection properties than cellulose acetate (CA) membranes, but have the disadvantage of being more prone to fouling when surface water sources are used. As a single barrier, CA membranes were demonstrated to be inadequate for pesticide removal and they recommend granular activated carbon (GAC) post treatment (Kruithof et.al. 1995). However, at PWN, TFC membranes were shown to reject 90 to 95% of applied pesticide cocktails while CA membranes offered, as expected, less rejection of the SOCs. Moreover, chlorophenols were removed 25 to 90% with CA membranes. Experiments conducted in Leiduin, the Netherlands also showed significant pesticide rejection. Using a 4-2-1 array equipped with six 4" single elements, Toray SU 710 L type membranes achieved 97 to greater than 99% rejection for all pesticides except 2,4 dichlorophenol (50%) and diuron (87%). Specifically, the highly rejected SOCs in this mixture were atrazine (99%), bentazone (>99%), DNOC (97%), and isoproturon (97%) with feed concentrations ranging from 5.1 to 6.3 µg/L. Bench-scale experiments conducted at PWN, which compared Hydranautics CPA2 and Toray SU 710 L, revealed comparable pesticide rejection for the two composite membranes. The least rejected SOCs were diuron and simazine of the trace concentration SOC mixture that included atrazine, bentazone, and DNOC. However, each individual SOC was rejected at or greater than 96% by both membranes except for diuron as treated by the Toray SU 710 L single element.

4.3   Membrane System Design Considerations

Conventional NF or RO membrane systems consist of pretreatment, membrane processing and post-treatment. These processes are discussed in the following sections.

4.3.1 Pretreatment

The purpose of pretreatment is to control and minimize membrane fouling and reduce flux decline. The conventional pretreatment process consists of scale inhibitor (anti-scalant) and/or acid addition in combination with microfiltration. These pretreatment process are used to control scaling and protect the membrane elements; they are required for conventional RO or NF membrane systems. The membranes can be fouled or scaled during operation. Fouling is caused by particulate materials such as colloids and organics that are present in the raw water attaching to the membrane surface, and will reduce the productivity of the membrane. Scaling is caused by the precipitation of a sparingly soluble salt within the membrane because of the solute concentration exceeding solubility. If a raw water is excessively fouling, additional or advanced pretreatment is required.

Flux decline indicated by a reduction in membrane process productivity can be a result of scaling, colloidal fouling, microbiological fouling and organic chemical fouling. Scaling can be approximated by chemical analysis and equilibrium calculations. Fouling indices can approximate colloidal fouling. Microbiological and organic chemical fouling can only be approximated at this time by pilot testing. These mechanisms should be recognized and understood, and are presented below in order to develop strategies to control flux decline.

4.3.1.1 Scaling. In an RO/NF membrane process, salts present in the feedwater are concentrated on the feed side of the membrane. This concentration process continues until saturation and salt precipitation (scaling) occurs. Scaling will reduce membrane productivity, and consequently, will limit the rate of water that may be recovered as permeate on a sustained basis. The maximum recovery is the recovery at which the limiting salt first begins to precipitate.

Limiting salts can be identified from the solubility products of potential limiting salts in the raw feedwater. Since ionic strength increases on the feed side of the membrane, the effect of ionic strength upon the solubility products must also be considered and taken into account for these calculations. Some limiting salts may be controlled via the addition of acid or scale inhibitor or both to the feedwater prior to membrane treatment. Typical sparingly soluble salts that may limit recovery in pressure-driven membrane processes include, but are not limited to, $CaCO_3$, $CaSO_4$, $BaSO_4$, $SrSO_4$, CaF_2 and SiO_2.

As the feedwater passes through the membrane element from the feed side to the concentrate end of the membrane system, and the permeate water is removed, the feedwater salts become more concentrated. For instance, in a 75% recovery membrane system, the concentrate contains almost four times the concentration of salts that were present in the feedwater. This is called concentration polarization. Concentration polarization is the term used to describe the increased salt concentration that occurs at the surface of the membrane elements. As the permeate water passes through the membrane, the concentration of the rejected salts build up on the high-pressure side of the membrane surface. The amount of increased salt concentration over the bulk stream depends on how quickly the salts diffuse back into the bulk stream.

A high salt concentration at the membrane surface results in an increase in salt passage through the membrane. The increase in local salt concentration can lead to saturation of solution components resulting in precipitation on the membrane surface.

4.3.1.2   Colloidal Fouling. Colloidal fouling results from particles that exist in the influent which buildup on the surface of the membrane. The build-up forms a cake, which eventually is compressed and reduces flow through the membrane. Initially, cake formation does not significantly reduce productivity. However, after the cake compresses, the productivity decreases and the compressed cake must be removed. MF or UF membranes can be backwashed to remove the cake. However, spiral-wound RO and NF membranes require chemical cleaning to remove the cake. Advanced pretreatment processes such as cross-flow MF and multi-media filtration should control colloidal fouling.

4.3.1.3   Microbiological Fouling. Microbiological fouling results from biological growth in the membrane element, which results in a reduction in membrane productivity or an increase in pressure drop through an element. No reliable methods have been demonstrated for prediction of biofouling. Microbiological growth can occur in the feed spacers or on the membrane surface. Microbiological growth will occur in membranes but this growth does not always result in significant productivity loss. Advanced pretreatment processes may aid in the control of microbiological fouling.

4.3.1.4   Chemical Fouling. Chemical fouling results from the interaction of dissolved solutes in the feed stream with the membrane surface, which results in a reduction in membrane productivity. Chemical interaction between solute and the membrane surface will occur to some degree, but membrane productivity may not be reduced. Advanced pretreatment processes may aid in the control of chemical fouling.

4.3.2   Advanced Pretreatment

Advanced pretreatment would include unit operations that precede scaling control and cartridge filtration. By definition, unit operations that precede conventional pretreatment would be advanced pretreatment. Examples of advanced pretreatment would be coagulation/flocculation/sedimentation, oxidation followed by greensand filtration, continuous cross-flow microfiltration, multi-media filtration, and granular activated carbon (GAC) filtration.

4.3.3   Membrane Processes

The membrane process follows pretreatment. The majority of dissolved contaminants are removed in the membrane process. If the membrane scales or fouls, the productivity of the membrane system declines and eventually the membranes must be chemically cleaned to restore productivity. Cleaning frequencies for RO or NF systems average about 6 months when treating ground waters (Taylor et.al. 1990) and can be as low as 1 to 2 weeks when treating surface water with integrated membrane systems (IMSs).

UF or MF membranes as a stand alone process cannot remove SOCs. However, powdered activated carbon (PAC) can used for SOC adsorption followed by UF or MF to remove the PAC from the flow stream. MF and UF membranes are sieving controlled and do not have a low enough molecular weight cut-off (MWCO) range to reject many of the known SOCs or inorganic compounds (IOCs). RO and NF membranes can achieve significant SOC rejection because the MWCO of these membranes are low and many SOCs cannot pass (Duranceau 1992). This is also the case with IOCs and radionuclides. Although RO and NF have been shown to be among the most promising processes for SOC and IOC removal, not all SOCs or IOCs are rejected by these processes. RO and NF membranes use both sieving and diffusion mechanisms to reject SOCs and IOCs from drinking water and rejection will increase as the MW and charge of the contaminant increases. Typically, charged solutes and solutes with MWCOs greater than 200 mg/mmol are highly rejected by RO and NF.

UF and MF membranes do not affect corrosivity because inorganic ions are not removed; however, RO and NF do remove inorganic solutes from water, and this can impact the corrosivity of the permeate water.

4.3.4   Post-Treatment

Typical post-treatment unit operations can consist of disinfection, aeration, stabilization and storage. Aeration may be required to strip dissolved gases (Duranceau 1993). Stabilization may be required to produce a non-corrosive finished water since membrane permeate can be corrosive. Alkalinity recovery is an effective process for recovering dissolved inorganic carbon (DIC) in the permeate. Alkalinity can be recovered by lowering the pH prior to membrane filtration converting the alkalinity to CO_2, and then raising the pH of the permeate in a closed system to recover dissolved CO_2 as alkalinity. Bypassing feedwater and blending it with membrane permeate is another way of stabilizing the finished water; however, blending would negate the benefit of the membrane treatment system to act as a physical barrier against microbial contaminants.

4.3.5   Waste Disposal

In addition to post treatment, the concentrate stream from the membrane processes must be treated and/or disposed of in some manner. Although membrane processes are at present often technically and economically well suited to produce drinking water, the disposal of membrane concentrate will become more difficult and more expensive because of increased regulation. Effective concentrate disposal methods depend on the concentrate water quality, local regulations and site-specific factors (AWWARF 1993). The handling and disposal of the wastes generated by treatment technologies removing SOCs from drinking water pose concerns to the water supplier, to local and State governments and to the public at large. The potential handling hazards associated with SOCs warrant the development of a viable membrane concentrate disposal method. Information regarding concentrate disposal options can be found in <u>Membrane Concentrate Disposal</u> (AWWARF 1993). The document investigates the application of regulations to the disposal of membrane concentrate. The document first addresses membrane concentrate and its characteristics, including the definitions and natures of

the wastes that are being generated. Then the disposal methods that are being regulated are addressed, including descriptions of how to dispose of the concentrate. Finally, the regulations and permits that apply to the various disposal options are addressed. The following are disposal options that must be approved by the State or local government prior to implementation of a waste disposal program.

Liquid Waste Disposal

- Direct discharge into storm sewers or surface water.

- Discharge into sanitary sewer.

- Deep well injection.

- Drying or chemical precipitation.

Solid Waste Disposal

- Temporary lagooning (surface impoundment).

- Disposal in landfill.

- Disposal without prior treatment.

a) With prior temporary lagooning.

b) With prior mechanical dewatering.

c) Application to land (soil spreading/conditioning).

- Disposal at State licensed waste facility.

5.0   DEFINITION OF OPERATIONAL PARAMETERS

The following terms are presented here for subsequent reference in this test plan:

Array – An array is the series flow stream configuration of pressure vessels through a train defined by stages (4:2:1 array).

Bulk Rejection - Percent solute concentration retained by the membrane relative to the bulk stream concentration.

$$1 - \frac{C_p}{C_f}$$

where:

C_f = feedwater concentration of specific constituent (mg/L)

C_p = permeate concentration of specific constituent (mg/L)

Bulk Solution - The solution on the high-pressure side of the membrane that has a water quality between that of the influent and concentrate streams.

Cleaning Frequency - The loss or decrease of the mass transfer coefficient (MTC) for water measures membrane productivity over time of production. Membranes foul during operation. Constant production is achieved in membrane plants by increasing pressure. Cleaning is done when the pressure increases by 10 to 15 percent. Cleaning frequency (CF) and a measurement of productivity can be determined from the MTC decline.

$$CF = \frac{\Omega K_w}{\frac{dK_w}{dt}}$$

where:

  CF = cleaning frequency (days)

  Ω = acceptable rate of MTC loss

  dK_w/dt = rate of MTC decline (gsfd/psi-d)

Concentrate (Q_c, C_c) - One of the membrane output streams that has a more concentrated water quality than the feed stream.

Conventional RO/NF Process - A treatment system consisting of acid and/or scale inhibitor addition for scale control, cartridge filtration, RO/NF membrane filtration, aeration, chlorination and corrosion control.

Feed (Q_f, C_f) - Input stream to the membrane process after pretreatment.

Feedwater - Water introduced to the membrane module.

Field Testing Organization (FDO) - An organization qualified to conduct studies and testing of drinking water treatment systems in accordance with protocols and test plans. The role of the field testing organization is to complete the application on behalf of the Company; to enter into contracts with NSF, as discussed herein; and arrange for or conduct the skilled operation of equipment during the intense periods of testing during the study and the tasks required by the Protocol.

Flux (F_w) - Mass (lb/ft^2-day) or volume (gal/ft^2-day, gsfd, gfd) rate of transfer through membrane surface.

$$F_w = K_w [\Delta P - \Delta \Pi] = \frac{Q_p}{A}$$

where:

  F_w = water flux (M/L^2·t)

  K_w = global water mass transfer coefficient (t^{-1})

  ΔP = transmembranic pressure gradient (M/L^2)

  $\Delta \Pi$ = osmotic pressure gradient (M/L^2)

  Q_p = permeate flow (L^3/t)

A = membrane surface area (L^2)

Fouling - Reduction of productivity measured by a decrease in the temperature normalized water MTC.

Fouling Indices - Fouling indices are simple measurements that provide an estimate of the required pretreatment for membrane processes. Fouling indices are determined from membrane tests and are similar to mass transfer coefficients for membranes used to produce drinking water. Fouling indices can be quickly developed from simple filtration tests, are used to qualitatively estimate pretreatment requirements and possibly could be used to predict membrane fouling. The silt-density index (SDI), modified fouling index (MFI) and mini plugging factor index (MPFI) are the most common fouling indices. The SDI, MFI and the MPFI are defined using the basic resistance model, and are quantitatively related to water quality and NF membrane fouling.

Some approximations for required indices prior to conventional membrane treatment are given below (Sung et. al. 1994).

Fouling Index Approximations for NF

Fouling Index	Range
SDI	< 3
MFI	< 10 s/L^2

Silt-Density Index (SDI): The SDI is the most commonly used test to predict a water's potential to foul a membrane by colloidal particles smaller than 0.45 microns. SDI is only a guide for pretreatment and is not an indication of adequate pretreatment. The SDI is a static measurement of resistance, which is determined by samples taken at the beginning and the end of the test. The SDI test is performed by timing the anaerobic hydraulic flow through a 47 mm diameter, 0.45 micron membrane filter at a constant pressure of 30 psi. The time required for 500 mL of the feedwater to pass through the filter is measured when the test is first initiated, and is also measured at time intervals of 5, 10, and 15 minutes after the start of the test. The value of the SDI is then calculated as follows (ASTM D-4189-82).

$$SDI = \left[\frac{1 - \dfrac{t_i}{t_f}}{t_T} \right] (100\%)$$

where:

t_i = time to collect initial 500 mL sample

t_f = time to collect 500 mL sample at time t = T

t_T = total running time of the test; 5, 10, or 15 minutes.

If the index is below a value of 3 then the water should be suitable for reverse osmosis. If the SDI is below 3, the impact of colloidal fouling is minimized.

Modified Fouling Index (MFI): The MFI is determined using the same equipment and procedure used for the SDI, except that the volume is recorded every 30 seconds over a 15 minute filtration period (Schippers and Verdouw 1980). The development of the MFI is consistent with Darcy's Law in that the thickness of the cake layer formed on the membrane surface is assumed to be directly proportional to the filtrate volume. The total resistance is the sum of the filter and cake resistance. The MFI is defined graphically as the slope of an inverse flow verses cumulative volume curve as shown in the following equations:

$$\frac{dV}{dt} = \frac{\Delta P}{\mu} \frac{A}{(R_f + R_k)}$$

$$t = \frac{\mu V R_f}{\Delta PA} + \frac{\mu V^2 I}{2\Delta PA^2}$$

$$\frac{1}{Q} = (a + MFI)V$$

where:

R_f = resistance of the filter

R_k = resistance of the cake

I = measure of the fouling potential

Q = average flow (liters/second)

a = constant

Typically the cake formation, build-up and compaction or failure can be seen in three distinct regions on a MFI plot. The regions corresponding to blocking filtration and cake filtration represent productive operation, whereas compaction would be indicative of the end of a productive cycle.

Hollow-Fiber – Fine hollow fibers of membrane material are extruded in either a cellulose triacetate or a polyamide. The ends of the fibers are sealed in an epoxy bock connected with the outside of the housing. The epoxy block is cut to allow the flow from the inside of the fine fibers to the other side of the epoxy block, where it is collected. The pressurized feedwater passes across the outside of the fibers. Pure water permeates the fibers and is collected at the end of the element.

The hollow-fiber housings are capable of holding a large quantity of fibers, this allowing a single element to produce a large permeate flow rate. Hollow-fiber elements are typically used for seawater desalination, and for brackish-water applications

Influent - Input stream to the membrane array after the recycle stream has been blended with the feed stream. If there is no concentrate recycle then the feed and influent streams are identical.

Mass Transfer Coefficient (MTC) (K_w) - Mass or volume unit transfer through membrane based on driving force (gfd/psi).

$$K_w = \frac{Q_p}{A(\Delta P - \Delta\Pi)}$$

where:

K_w = global water mass transfer coefficient (t^{-1})

ΔP = transmembranic pressure gradient (M/L^2)

$\Delta\Pi$ = osmotic pressure gradient (M/L^2)

Q_p = permeate flow (L^3/t)

A = membrane surface area (L^2)

Membrane Element - A single membrane unit containing a bound group of spiral wound or hollow-fiber membranes to provide a nominal surface area for treatment.

Membrane Molecular Weight Cutoff Determination - The membrane molecular weight cutoff (MWCO) of membranes a commonly used to characterize membrane rejection capability. Membrane MWCO is typically determined by measuring the rejection of different molecular weight nonionic polymers. Solute rejection is defined as:

$$\% \text{ Solute Rejection} = \left(1 - \frac{C_p}{C_f}\right)(100\%)$$

Given the narrow molecular weight bands of polyethylene glycol (PEG) solutions, these nonionic random coil polymers can be applied to membranes for MWCO estimation. Although the percent PEG rejection varies by manufacturer, 80 to 90 percent PEG rejection has been used. Neither the percent rejection nor the material is fixed except by membrane manufacturer. The standard molecular weight solutions can be measured as TOC and correlated to PEG concentration. This correlation can then be applied for assessment of PEG rejection by the membrane and subsequent MWCO determination.

Membrane Productivity - Membrane productivity will be assessed by the rate of mass transfer coefficient (MTC_w) decline over time of operation. As flux declines, a constant product can be achieved by increasing pressure to maintain a constant flux.

Net Driving Pressure (NDP): The net driving pressure (NDP) is calculated using the influent, concentrate and permeate pressure.

$$NDP = \left[\frac{(P_f + P_c)}{2}\right] - P_p - \Delta\Pi$$

where:

NDP = net driving pressure for solvent transport across the membrane (psi, bar)

P_f = feedwater pressure to the feed side of the membrane (psi, bar)

P_c = concentrate pressure on the reject side of the membrane (psi, bar)

P_p = permeate pressure on the treated water side of the membrane (psi, bar)

$\Delta\pi$ = osmotic pressure (psi)

Osmotic Pressure Gradient ($\Delta\pi$):** The term osmotic pressure gradient refers to the difference in osmotic pressure generated across the membrane barrier as a result of different concentrations of dissolved salts. In order to determine the NDP, the osmotic pressure gradient must be estimated from the influent, concentrate and permeate TDS.

$$?? = \left(\left[\frac{(TDS_f + TDS_c)}{2} \right] - TDS_p \right) \left(\frac{1\,psi}{100\frac{mg}{L}} \right)$$

where:

TDS_f = feedwater total dissolved solids (TDS) concentration (mg/L)

TDS_c = concentrate TDS concentration (mg/L)

TDS_p = permeate TDS concentration (mg/L)

Mass Transfer Coefficient (MTC_w): The MTC_w is calculated by dividing the permeate flow by the membrane surface area.

$$F_w = \frac{Q_p}{A} = \left(MTC_w \right) NDP)$$

From this the MTC_w can be calculated. However, given the relationship between temperature and the viscosity of water, flux should be normalized to a standard temperature condition (25°C). These relationships should be provided by the membrane manufacturer and used to normalize the flux data set as shown below.

$$MTC_{w, 25°C} = \frac{F_{w, 25°C}}{NDP}$$

Temperature Adjustment for Flux Calculation: If manufacture does not specify a temperature correction equation the following equation may be used so that water production can be compared on an equivalent basis.

$$F_{w, 25°C} = F_{w, T°C} \left(1.03^{(25°C - T°C)} \right)$$

Recovery: Recovery should also be calculated using the permeate and influent flow.

$$R = \frac{Q_p}{Q_i}$$

Using the above equations the MTC_w, normalized flux and recovery for each stage and the system can be calculated for each set of operational data and plotted as a function of cumulative operating time.

Package Plant - A complete water treatment system including all components from the connection to the raw water(s) intake through discharge to the distribution system.

Permeate (Q_p, C_p) - The membrane output stream that has convected through the membrane.

$$Q_p C_p = Q_f C_f - Q_c C_c$$

Permeate - Water produced by the membrane process.

Permeate Flux - The average permeate flux is the flow of permeate divided by the surface area of the membrane. Permeate flux is calculated according to the following formula:

$$J_t = \frac{Q_p}{S}$$

where:

J_t = permeate flux at time t (gfd, L/(h·m^2))

Q_p = permeate flow (gpd, L/h)

S = membrane surface area (ft^2, m^2)

It should be noted that only gfd and L/(h·m^2) shall be considered acceptable units of flux for this testing plan.

Pressure Vessel - A single tube or housing that contains several membrane elements in series.

Product-Specific Test Plan (PSTP) - A written document of procedures for on-site/in-line testing, sample collection, preservation, and shipment and other on-site activities described in the EPA/NSF ETV Protocol(s) and Test Plan(s) that apply to a specific make and model of equipment.

Raw - Input stream to the membrane process prior to any pretreatment.

Recovery - The recovery of feedwater as permeate water is given as the ratio of permeate flow to feedwater flow:

$$\% \text{ System Recovery} = \left[\frac{Q_p}{Q_f}\right](100\%)$$

where:

Q_f = feedwater flow to the membrane (gpm, L/h)

Q_p = permeate flow (gpm, L/h)

Recycle Ratio (r) - The recycle ratio represents the ratio of the total flow of water that is used for cross-flow and the net feedwater flow to the membrane. This ratio provides an idea of the recirculation

pumping that is applied to the membrane system to reduce membrane fouling and specific flux decline.

$$\text{Recycle Ratio} = \left[\frac{Q_r}{Q_f}\right]$$

where:

Q_f = feedwater flow to the membrane (gpm, L/h)

Q_r = recycle hydraulic flow in the membrane element (gpm, L/h)

Rejection (mass) – The mass of a specific solute entering a membrane system that does not pass through the membrane.

$$\left(1 - \frac{Q_p C_p}{Q_f C_f}\right)$$

Scaling Control - Controlling precipitation or scaling within the membrane element requires identification of a limiting salt, acid addition for prevention of $CaCO_3$ and/or addition of a scale inhibitor. The limiting salt determines the amount of scale inhibitor or acid addition. A diffusion controlled membrane process will concentrate salts on the feed side of the membrane. If excessive water is passed through the membrane, this concentration process will continue until a salt precipitates and scaling occurs. Scaling will reduce membrane productivity and consequently recovery is limited by the allowable recovery just before the limiting salt precipitates. The limiting salt can be determined from the solubility products of potential limiting salts and the actual feed stream water quality. Ionic strength must also be considered in these calculations as the natural concentration of the feed stream during the membrane process increases the ionic strength, allowable solubility and recovery.

Calcium carbonate scaling is commonly controlled by sulfuric acid addition however sulfate salts are often the limiting salts. Commercially available scale inhibitors can be used to control scaling by complexing the metal ions in the feed stream and preventing precipitation. Equilibrium constants for these scale inhibitors are not available which prevents direct calculation. However some manufacturers provide computer programs for estimating the required scale inhibitor dose for a given recovery, water quality and membrane. The following are general equations for the solubility products and ionic strength approximations.

Solubility Product: Calculation of the solubility product of selected sparingly soluble salts will be important exercise for the test plan in order to determine if there are operational limitations caused by the accumulation of limiting salts at the membrane surface. Text book equilibrium values of the solubility product should be compared with solubility values calculated from the results of experimental Verification Testing, as determined from use of the following equation:

$$K_{sp} = ?_A^x \left[A^{y-}\right]^x ?_B^y \left[B^{x+}\right]^y$$

where:

K_{sp} = solubility product for the limiting salt being considered

γ = free ion activity coefficient for the ion considered (i.e., A or B)

[A] = molal solution concentration of the anion A for sparingly soluble salt A_xB_y

[B] = solution concentration of the anion B

x, y = stiochiometric coefficients for the precipitation reaction of A and B

Mean Activity Coefficient: The mean activity coefficients for each of the salt constituents may be estimated for the concentrated solutions as a function of the ionic strength:

$$\log ?_{A,B} = -0.509 Z_A Z_B \sqrt{\mu}$$

where:

γ = free ion activity coefficient for the ion considered (i.e., A or B)

Z_A = ion charge of anion A

Z_B = ion charge of cation B

μ = ionic strength

Ionic Strength: A simple approximation of the ionic strength can calculated based upon the concentration of the total dissolved solids in the feedwater stream:

$$\mu = (2.5 \cdot 10^{-5})(TDS)$$

where:

μ = ionic strength

TDS = total dissolved solids concentration (mg/L)

Solute - The dissolved constituent (mg/L) in a solution or process stream.

Solute Rejection - Solute rejection is controlled by a number of operational variables that must be reported at the time of water sample collection. Bulk rejection of a targeted inorganic chemical contaminant may be calculated by the following equation.

$$\% \text{ Solute Rejection} = \left[\frac{C_f - C_p}{C_f} \right] (100\%)$$

where:

C_f = feedwater concentration of specific constituent (mg/L)

C_p = permeate concentration of specific constituent (mg/L)

Solvent - A substance, usually a liquid such as water, capable of dissolving other substances.

Solvent and Solute Mass Balance - Calculation of solvent mass balance is performed to verify the reliability of flow measurements through the membrane. Calculation of solute mass balance across the

membrane system is performed to estimate the concentration of limiting salts at the membrane surface.

$$Q_f = Q_p + Q_c$$

$$Q_f C_f = Q_p C_p + Q_c C_c$$

where:

Q_f = feedwater flow to the membrane (gpm, L/h)

Q_p = permeate flow (gpm, L/h)

Q_c = concentrate flow (gpm, L/h)

C_f = feedwater concentration of specific constituent (mg/L)

C_p = permeate concentration of specific constituent (mg/L)

C_f = concentrate concentration of specific constituent (mg/L)

Specific Flux - At the conclusion of each chemical cleaning event and upon return to membrane operation, the initial condition of transmembrane pressure shall be recorded and the specific flux calculated. The efficiency of chemical cleaning shall be evaluated by the recovery of specific flux after chemical cleaning as noted below, with comparison drawn from the cleaning efficiency achieved during previous cleaning evaluations. Comparison between chemical cleanings shall allow an evaluation of irreversible fouling. Two primary indicators of cleaning efficiency and restoration of membrane productivity will be examined in this task.

Percent Recovery of Specific Flux: The immediate recovery of membrane productivity, as expressed by the ratio between the final specific flux (F_{sf}) and the initial specific flux (F_{si}) measured for the subsequent run.

$$\% \text{ Recovery of Specific Flux} = \left[1 - \frac{F_{sf}}{F_{si}}\right](100\%)$$

where:

F_{sf} = Specific flux (gfd/psi, L/(h-m^2)/bar) at end of run (final)

F_{si} = Specific flux (gfd/psi, L/(h-m^2)/bar) at beginning of run (initial).

Percent Loss of Original Specific Flux: The loss of original specific flux capabilities, as expressed by the ratio between the initial specific flux for any given filtration run (F_{si}) divided by the original specific flux (F_{sio}), as measured at the initiation of the first filtration run in a series.

$$\% \text{ Loss of Original Specific Flux} = \left[1 - \frac{F_{si}}{F_{sio}}\right](100\%)$$

Spiral-Wound - Spiral-wound membrane elements are constructed of flat sheet membranes folded and glued on three edges to create several membrane envelopes. The open edge of the each envelope is glued to a central collection pipe with perforations to allow water from inside the envelope to pass into the pipe. The envelopes are spun around the central collection pipe. Layered inside each envelope is a

thin layer of fabric that prevents the envelope from sealing itself off when the outside of the envelope is exposed to high pressure. The fabric allows the passage of permeate water to the center collection tube.

The feed water enters the end of the spiral-wound element and moves across the surface of the rolled-up membrane envelopes. Spacers between the envelopes promote turbulence so that pure water permeates the envelopes, any salts left behind will diffuse back into the bulk solution. Inside the envelope the pressure is near atmospheric, whereas the pressure on the feedwater side can be as high as 1,000 psi. The pressure differential drives the pure water into the membrane envelope. In the envelope the permeate passes through fabric material and finds its way into the central collection pipe. The water in the collection pipe travels to the end where it either enters the collection tube of another element, or is transferred to the permeate port of the end cap of the housing.

Stage – A stage is the configuration of an array.

Train – A train is a parallel flow stream through the membrane system. For instance a 5 MGD membrane system may be comprised of five 1 MGD trains.

Verification Statement - A written document that summarizes a final report reviewed and approved by NSF on behalf of the USEPA or directly by the USEPA.

Water System - The water system that operates using water treatment equipment to provide potable water to its customers.

6.0   OVERVIEW OF TASKS

This Plan is applicable to the testing of water treatment equipment utilizing membrane processes. Testing of membrane processes will be conducted by a NSF-qualified Field Testing Organization that is selected by the Manufacturer. Water quality analyses will be performed by a state-certified or third party-, or EPA-qualified analytical laboratory. This Plan provides objectives, work plans, schedules, and evaluation criteria for the required tasks associated with the equipment testing procedure.

The following is a brief overview of the tasks that shall be included as components of the Verification Testing Program and PSTP for removal of SOCs.

- **Task 1: Characterization of Raw Water** – Obtain chemical, biological and physical characterization of the raw water. Provide a brief description of the watershed that provides the raw water to the water treatment plant.

- **Task 2: Membrane Productivity** - Demonstrate operational conditions for the membrane equipment; permeate water recovery achieved by the membrane equipment; and rate of flux decline observed over an extended membrane process operation.

- **Task 3: Finished Water Quality** – Evaluate the water quality produced by membrane processes as it relates to raw water quality and operational conditions.

- **Task 4: Cleaning Efficiency** – Evaluate the effectiveness of chemical cleaning to the membrane system and confirm that the Manufacturer-recommended cleaning practices are sufficient to restore membrane productivity.

- **Task 5: Operations and Maintenance (O&M)** - Develop an O&M manual for each system submitted. The O&M manual shall characterize membrane process design, outline a membrane process cleaning procedure or procedures, and provide a concentrate disposal plan.

- **Task 6: Data Collection and Management** – Establish an effective field protocol for data management between the Field Testing Organization and NSF.

- **Task 7: Quality Assurance / Quality Control (QA/QC)** – Develop a QA/QC protocol for Verification Testing. This is an important item that will assist in obtaining an accurate measurement of operational and water quality parameters during membrane equipment Verification Testing.

- **Task 8: Cost Evaluation** - Develop capital and O&M costs for the submitted NF membrane technology and equipment.

7.0   TESTING PERIODS

The required tasks of the ETV Testing Plan (Tasks 1 through 9) are designed to be completed over a 60-day period, not including mobilization, shakedown and start-up. The schedule for equipment monitoring during the 60-day testing period shall be stipulated by the FTO in the PSTP, and shall meet or exceed the minimum monitoring requirements of this testing plan. The FTO shall ensure in the PSTP that sufficient water quality data and operational data will be collected to allow estimation of statistical uncertainty in the Verification Testing data, as described in the "EPA/NSF ETV Protocol For Equipment Verification Testing For The Removal Of Synthetic Organic Chemical Contaminants: Requirements For All Studies". The FTO shall therefore ensure that sufficient water quality and operational data is collected during Verification Testing for the statistical analysis described herein.

For membrane process treatment equipment, factors that can influence treatment performance include:

- Feedwaters with high seasonal concentrations of inorganic constituents and TDS. These conditions may increase finished water concentrations of inorganic chemical contaminants and may promote precipitation of inorganic materials in the membrane;

- Feedwaters with variable pH; increases in feedwater pH may increase the tendency for precipitation of sparingly soluble salts in the membrane module and may require variable strategies in anti-scalant addition and pH adjustment;

- Cold water, encountered in winter or at high altitude locations;

- High concentrations of natural organic matter (measured as TOC), which may be higher in some waters during different seasonal periods;

- High turbidity, often occurring in spring, as a result of high runoff resulting from heavy rains or snowmelt.

It is highly unlikely that all of the above problems would occur in a water source during a single 60-day period during the Verification Testing Program. Membrane testing conducted beyond the required 60-day testing may be used for fine-tuning of membrane performance or for evaluation of additional operational conditions. During the testing periods, evaluation of cleaning efficiency and finished water quality can be performed concurrent with membrane operation testing procedures.

During the time intervals between equipment verification runs, the water treatment equipment may be used for production of potable water. If the equipment is being used for the production of potable water, routine operation for water production is expected. The operating and water quality data collected and furnished to the local regulatory agency should also be supplied to the NSF-qualified FTO.

8.0   TASK 1: CHARACTERIZATION OF RAW WATER

8.1   Introduction

A characterization of raw water quality is needed to determine if the concentrations of SOCs or other raw water contaminants are appropriate for the use of NF membrane processes. The feedwater quality can influence the performance of the equipment as well as the usefulness of testing results to readers of the verification report.

8.2   Objectives

One reason for performing a raw water characterization is to obtain at least one-year of historical raw water quality data from the raw water source. The objective is to:

- demonstrate seasonal effects on the concentration of SOCs; and

- develop maximum and minimum concentrations for the contaminant.

If historical raw water quality is not available, a raw water quality analysis of the proposed feedwater shall be performed prior to equipment Verification Testing.

8.3   Work Plan

The characterization of raw water quality is best accomplished through the performance of laboratory testing and the review of historical records. Sources for historical records may include municipalities, laboratories, USGS (United States Geographical Survey), USEPA, and local regulatory agencies. If historical records are not available preliminary raw water quality testing shall be performed prior to equipment Verification Testing. The specific parameters of characterization will depend on the NF membrane process that is being tested. The following characteristics should be reviewed and documented:

• Specific SOC	• True Color	• Nitrate
• Temperature	• Chloride	• Sodium

- pH
- TDS/Conductivity
- Total Hardness
- Calcium Hardness
- Total Organic Carbon
- Total Alkalinity
- Turbidity

- Fluoride
- Sulfate
- Ammonia
- Iron
- Manganese
- Silica
- Barium

- Potassium
- Strontium
- Phosphate
- SDI
- MFI

Data collected should reflect seasonal variations in the above data if applicable. This will determine variations in water quality parameters that will occur during Verification Testing. The data that is collected will be shared with NSF so that the FTO can determine the significance of the data for use in developing a test plan. If the raw water source is not characterized, the testing program may fail, or results of a testing program may not be considered acceptable. A description of the raw water source should also be included with the feedwater characterization. The description may include items such as:

- size of watershed;
- topography;
- land use;
- nature of the water source; and
- potential sources of pollution.

8.4   Schedule

The schedule for compilation of adequate water quality data will be determined by the availability and accessibility of historical data. The historical water quality data can be used to determine the suitability of NF membrane processes for the treatment for the raw source water. If raw water quality data is not available, a preliminary raw water quality testing should be performed prior to the Verification Testing of the NF membrane equipment.

8.5   Evaluation Criteria

The feedwater quality shall be evaluated in the context of the Manufacturer's Statement of Performance Objectives for the removal of SOCs. The feedwater should challenge the capabilities of the chosen equipment, but should not be beyond the range of water quality suitable for treatment by the chosen equipment. For NF membrane processes, a complete scan of water quality parameters may be required in order to determine limiting salt concentrations, necessary for establishing pretreatment criteria.

9.0   TASK 2: MEMBRANE PRODUCTIVITY

9.1   Introduction

The removal of SOCs from drinking water supplies is accomplished by NF membrane filtration. The effectiveness of NF membrane processes for SOC removal will be evaluated in this task. Membrane mass transfer coefficient, flux and recovery will be evaluated in this task. After installation of a NF membrane, compaction and ripening of the membrane will cause a characteristic flux decline with time until the membrane stabilizes. After this initial flux decline, the rate of flux decline will be used to demonstrate membrane performance for the specific operating conditions to be verified. The operational conditions to be verified shall be specified by the Manufacturer in terms of a temperature-corrected flux (normalized flux) value (e.g., gsfd at 77°F or L/(m^{2}hr) at 25°C) before the initiation of the Program.

Flux decline is a function of water quality, membrane type, configuration and operational conditions. In establishing the range of operation for the membrane performance evaluations, limiting salt information should be used to define the run scenarios. The run conditions should include operating scenarios, which approach and exceed these projected limits. Subsequent water quality analysis will allow for assessment of the degree of saturation of the sparingly soluble salts in the final concentrate. The degree of saturation of the salts should then be compared to resulting membrane productivity decline. Table 9.1 presents an example of membrane pretreatment data required to provide baseline conditions and assist in evaluating membrane productivity.

Some Manufacturers may wish to employ the NF membrane process with a pretreatment process in order to reduce flux decline and improve removal of SOCs. Any pretreatment included in the membrane treatment system that is designed for removal of SOCs shall be considered an integral part of the membrane treatment system and shall not be tested independently. In such cases, the system shall be considered as a single unit and the pretreatment process shall not be separated for optional evaluation purposes.

9.2   Experimental Objectives

The objectives of this task are to demonstrate:

- Operational conditions for the membrane equipment;

- Permeate water recovery achieved by the membrane equipment; and

- Rate of flux decline observed over extended membrane process operation.

Raw water quality shall be measured prior to system operation and then monitored every two weeks during the 60-day testing period at a minimum. It should be noted that the objective of this task is not process optimization, but rather verification of membrane operation at the operating conditions specified by the Manufacturer, as it pertains to permeate flux and transmembrane pressure, and SOC removal.

9.3   Work Plan

Determination of ideal membrane operating conditions for a particular water may require as long as one year of operation. For this task the Manufacturer shall specify the operating conditions to be evaluated in this Verification Testing Plan and shall supply written procedures on the operation and maintenance of the membrane treatment system. The Manufacturer shall evaluate flux decline. The Manufacturer shall also determine the limiting salt and identify possible foulants and scalants, and use this for performance evaluation for their particular membrane equipment. The set of operating conditions shall be maintained for the 60-day testing period (24-hour continuous operation). The Manufacturer shall specify the primary permeate flux at which the equipment is to be verified. Additional operating conditions can be verified in separate 60-day testing periods.

After set-up and "shakedown" of membrane equipment, membrane operation should be established at the flux condition to be verified. Testing of additional operational conditions could be performed by extending the number of 60-day testing periods beyond the initial 60-day period required by the Verification Testing Program at the discretion of the Manufacturer and their designated FTO.

Additional 60-day periods of testing may also be included in the Verification Testing Plan in order to demonstrate membrane performance under different feedwater quality conditions. For membrane processes, extremes of feedwater quality (e.g., low temperature, high TOC concentration, variable SOC concentrations, high SDI and high turbidity) are the conditions under which membranes are most prone to fouling and subsequent failure. At a minimum the performance of the NF membrane equipment relative to SOC removal shall be documented during those periods of variable feedwater conditions. The Manufacturer shall perform testing with as many different water quality conditions as desired for verification status. Testing under each different water quality condition shall be performed during an additional 60-day testing period, as required above for each additional set of operating conditions.

The testing runs conducted under this task shall be performed in conjunction with finished water quality and if applicable, cleaning efficiency. With the exception of additional testing periods conducted at the Manufacturer's discretion, no additional membrane test runs are required for performance of cleaning efficiency and finished water quality. A continuous yearlong evaluation, although not required, may be of benefit to the Manufacturer for verification of long term trends.

9.3.1   Operational Data Collection

Measurement of membrane feedwater flow and permeate flow (recycle flow where applicable) and system pressures shall be collected at a minimum of 3 eight-hour shifts per day. Table 9.2 is an example of a daily operational data sheet for a two-stage membrane system. This table is presented for informational purposes only. Figure 9.1 presents the sample locations for the daily operational data sheet. The actual forms will be submitted as part of the test plan and may be site-specific. Measurement of feedwater temperature to the membranes shall be made along with these three daily measurements in order to provide data for normalizing flux with respect to temperature

Water quality should be analyzed from the same locations identified for TDS in Table 9.2 prior to start-up and then twice a month for the parameters identified in Table 9.3, except for each SOC, which will be monitored weekly. Power costs for operation of the membrane equipment (pumping requirements, chemical usage, etc.) shall also be closely monitored and recorded by FTO during the 60-day testing period. Power usage shall be estimated by inclusion of the following details regarding equipment operation requirements: pumping requirements; size of pumps; name-plate; voltage; current draw; power factor; peak usage; etc. In addition, measurement of power consumption and chemical consumption shall be quantified by recording such items as day tank concentration, daily volume consumption and unit cost of chemicals.

9.3.2   Feedwater Quality Limitations

The characteristics of feedwaters used during the 60-day testing period (and any additional 60-day testing periods) shall be explicitly stated in reporting the membrane flux and recovery data for each period. Accurate reporting of such feedwater characteristics are critical for the Verification Testing Program, as these parameters can substantially influence the range of achievable membrane performance and treated water quality under variable raw water quality conditions. The following criteria and trends should also be presented in the Verification Testing Program:

- Evaluation criteria and minimum reporting requirements.

- Plot graph of SOC removed over time for each 30-day period of operation.

- Plot graph of NDP over time for each 30-day period of operation.

- Plot graph of TDS over time for each 30-day period of operation.

- Plot graph of $F_{w25°C}$ over time for each 30-day period of operation.

- Plot graph of MTC_w over time for each 30-day period of operation.

- Plot graph of recovery over time for each 30-day period of operation.

TABLE 9.1: NF Membrane Pretreatment Data

Foulants and Fouling Indices of the Feedwater Prior to Pretreatment	
Alkalinity (mg/L of $CaCO_3$)	
Ca Hardness (mg/L of $CaCO_3$)	
LSI	
Dissolved iron (mg/L)	
Total iron (mg/L)	
Dissolved aluminum (mg/L)	
Total aluminum (mg/L)	
Fluoride (mg/L)	
Phosphate (mg/L)	
Sulfate (mg/L)	
Calcium (mg/L)	
Barium (mg/L)	
Strontium (mg/L)	
Reactive silica (mg/L as SiO_2)	
Turbidity (NTU)	
SDI	
Pretreatment Processes Used Prior to Nanofiltration or Reverse Osmosis	
Pre-filter listed pore size (μm)	
Type of acid used	
Acid concentration (units)	
mL of acid per L of feed	
Type of scale inhibitor used	
Scale inhibitor concentration (units)	
mL of scale inhibitor per L of feed	
Type of coagulant used	
Coagulant dose (mg/L)	
Type of polymer used during coagulation.	
Polymer dose (mg/L)	

TABLE 9.2: Daily Operations Log Sheet for a Two-Stage Membrane System

Date:

Parameter	Shift 1	Shift 2	Shift 3
Time			
Initial			
Feed			
Q_{feed} (gpm)			
TDS_{feed} (before pretreatment) (mg/L)			
TDS_{feed} (after pretreatment) (mg/L)			
P_{feed} (psi)			
pH_{feed} (before pretreatment)			
pH_{feed} (after pretreatment)			
T_{feed} (°C)			
Permeate - Stage 1			
Q_{p-S1} (gpm)			
TDS_{p-S1} (mg/L)			
P_{p-S1} (psi)			
Concentrate - Stage 1			
Q_{c-S1} (gpm)			
TDS_{c-S1} (mg/L)			
P_{c-S1} (psi)			
T_{c-S1} (°C)			
Permeate - Stage 2			
Q_{p-S2} (gpm)			
TDS_{p-S2} (mg/L)			
P_{p-S2} (psi)			
Concentrate - Stage 2			
Q_{c-S2} (gpm)			
TDS_{c-S2} (mg/L)			
P_{c-S2} (psi)			
Finished			
Q_{fin} (gpm)			
TDS_{fin} (mg/L)			
Recovery (Q_{fin}/Q_{feed}) (%)			
Recycle			
$Q_{recycle}$ (gpm)			

FIGURE 9.1: Sample Locations for a Two-Stage Membrane Process
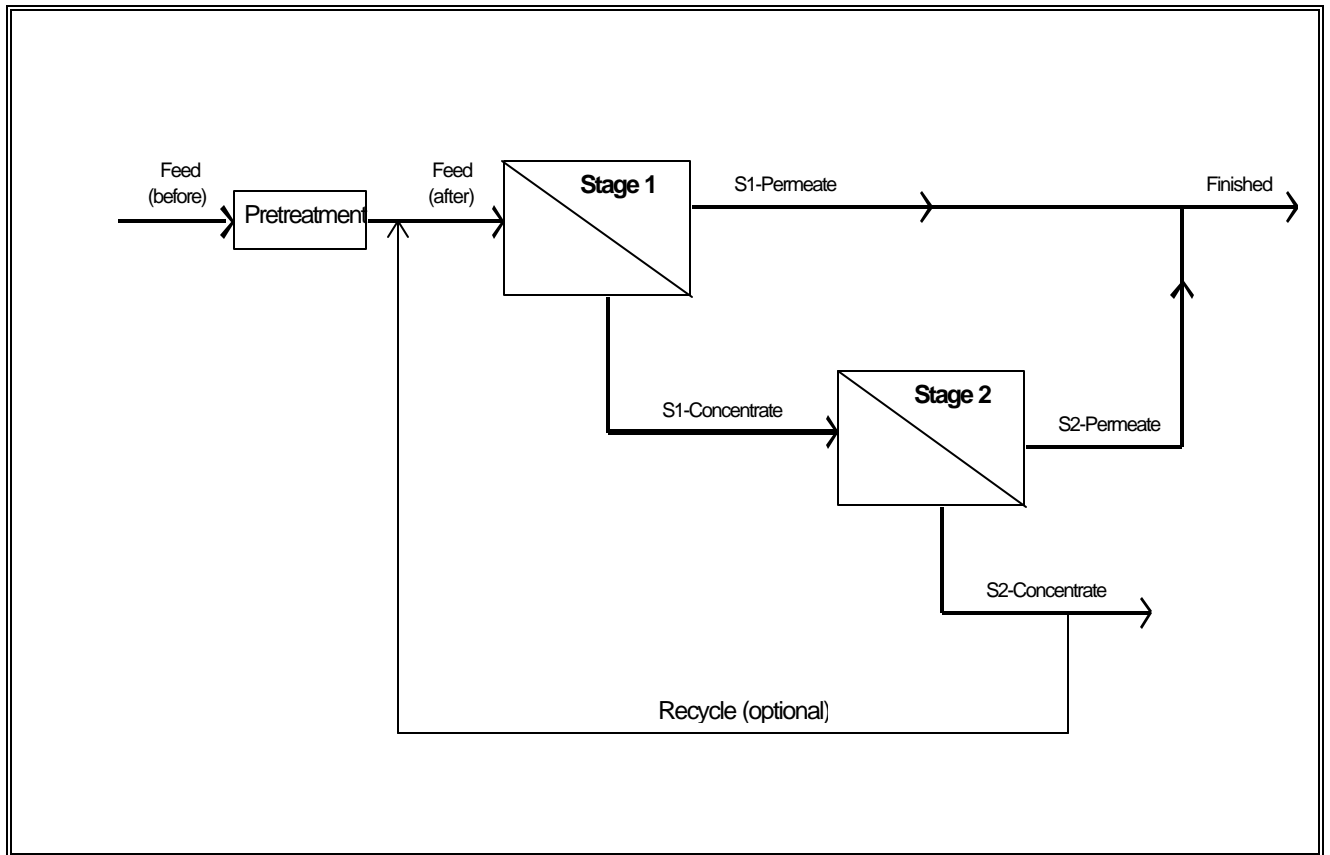
TABLE 9.3: Operating and Water Quality Data Requirements for Membrane Processes

Parameter	Frequency and Importance for Sampling
Feedwater Flow	3 * Daily (1)
Permeate Water Flow	3 * Daily (1)
Concentrate Water Flow	3 * Daily (1)
Feedwater Pressure	3 * Daily (1)
Permeate Water Pressure	3 * Daily (1)
Concentrate Water Pressure	3 * Daily (1)
List Each Chemical Used, And Dosage	Daily Data Or Monthly Average (1)
Hours Operated Per Day	Daily (1)
Hours Operator Present Per Day	Monthly Average (2)
Power Costs (Kwh/Million Gallons)	Monthly (2)
Independent check on rates of flow	Weekly (1)
Independent check on pressure gages	Weekly (2)
Verification of chemical dosages	Monthly (1)
SOCs	1, Weekly
Temperature	3 * Daily (1)
pH	3 * Daily (1)
TDS/Conductivity	3 * Daily (1)
Turbidity	Every two weeks (1)
True Color	Every two weeks (1)
Total Organic Carbon	Every two weeks (1)
UV Absorbance (254 nm)	Every two weeks (1)
Total Alkalinity	Every two weeks (1)
Total Hardness	Every two weeks (1)
Calcium Hardness	Every two weeks (1)
Sodium	Every two weeks (1)
Chloride	Every two weeks (1)
Iron	Every two weeks (1)
Manganese	Every two weeks (1)
Sulfate	Every two weeks (1)
Fluoride	Every two weeks (1)
Silica	Every two weeks (1)
Ammonia	Every two weeks (1)
Potassium	Every two weeks (1)
Strontium	Every two weeks (1)
Barium	Every two weeks (1)
Nitrate	Every two weeks (1)
TTHM	Every two weeks (2)
THAA	Every two weeks (2)
TOX	Every two weeks (2)

1 = Required   2 = Desired But Not Necessary

10.0   TASK 3: FINISHED WATER QUALITY

10.1   Introduction

Water quality data shall be collected for the raw and finished water as provided previously in Table 9.3. (Note, in some instances sampling concentrate water quality may be required because detection limits may be too low for a specified parameter.) At a minimum, the required sampling shall be one sampling at start-up and two sampling events per month while raw water samples are collected. Water quality goals and target removal goals for the membrane equipment should be proved and reported in the PSTP.

10.2   Objectives

The objective of this task is to verify the Manufacturer's performance objectives. Table 9.3 presented a list of the minimum number of water quality parameters to be monitored during equipment Verification Testing has been provided in this document. The actual water quality parameters selected for testing and monitoring shall be stipulated in the PSTP.

10.3   Work Plan

The PSTP shall identify the treated water quality objectives to be achieved in the Statement of Performance Objectives of the equipment to be evaluated in the Verification Testing Program. The PSTP shall also identify in the Statement of Performance Objectives the specific SOCs that shall be monitored during equipment testing. The Statement of Performance Objectives prepared by the PSTP shall indicate the range of water qualities and operating conditions under which the equipment can be challenged while successfully treating the contaminated water supply.

It should be noted that many of the drinking water treatment systems participating in the SOC Removal Verification Testing Program will be capable of achieving multiple water treatment objectives. Although the SOC Verification Testing Plan is oriented towards removal of SOCs, the Manufacturer may want to look at the treatment system's removal capabilities for additional water quality parameters.

Many of the water quality parameters described in this task shall be measured on-site by the NSF-qualified FTO. A state-certified or third-party- or EPA-qualified analytical laboratory shall perform analysis of the remaining water quality parameters. Representative methods to be used for measurement of water quality parameters in the field and lab are identified in Table 10.1. The analytical methods utilized in this study for on-site monitoring of raw and finished water qualities are described in Quality Assurance/ Quality Control (QA/QC). Where appropriate, the Standard Methods reference numbers and EPA method numbers for water quality parameters are provided for both the field and laboratory analytical procedures.

TABLE 10.1: Water Quality Analytical Methods

Parameter	Standard Method [1]	EPA Method [2]
Phase II SOCs		
2,4,5-TP (Silvex)	6640 B	515.1; 515.2; 555
2,4-D (Formula 40, Weedar 64)	6640 B	515.1; 515.2; 555
Acrylamide		
Alachlor (Lasso)		505; 507; 525.2; 508.1
Aldicarb	6610 B	531.1
Aldicarb sulfone	6610 B	531.1
Aldicarb sulfoxide	6610 B	531.1
Atrazine		505; 507; 508.1; 525.2
Carbofuran (Furdan 4F)	6610 B	531.1
Chlordane	6410 B; 6630 B,C	505; 508; 508.1; 525.2
Dibromochloropropane (DBCP, Nemafume))	6210 C,D; 6230 D; 6231 B	504.1; 551
Ethylene dibromide (EDB, Bromofume)		504.1; 551
Heptachlor (H-34, Heptox)	6410 B; 6630 B, C	505; 508; 508.1; 525.2
Heptachlor epoxide	6410 B; 6630 B, C	505; 508; 508.1; 525.2
Lindane	6630 B	505; 508; 508.1; 525.2
Methoxychlor (DMDT, Marlate)	6630 B	505; 508; 508.1; 525.2
Pentachlorophenol	6410 B; 6420 B; 6640 B	515.1; 515.2; 525.2; 555
Polychlorinated biphenyls (PCBs, Aroclor)	6410 B; 6630 C	505; 508; 508A
Toxaphene	6410 B; 6630 B, C	505; 508; 525.2
Phase V SOCs		
Adipate (diethylhexyl)		506; 525.2
Dalapon	6640 B	515.1; 552.1
Dichloromethane		
Dinoseb	6640 B	515.1; 515.2; 555
Dioxin		1613
Diquat		549.1

TABLE 10.1: Water Quality Analytical Methods (Cont.)

Parameter	Standard Method [1]	EPA Method [2]
Endothall		548.1
Endrin	6410 B; 6630 B, C	505; 508; 508.1; 525.2
Glyphosate	6651 B	547
Hexachlorobenzene	6040 B; 6410 B	505; 508; 508.1; 525.2
Hexachlorocyclopentadiene	6410 B	505; 508; 508.1; 525.2
Oxamyl (Vydate)	6610 B	531.1
Phathalate		506; 525.2
Phenanthrene (PAH)	6040 B; 6410 B; 6440 B	525.1; 550; 550.1
Picloram	6640 B	515.1; 515.2; 555
Simazine		505; 507; 508.1; 525.2
Trichlorobenzene (1,2,4-)	6040 B; 6210 D; 6220 C; 6230 D; 6410 B	
Trichloroethane (1,1,2,-)	6040 B; 6210 B, C, D; 6220 C; 6230 B, C, D	
Physical Parameters		
Temperature	2550 B	
pH	4500-H^+ B	150.1; 150.2
Conductivity	2510 B	120.1
Total Dissolved Solids	2540 C	
Total Suspended Solids	2540 D	
Turbidity	2130 B; Method 2	180.1
Dissolved Oxygen	4500-O B	
Organics		
True color	2120 B	
Total Organic Carbon	5310 C	
UV$_{254}$ absorbance	5910 B	
Total Trihalomethanes (TTHMs)	6232 B	524.3
Total Haloacetic Acids (THAAs)	6251 B	552.1

TABLE 10.1: Water Quality Analytical Methods (Cont.)

Parameter	Standard Method [1]	EPA Method [2]
Total Organic Halogens (TOX)	5320 B	
Inorganics		
Total Alkalinity	2320 B	
Total Hardness	2340 C	
Calcium Hardness	$3500\text{-}Ca^{+2}$ D	
Sodium	3111 B	200.7
Chloride	4110 B; $4500\text{-}Cl^-$ D	300.0
Iron	3111 D; 3113 B; 3120 B	200.7; 200.8; 200.9
Manganese	3111 D; 3113 B; 3120 B	200.7; 200.8; 200.9
Sulfate	4110 B; $4500\text{-}SO_4^{-2}$ C, D, F	300.0; 375.2
Fluoride	4110 B; $4500\text{-}F^-$ B, C, D, E	300.0
Silica (total and dissolved)	3120 B; 4500-Si D, E, F	200.7
Ammonia, NH_3	$4500\text{-}NH_3$ B, C, D	350.3
Potassium	3111 B; 3500-K C, D, E	200.7
Strontium	3111 B; 3500-Sr C,D,E	200.7
Barium	3111 D; 3113 B; 3120 B	200.7; 200.8
Nitrate	4110 B; $4500\text{-}NO_3^-$ D, F	300.0; 353.2

1) AWWA, Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1999.

2) EPA, Methods and Guidance for Analysis of Water, EPA 821-C-97-001, April 1997.

For the water quality parameters requiring analysis at an off-site laboratory, water samples shall be collected in appropriate containers (containing necessary preservatives as applicable) prepared by the state-certified or third-party- or EPA-qualified laboratory. These samples shall be preserved, stored, shipped and analyzed in accordance with appropriate procedures and holding times, including chain-of custody requirements, as specified by the analytical lab.

10.4 Analytical Schedule

10.4.1 Removal of SOCs

During the steady-state operation of each membrane testing period, SOC mass balances shall be performed on the membrane feed, permeate and concentrate water in order to determine the SOC removal capabilities of the membrane system.

10.4.2 Feed and Permeate Water Characterization

At the beginning of each membrane testing period, the raw water, permeate and in some cases concentrate water shall be characterized at a single set of operating conditions by measurement of the water quality parameters identified in Table 9.3.

10.4.3 Water Quality Sample Collection

Water quality data shall be collected at regular intervals during each period of membrane equipment testing. The minimum monitoring frequency for the required water quality parameters is once at start-up and weekly for SOCs and every two weeks for the remaining water quality parameters. The water quality sampling program may be expanded to include a greater number of water quality parameters and to require a greater frequency of parameter sampling. Analyses for organic water quality parameters shall be performed on water sample aliquots that were obtained simultaneously from the same sampling location, in order to provide the maximum degree of comparability between water quality analytes.

No monitoring of microbial populations shall be required in this Equipment Verification Testing Plan. However, the Manufacturer may include optional monitoring of indigenous microbial populations to demonstrate removal capabilities.

10.4.4 Raw Water Quality Limitations

The characteristics of feedwaters encountered during each 60-day testing period shall be explicitly stated. Accurate reporting of such raw water characteristics such as those identified in Table 9.3 are critical for the Verification Testing Program, as these parameters can substantially influence membrane performance.

10.5 Evaluation Criteria and Minimum Reporting Requirements

- Removal or reduction of SOCs.
- Water quality and removal goals specified by the Manufacturer.

11.0 TASK 4: CLEANING EFFICIENCY

11.1 Introduction

There are certain types of foulant scales that pose an immediate threat to the operational integrity of a membrane process. Examples of scale include calcium carbonate scale and silica or sulfate scale.

Should scaling or fouling occur during or following the test runs, the membrane equipment shall require chemical cleaning to restore membrane productivity. The number of cleaning efficiency evaluations shall be determined by the fouling frequency of the membrane during each specified test period. In the case where the membrane does not fully reach the operational criteria for fouling as specified by the Manufacturer, chemical cleaning shall be performed after the 30 days of operation, with a record made of the operational conditions before and after cleaning.

The membrane treatment process will be optimized for sustained production under high product water recovery and solvent flux. Productivity goals shall be stated in the PSTP in terms of productivity decline and/or operational time.

Either normalized flux decline or solvent mass transfer (MTCw) reduction will determine productivity decline. The use of the normalized MTC_w for productivity decline would eliminate the need for constant system pressure for productivity decline determination. Chemical cleaning of the membranes will be performed as necessary for the removal of reversible foulants per Manufacturer specifications. These cleaning events are to be documented and used as an aid in determining the nature of the fouling or scaling conditions experienced by the system. The cleaning solutions should also be analyzed to determine which constituents may have adsorbed or precipitated onto the membrane surface during cleaning. This may also prove useful for establishing the mechanism of removal for some SOCs.

11.2   Experimental Objectives

The objective of this task is to evaluate the effectiveness of chemical cleaning to the membrane systems. The intent of this task is to confirm that standard Manufacturer-recommended cleaning practices are sufficient to restore membrane productivity for the systems under consideration. Cleaning chemicals and cleaning routines shall be based on the Manufacturer recommendations. This task is considered a "proof of concept" effort, not an optimization effort.

11.3   Work Plan

The membrane systems may become fouled during the membrane test runs. These fouled membranes shall be utilized for the cleaning assessments herein. Each system shall be chemically cleaned using the recommended cleaning solutions and procedures specified by the Manufacturer, which will vary according to identified foulants or scale. After each chemical cleaning of the membranes, the system shall be restarted and then returned to the flux condition being tested.

The Manufacturer shall specify in detail the procedure(s) for chemical cleaning of the membranes. At a minimum, the following shall be specified:

- cleaning chemicals

- quantities and costs of cleaning chemicals

- hydraulic conditions of cleaning

- duration of each cleaning step

- chemical cleaning solution

- quantity and characteristics of residual waste volume to be disposed

11.4   Recommended Disposal Procedures

Methods of disposal of membrane concentrate include, but are limited to the following:

- Public works wastewater plant;

- Deep well injection; or

- Discharge to a surface water with accordance to the National Pollutant Discharge Elimination System (NPDES) Program.

However SOCs are considered a potentially hazardous waste and the effluent must be monitored since it is concentrated. The concentrate disposal may require other State and/or Federal permits. In addition, a description of all cleaning equipment and its operation shall be described and included in the O&M manual.

11.5 Analytical Schedule

11.5.1 Sampling

The pH of each cleaning solution shall be determined and recorded during various periods of the chemical cleaning procedure. Conductivity and turbidity should also be used to monitor flush periods.

11.5.2 Operational Data Collection

Flow and pressure data shall be collected before system shutdown due to membrane fouling; flow and pressure data shall also be collected after chemical cleaning.

12.0 TASK 5: OPERATIONS AND MAINTENANCE MANUAL

An operations and maintenance (O&M) manual for the membrane system to be tested for SOC removal shall be included in the Verification Testing evaluation.

12.1 Objectives

The objective of this task is to provide an O&M manual that will assist in operating, troubleshooting and maintaining the membrane system performance. The O&M manual shall:

- characterize the membrane process design;

- outline a membrane process cleaning procedure or procedures; and

- provide a concentrate disposal plan.

The concentrate disposal plan must be approved by the State in question for permanent installation. A fully developed concentrate disposal plan would be required because of the SOCs that have been concentrated in the waste stream. Criteria for evaluation of the equipment's O&M Manual shall be compiled and then evaluated and commented upon during verification by the FTO. An example is provided in Table 12.1.

Each specific test plan will include a list of criteria for evaluating O&M information. This shall be compiled and submitted for evaluation by EPA, NSF and technical peer reviewers. An example is provided in Table 12.2. The purpose of this O&M information is to allow utilities to effectively choose

a technology that their operators are capable of operating, and provide information on how many hours the operators can be expected to work on the system. Information about obtaining replacement parts and ease of operation of the system would also be valuable.

TABLE 12.1: OPERATIONS & MAINTENANCE MANUAL CRITERIA -
NF Membrane Process Systems

MAINTENANCE:

The manufacturer should provide readily understood information on the recommended or required maintenance schedule for each piece of operating equipment such as:

- flow meters
- pressure gauges
- pumps
- motors
- valves
- chemical feeders
- mixers

The manufacturer should provide readily understood information on the recommended or required maintenance for non-mechanical or non-electrical equipment such as:

- membranes
- pressure vessels
- piping

OPERATION:

The manufacturer should provide readily understood recommendation for procedures related to proper operation of the equipment. Among the operating aspects that should be discussed are:

Chemical feeders:

- calibration check
- settings and adjustments - how they should be made
- dilution of chemicals and scale inhibitors - proper procedures

Monitoring and observing operation:

- mass balance calculations
- recovery calculation

OPERATION (continued):

Monitoring and observing operation (continued):

- pressure losses

The manufacturer should provide a troubleshooting guide; a simple check-list of what to do for a variety of problems including:

- flux decline;

- no raw water (feedwater) flow to plant;

- when the water flow rate through the equipment can not be measured;

- no chemical feed;

- automatic operation (if provided) not functioning;

- no electric power; and

- sand or silt entrainment (such as plugging of prefilters).

The following are recommendations regarding operability aspects of membrane processes. These aspects of plant operation should be included if possible in reviews of historical data, and should be included to the extent practical in reports of equipment testing when the testing is done under the ETV Program. During Verification Testing and during compilation of historical equipment operating data, attention shall be given to equipment operability aspects.

- are chemical feed pumps calibrated?

- are flow meters present and have they been calibrated?

- are pressure gauges calibrated?

- are pH meters calibrated?

- are TDS or conductivity meters calibrated?

- can cleaning be done automatically?

- can membrane seals be easily replaced?

- does remote notification occur (alarm) when pressure increases > 15% or flow drops > 15%?

The reports on Verification Testing should address the above questions in the written reports. The issues of operability should be dealt with in the portion of the reports that are written in response to Operating Conditions and Treatment Equipment Performance, in the Membrane Process Test Plan.

TABLE 12.2: Requirements for Maintenance and Operability of
NF Membrane Process Systems

MAINTENANCE INFORMATION		
Equipment	**Maintenance Frequency**	**Replacement Frequency**
Membranes		
Pumps		
Valves		
Motors		
Mixers		
chemical mixers		
water meters		
pressure gauges		
cartridge filters		
Seals		
Piping		

OPERABILITY INFORMATION: (rank from 1 (easy) to 3 (difficult), or N/A)	
Operation Aspect	**Response**
Chemical feed pumps calibration	
Flow meters calibration	
Pressure gauges calibration	
pH meters calibration	
TDS or conductivity meters calibration	
Cleaning	
Replacement of membrane seals	
Measurement and control of flux decline	

Notes:

12.2 O&M Work Plan

Descriptions for pretreatment, membrane process, and post-treatment to characterize the membrane system unit process design shall be developed. Membrane processes shall include the design criteria and membrane element characteristics. Examples of information required relative to the membrane design criteria and element characteristics are presented in Tables 12.3 and 12.4, respectively.

TABLE 12.3: NF Membrane Plant Design Criteria Reporting Items

Parameter	Value
Number of trains	
Number of stages	
Stage configuration	
Number of pressure vessels in stage 1	
Number of pressure vessels in stage 2	
Number of elements per pressure vessel	
Recovery per stage (%)	
Recovery for system (%)	
Design flow (gpm)	
Design temperature (°C)	
Design flux (gsfd)	
Surface area per element (ft^2)	
MTC$_W$ (gsfd/psi)	
Maximum flow rate to an element (gpm)	
Minimum flow rate to an element (gpm)	
Pressure loss per element (psi)	
Pressure loss in stage entrance and exit (psi)	
Feed stream TDS (mg/L)	
SOC rejection (%) *	

* Specify SOC name(s), chemical and trade name(s).

TABLE 12.4: NF Membrane Element Characteristics

Membrane manufacturer			
Membrane module model number			
Size of element used in study (e.g. 4" x 40")			
Active membrane area of element used in study			
Active membrane area of an equivalent 8" x 40" element			
Purchase price for an equivalent 8" x 40" element ($)			
Molecular weight cutoff (Daltons)			
Membrane material / construction			
Membrane hydrophobicity (circle one)	Hydrophilic		Hydrophobic
Membrane charge (circle one)	Negative	Neutral	Positive
Design pressure (psi)			
Design flux at the design pressure (gfd)			
Variability of design flux (%)			
MTC_W (gfd/psi)			
Standard testing recovery (%)			
Standard testing pH			
Standard testing temperature (°C)			
Design cross-flow velocity (fps)			
Maximum flow rate to the element (gpm)			
Minimum flow rate to the element (gpm)			
Required feed flow to permeate flow rate ratio			
Maximum element recovery (%)			
Rejection of reference solute and conditions of test (e.g. solute type and concentration)			
Variability of rejection of reference solute (%)			
Spacer thickness (ft)			
Scroll width (ft)			
Acceptable range of operating pressures			
Acceptable range of operating pH values			
Typical pressure drop across a single element			
Maximum permissible SDI			
Maximum permissible turbidity (NTU)			
Chlorine/oxidant tolerance			
Suggested cleaning procedures			

Note: Some of this information may not be available, but this table should be filled out as completely as possible for each membrane tested.

The membrane treatment process will be optimized for sustained production under high product water recovery and solvent flux. Productivity goals shall be stated in the PSTP.

Productivity decline will be indicated and signaled by either normalized flux decline or normalized solvent mass transfer (MTC_w) reduction. Normalized means that the flux has been adjusted for temperature and pressure. The use of the normalized MTC_w for productivity decline would eliminate the need for constant system pressure for productivity decline determination.

Chemical cleaning of the membranes will be performed as necessary for the removal of reversible foulants per manufacturer specifications. These cleaning events are to be documented and used as an aid in determining the nature of the fouling or scaling conditions experienced by the system. The cleaning solutions could also be analyzed for determining which constituents may have adsorbed or precipitated onto the membrane surface. Analysis of cleaning solutions can be coupled with mass balances on the same solutes monitored during operation to determine solute accrual in membrane elements. This may prove useful for establishing the mechanism of removal for some SOCs. A cleaning efficiency evaluation is described in Section 11.0.

The potential handling hazards associated with SOCs warrant the development of a viable membrane concentrate disposal method and safety program. Provisions for concentrate disposal from the system must be developed as part of the work plan.

13.0   TASK 6: DATA COLLECTION AND MANAGEMENT

13.1   Introduction

The data management system used in the Verification Testing Program shall involve the use of computer spreadsheets, in addition to manual recording of operational parameters for the membrane processes on a daily basis.

13.2   Objectives

The objective of this task is to establish a viable structure for the recording and transmission of field testing data such that the FTO provides sufficient and reliable operational data for verification purposes. Chain-of-Custody protocols will be developed and adhered to.

13.3   Work Plan

13.3.1 Data Handling Work Plan

The following protocol has been developed for data handling and data verification by the FTO. In addition to daily operational data sheets, a Supervisory Control and Data Acquisition (SCADA) system could be used for automatic entry of testing data into computer databases. Specific parcels of the computer database for operational and water quality parameters should then be downloaded by manual importation into electronic spreadsheets. These specific database parcels shall be identified based upon discrete time spans and monitoring parameters.

In spreadsheet form, the data shall be manipulated into a convenient framework to allow analysis of membrane process operation. At a minimum, backup of the computer databases to diskette should be performed on a monthly basis.

Field testing operators shall record data and calculations by hand in laboratory notebooks for three eight-hour shifts per day. (Daily measurements shall be recorded on specially prepared data log sheets as appropriate. Table 9.2 presents an example of a daily log sheet). The laboratory notebook shall provide copies of each page. The original notebooks shall be stored on-site; the copied sheets shall be forwarded to the project engineer of the FTO at least once per week during the 60-day testing period. This protocol will not only ease referencing the original data, but offer protection of the original record of results. Operating logs shall include

- descriptions of the and test runs;

- names of visitors; and

- descriptions of any problems.

Such descriptions shall be provided in addition to experimental calculations and other items.

13.3.2 Data Management

The database for the project shall be set up in the form of custom designed spreadsheets. The spreadsheets shall be capable of storing and manipulating each monitored water quality and operational parameter from each task, each sampling location, and each sampling time. All data from the field laboratory analysis notebooks and data log sheets shall be entered into the appropriate spreadsheet. Data entry shall be conducted on-site by the designated field testing operators. All recorded calculations shall also be checked at this time.

Following data entry, the spreadsheet shall be printed and the printout shall be checked against the handwritten data sheet. Any corrections shall be noted on the hardcopies and corrected on the screen, and then the corrected recorded calculations will also be checked and confirmed. The field testing operator or engineer performing the data entry or verification step shall initial each step of the verification process.

Each experiment (e.g. each membrane process test run) shall be assigned a run number, which will then be tied to the data from that experiment through each step of data entry and analysis. As samples are collected and sent to state-certified or third-party- or EPA-qualified laboratories, the data shall be tracked by use of the same system of run numbers. Data from the outside laboratories shall be received and reviewed by the FTO. These data shall be entered into the data spreadsheets, corrected, and verified in the same manner as the field data.

13.3.3 Statistical Analysis

For the analytical data obtained during Verification Testing, 95 percent confidence intervals shall be calculated by the FTO for selected water quality parameters. The specific Plans shall specify which water quality parameters shall be subjected to the requirements of confidence interval

calculation. As the name implies, a confidence interval describes a population range in which any individual population measurement may exist with a specified percent confidence. When presenting the data, maximum, minimum, average and standard deviation should be included.

Calculation of confidence intervals shall not be required for equipment performance obtained during the equipment Verification Testing Program. In order to provide sufficient analytical data for statistical analysis, the FTO shall collect three discrete water samples at one set of operational conditions for each of the specified water quality parameters during a designated testing period.

14.0 TASK 7: QUALITY ASSURANCE/QUALITY CONTROL

14.1 Introduction

Quality assurance and quality control (QAQC) of the operation of the membrane process equipment and the measured water quality parameters shall be maintained during the Equipment Verification Testing Program.

14.2 Experimental Objectives

The objective of this task is to maintain strict QA/QC methods and procedures during the Equipment Verification Testing Program. Maintenance of strict QA/QC procedures is important, in that if a question arises when analyzing or interpreting data collected for a given experiment, it will be possible to verify exact conditions at the time of testing.

14.3 QA/QC Work Plan

Equipment flow rates should be calibrated and verified and verification recorded on a routine basis. A routine daily walk through during testing shall be established to check that each piece of equipment or instrumentation is operating properly. Particular care shall be taken to verify that chemicals are being fed at the defined flow rate, and into a flow stream that is operating at the expected flow rate. This will provide correct chemical concentrations in the flow stream. In-line monitoring equipment such as flow meters, etc. shall be checked as indicated below to verify that the readout matches with the actual measurement (i.e. flow rate) and that the signal being recorded is correct. The items listed are in addition to any specified checks outlined in the analytical methods.

When collecting water quantity data, all system flow meters will be calibrated using the classic bucket and stopwatch method where appropriate. Hydraulic data collection will include the measurement of the finished water flow rate by the "bucket test" method. This would consist of filling a calibrated vessel to a known volume and measuring the time to fill the vessel with a stopwatch. This will allow for a direct check of the system flow measuring devices.

Mass balances will be performed on the system for water quality parameters measured in the feed, permeate and concentrate streams. This will enable an additional quality control check on the accuracy and reliability of the analyzed data. SOCs in particular will be analyzed in each process stream.

However, the difficulty in measuring some low level SOCs may limit the mass balance to be calculated based on feed and concentrate. Mass balances may provide insight into the mechanism for rejection of individual SOCs. For example, mass balances showing incomplete recovery for a particular SOC may suggest possible adsorption onto the membrane surface.

14.3.1 Daily QA/QC Verifications

- Chemical feed pump flow rates (check and verify components)

- On-line conductivity meters (check and verify components)

- On-line pH meters (standardize and recalibrate)

- On-line turbidimeter flowrates (verified volumetrically over a specific period of time)

- On-line turbidimeter readings checked against a properly calibrated bench model

14.3.2 QA/QC Verifications Performed Every Two Weeks

- Chemical feed pump flow rates (verify volumetrically over a specific time period)

- On-line conductivity meters (recalibrate)

- On-line flow meters/rotameters (clean equipment to remove any debris or biological buildup and verify flow volumetrically to avoid erroneous readings)

14.3.3 QA/QC Verifications Performed Every Testing Period

- Differential pressure transmitters (verify gauge readings and electrical signal using a pressure meter)

- Tubing (verify good condition of all tubing and connections, replace if necessary)

14.4   On-Site Analytical Methods

Use of either bench-top field analytical equipment will be acceptable for the Verification Testing; however, on-line equipment is recommended for ease of operation. Use of on-line equipment is also preferable because it reduces the introduction of error and the variability of analytical results generated by inconsistent sampling techniques. However, standard and uniform calibration and standardization techniques that are approved should be employed. Table 10.1 lists Standard Methods and EPA methods of analysis.

14.4.1 pH

Analysis for pH shall be performed according to *Standard Method* 4500-H$^+$. A three-point calibration of the pH meter used in this study will be performed once per day when the instrument is in use. Certified pH buffers in the expected range shall be used. The pH probe shall be stored in the appropriate solution defined in the instrument manual. Transport of carbon dioxide across the air-water interface can confound pH measurement in poorly buffered waters. Therefore, measure the pH under a continuous stream of sample by placing the tip of the probe in the sample container allowing the sample to overflow the container while the probe reaches

equilibrium. If this is a problem, measurement of pH in a confined vessel is recommended to minimize the effects of carbon dioxide loss with the atmosphere.

14.4.2 Turbidity

Turbidity analyses shall be performed according to Standard Method 2130 or EPA Method 180.1 with either a bench-top or in-line turbidimeter. Grab samples shall be analyzed using a bench-top turbidimeter; readings from this instrument will serve as reference measurements throughout the study. The bench-top turbidimeter shall be calibrated within the expected range of sample measurements at the beginning of Verification Testing and on a weekly basis using primary turbidity standards of 0.1, 0.5 and 3.0 NTU. Secondary turbidity standards shall be used on a daily basis to verify calibration of the turbidimeter and to recalibrate when more than one turbidity range is used.

During each verification testing period, the bench-top and in-line turbidimeters will be left on continuously. Once each turbidity measurement is complete, the unit will be switched back to its lowest setting. All glassware used for turbidity measurements will be cleaned and handled using lint-free tissues to prevent scratching. Sample vials will be stored inverted to prevent deposits from forming on the bottom surface of the cell.

The Field Testing Organization shall be required to document any problems experienced with the monitoring turbidity instruments, and shall also be required to document any subsequent modifications or enhancements made to monitoring instruments.

14.4.2.1   Bench-Top Turbidimeters. The method for collecting grab samples will consist of running a slow, steady stream from the sample tap, triple-rinsing a dedicated sample beaker in this stream, allowing the sample to flow down the side of the beaker to minimize bubble entrainment, double-rinsing the sample vial with the sample, carefully pouring from the beaker down the side of the sample vial, wiping the sample vial clean, inserting the sample vial into the turbidimeter, and recording the measured turbidity.

When cold water samples cause the vial to fog and prevent accurate readings, allow the vial to warm up by submersing partially into a warm water bath for approximately 30 seconds.

14.4.2.2   In-Line Turbidimeters. In-line turbidimeters may be used during verification testing and must be calibrated as specified in the manufacturer's operation and maintenance manual. It will be necessary to periodically verify the in-line readings using a bench-top turbidimeter; although the mechanism of analysis is not identical between the two instruments the readings should be comparable. Should these readings suggest inaccurate readings then all in-line turbidimeters should be recalibrated. In addition to calibration, periodic cleaning of the lens should be conducted using lint-free paper, to prevent any particle or microbiological build-up that could produce inaccurate readings. Periodic verification of the sample flow should also be performed using a volumetric measurement. Instrument bulbs should be replaced on an as-

needed basis. It should also be verified that the LED readout matches the data recorded on the data acquisition system, if the latter is employed.

14.4.3 Temperature

Readings for temperature shall be conducted in accordance with *Standard Method* 2550. Raw water temperatures shall be obtained at least once daily. The thermometer shall have a scale marked for every 0.1°C, as a minimum, and should be calibrated weekly against a precision thermometer certified by the National Institute of Standards and Technology (NIST). (A thermometer having a range of -1°C to +51°C, subdivided in 0.1° increments, would be appropriate for this work.)

14.4.4 Dissolved Oxygen

Analysis for dissolved oxygen shall be performed on raw ground water samples according to *Standard Method 4500-O* using an iodometric method or the membrane electrode method. The techniques described for sample collection must be followed very carefully to avoid causing changes in dissolved oxygen during the sampling event. Sampling for dissolved oxygen does not need to be coordinated with sampling for other water quality parameters, so dissolved oxygen samples should be taken at times when immediate analysis is going to be possible. This will eliminate problems that may be associated with holding samples for a period of time before the determination is made.

If the sampling probe is not mounted such that the probe is continuously exposed to the process stream, then care must be taken when measuring the dissolved oxygen concentration. For best results, collect the dissolved oxygen sample with minimal agitation and measure the dissolved oxygen concentration immediately. If possible, measure the dissolved oxygen under a continuous stream of sample by placing the tip of the probe in the sample container, allowing the sample to overflow the container while the probe reaches equilibrium (usually less than 5 minutes).

14.5   Chemical Samples Shipped Off-Site for Analysis

The analytical methods that shall be used during testing for chemical samples that are shipped off-site for analyses are described in the section below.

14.5.1 Organic Samples

Samples for analysis of total organic carbon (TOC), UV_{254} absorbance, and dissolved organic carbon (DOC) shall be collected in glass bottles supplied by the state-certified or third party- or EPA-accredited laboratory and shipped at 4 °C to the analytical laboratory within 24 hours of sampling. These samples shall be preserved in accordance with Standard Method 5010 B. Storage time before analysis shall be minimized, according to Standard Methods.

14.5.2 Inorganic Samples

Inorganic chemical samples shall be collected and preserved in accordance with Standard Methods or EPA-approved methods. The samples shall be refrigerated at approximately 2 to 8°C. Samples shall be processed for analysis by a state-certified or third party- or EPA-accredited laboratory within 24 hours of collection. The laboratory shall keep the samples at approximately 2 to 8°C until initiation of analysis.

14.5.3 SOC Analysis

Analysis of SOCs requires a trained analyst using sophisticated instrumentation. Only state-certified or third party- or EPA-accredited laboratories shall analyze SOC samples that are collected during Initial Operations and Verification Testing. As stated in the " EPA/NSF ETV Protocol For Equipment Verification Testing For The Removal Of Synthetic Organic Chemical Contaminants: Requirements For All Studies," approved methods for some SOCs may not be available, and for these SOCs, a proposed, peer-reviewed method may be used.

There are many approved methods for analyzing Phase II and Phase V SOCs. Depending on the laboratory, gas chromatography (GC) or high performance liquid chromatography (HPLC) methods can be used to analyze SOCs. For both methods, the equipment is highly specialized and proper operation of these instruments requires a skilled laboratory technician.

Mass spectrometry is not required for all SOCs, however it is recommended for SOC identification. Retention times relative to the internal standard can also be used to identify SOCs. Either peak height or peak area can be used to determine the SOC concentrations.

SOCs shall be analyzed with an internal standard similar in analytical behavior and not affected by the matrix for QA/QC. An appropriate surrogate standard shall also be used during SOC analysis. Data pertaining to the internal and surrogate standards shall be reported with the SOC concentrations of the samples being analyzed. A method blank shall also be prepared and analyzed by the state-certified or third party- or EPA-accredited laboratory to verify minimal contamination in the laboratory.

At least three standards shall be used to develop the standard curve for SOC quantification and these three standards shall be extracted and analyzed (by GC or HPLC) on the same day as the samples.

During each Verification Test period, one treated water sample shall be analyzed by scanning for the presence and concentration of potential by-products of SOC disinfection by oxidation. Gas chromatography followed by mass spectrometry can be used to identify many of the organic by-products formed during oxidation disinfection. The spectra obtained by this analysis can be matched to a compound library in a computer database to identify the various by-products. This analysis shall be performed by a state-certified or third party- or EPA-

accredited analytical laboratory. The scan should be targeted toward the SOC of interest, and the potential by-products associated with oxidation of that SOC.

Spiked samples shall be analyzed once, at the beginning of each Verification Test Run. The laboratory shall spike a feed water sample with a known quantity of the SOC(s) of interest and analyze this spiked sample. SOC analysis of the spiked sample will indicate if there are any interferences present in the feed water. The broad scan can be a performance-based scan (i.e., the scan is not used for compliance, and therefore undergoes less rigorous QA/QC and is less expensive than a compliance based scan analysis.)

14.6   Trip Control

For tests utilizing spiked SOCs, a replicate or subsample of the spiking solution shall accompany the actual spiking solution from the analytical laboratory. This replicate sample shall undergo all of the processes used on the actual solution including dose preparation, shipping, preparation for spiking, and return to the laboratory for analysis. The trip control samples should show minimal loss of SOC(s). Significant decreases in the SOC concentration of the trip control sample indicates that some step in handling the solution contributed to the reduction in the SOC concentration. The seeding tests must be repeated when significant loss of SOCs in the trip control sample is observed.

15.0   TASK 8: COST EVALUATION

This Plan includes the assessment of costs of verification with the benefits of testing NF membrane processes over a wide range of operating conditions. Therefore, this Plan requires that one set of operating conditions be tested over a 60-day testing period. The equipment Verification Tests will provide information relative to systems, which provide desired results and the cost, associated with the systems. Design parameters are summarized in Table 15.1. These parameters will be used with the equipment Verification Test costs to prepare cost comparisons for Verification Testing purposes.

Capital and operation and maintenance (O & M) costs realized in the equipment Verification Test may be utilized for calculating cost estimates. O & M costs for each system will be determined during the equipment Verification Tests. The equipment costs will vary based on the cost of membrane equipment. The O & M costs that will be recorded and compared during the Verification Test include:

- Labor;
- Electricity;
- Chemical Dosage, and
- Equipment Replacement Frequency.

The capital and O & M costs will vary based on geographic location.

Table 15.1: Design Parameters for Cost Analysis

Design Parameter	Specific Utility Values
Raw water feed rate(mgd)	
Total required plant production rate(mgd)	
By-pass flow rate (mgd)	
Membrane flow rate (mgd)	
High/Low plant feedwater temperature (°C)	
Average Flux (gsfd/psi)	
Maximum Flux (gsfd/psi)	
Average cleaning frequency (days)	
High/Low feed TDS (mg/L)	

O & M costs should be provided for each membrane process that is tested. In order to receive the full benefit of the equipment Verification Test Programs, these costs should be considered along with quality of system operations. Other cost considerations may be added to the cost tables presented in this section as is needed prior to the start-up of the Verification Tests. A summary of O & M costs are outlined in Table 15.2.

Table 15.2: Operations and Maintenance Cost

Cost Parameter	Specific Values	
Labor rate + fringe ($/personnel-hour)		
Labor overhead factor (% of labor)		
Number of O&M personnel hours per week		
Electric rate ($/kWh)		
Membrane replacement frequency (%/year)		
Chemical Dosage (per week)		
O&M cost ($/Kgal)		
	Dose	Bulk Chemical Cost
Chlorine (Disinfectant)		
Sulfuric acid (Pretreatment)		
Alum (Pretreatment)		
Hydrochloric acid (Pretreatment)		
Scale inhibitor [2](Pretreatment)		
Caustic (Post-treatment)		
Sodium hydroxide (Membrane cleaning)		
Phosphoric acid (Membrane cleaning)		

[1]Information for cleaning chemicals and pretreatment chemicals (such as alum) should also be provided in this table. For cleaning agents, the concentration of the cleaning solution used to clean the membranes should be reported as the chemical dosed.

[2]Report the product name and manufacturer of the specific scale inhibitor used.

16.0   SUGGESTED READING

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APPENDIX A - SOC HEALTH EFFECTS INFORMATION

TABLE A.1: Regulated SOCs under Phase II of the SDWA

PARAMETER	MCLG (mg/L)	MCL (mg/L)	Sources of Drinking Water Contamination	Potential Health Effects
2,4,5-TP (Silvex)	0.05	0.05	Herbicide on crops, right-of-ways, golf courses; canceled in 1982	Liver and kidney damage
2,4-D (Formula 40, Weedar 64)	0.07	0.07	Runoff from herbicide on wheat, corn, range lands, lawns	Liver and kidney damage
Acrylamide	Zero	TT	Polymers used in sewage and wastewater treatment	Cancer, nervous system effects
Alachlor (Lasso)	Zero	0.002	Runoff from herbicide on corn, soybeans, other crops	Cancer
Aldicarb	0.007	0.007	Insecticide on cotton, potatoes, other crops; widely restricted	Nervous system effects
Aldicarb sulfone	0.007	0.007	Biodegradation of Aldicarb	Nervous system effects
Aldicarb sulfoxide	0.007	0.007	Biodegradation of Aldicarb	Nervous system effects
Atrazine	0.003	0.003	Runoff from use as herbicide on corn and non-crop land	Mammary gland tumors
Carbofuran (Furdan 4F)	0.04	0.04	Soil fumigant on corn and cotton; restricted in some areas	Nervous, reproductivity effects
Chlordane	Zero	0.002	Leaching from soil treatment for termites	Cancer
Dibromochloropropane (DBCP, Nemafume))	Zero	0.0002	Soil fumigant on soybeans, cotton, pineapple, orchards	Cancer
Ethyl benzene	0.7	0.7	Gasoline, insecticides, chemical manufacturing wastes	Liver, kidney, nervous system effects
Ethylene dibromide (EDB, Bromofume)	Zero	0.00005	Leaded gas additives, leaching of soil fumigant	Cancer
Heptachlor (H-34, Heptox)	Zero	0.0004	Leaching of insecticide for termites, very few crops	Cancer
Heptachlor epoxide	Zero	0.0002	Biodegradation of heptachlor	Cancer
Lindane	0.0002	0.0002	Insecticides for cattle, lumber, gardens; restricted in 1983	Liver, kidney, nervous system, immune system and circulatory system effects
Methoxychlor (DMDT, Marlate)	0.04	0.04	Insecticides for fruits, vegetables, alfalfa, livestock, pets	Growth, liver, kidney, and nervous system effects
Pentachlorophenol	Zero	0.001	Wood preservatives, herbicides, cooling tower wastes	Cancer, liver and kidney effects
Polychlorinated biphenyls (PCBs, Aroclor)	Zero	0.0005	Coolant oils from electrical transformers, plasticizers	Cancer
Toxaphene	Zero	0.003	Insecticide on cattle , cotton soybeans; canceled in 1982	Cancer

TABLE A.2: Regulated SOCs under Phase V of the SDWA

PARAMETER	MCLG (mg/L)	MCL (mg/L)	Sources of Drinking Water Contamination	Potential Health Effects
Adipate (diethylhexyl)	0.4	0.4	Synthetic rubber, food packaging, cosmetics	Decreased body weight
Dalapon	0.2	0.2	Herbicides on orchards, beans, coffee, lawns, roads, railways	Liver, kidney effects
Dinoseb	0.007	0.007	Runoff of herbicide from crop and non-crop allocations	Thyroid, reproductive organ damage
Dioxin	Zero	$3 * 10^{-8}$	Chemical production by-product, impurity in herbicides	Cancer
Diquat	0.02	0.02	Runoff of herbicides on land and aquatic weeds	Liver, kidney, eye effects
Endothall	0.1	0.1	Herbicide on crops and land and aquatic weeds; rapidly degraded	Liver, kidney, gastrointestinal effects
Endrin	0.002	0.002	Pesticides on insects, rodents, birds; restricted since 1980	Liver, kidney, heart damage
Glyphosate	0.7	0.7	Herbicide on grasses, weeds, brush	Liver, kidney damage
Hexachlorobenzene	Zero	0.001	Pesticide production waste by-product	Cancer
Hexachlorocyclopentadiene	0.05	0.05	Pesticide production intermediate	Kidney, stomach damage
Oxamyl (Vydate)	0.2	0.2	Insecticide on apples, potatoes, tomatoes	Kidney damage
Phathalate	Zero	0.006	PVC and other plastics	Cancer
Pheneanthrene (PAH)	Zero	0.0002	Coal tar coatings, burning organic matter, volcanoes, fossil fuels	Cancer
Picloram	0.5	0.5	Herbicide on broadleaf and woody plants	Kidney, liver damage
Simazine	0.004	0.004	herbicide on grass sod, some crops, aquatic algae	Cancer

APPENDIX B – PROPOSED SOCS FOR REGULATION

TABLE B.1: Proposed SOCs for Regulation

Parameters	Regulatory Status.	MCLG (mg/L)	MCL (mg/L)	Status HA	RID (mg/kg/day)	DWEL (mg/L)
Acetochlor	---	---	---	---	---	---
Acifluorfen	Tentative	zero	---	Final	0.013	0.4
Acrylonitrile	Tentative	zero	---	Draft	---	---
Aldrin	---	---	---	Draft	0.00003	0.001
Bromobenzene	Listed	---	---	Draft	---	---
Bromomethane	Tentative	---	---	Final	0.001	0.05
Cyanazine	Tentative	0.001	---	Draft	0.002	0.07
Diazinon	---	---	---	Final	0.00009	0.003
Dicamba	Listed	---	---	Final	0.03	1
Dichloroethane (1,1)	---	---	---	---	---	---
Dichloropropane (1,3-)	Listed	---	---	Draft	---	---
Dichloropropane (2,2-)	Listed	---	---	Draft	---	---
Dichloropropene (1,1-)	Listed	---	---	Draft	---	---
Dichloropropene (1,3-)	Tentative	zero	---	Final	0.0003	0.01
Dieldrin	---	---	---	Final	0.00005	0.002
Dinitrophenol (2,4)	---	---	---	---	---	---
Dinitrotoluene (2,4-)	Listed	---	---	Final	0.002	0.1
Dinitrotoluene (2,6-)	Listed	---	---	Final	0.001	0.04
Diphenylhydrazine (1,2)	---	---	---	---	---	---
Disulfoton	---	---	---	Final	0.00004	0.001
Diuron	---	---	---	Final	0.002	0.07
Fonofos	---	---	---	Final	0.002	0.07
Hexachlorobutadiene	Tentative	0.001	---	Final	0.002	0.07
Isopropyltoluene (p-)	---	---	---	---	---	---
Linuron	---	---	---	---	---	---
Methomyl	Listed	---	---	Final	0.025	0.9
Methyl Bromide	---	---	---	---	---	---
Methyl-Phenol (2-)	---	---	---	---	---	---
Methyl tert butyl ether (MTBE)	Listed	---	---	Draft	0.03	1
Metolachlor	Listed	---	---	Final	0.1	3.5
Metribuzin	Listed	---	---	Final	0.013	0.5
Molinate	---	---	---	---	---	---
Naphthalene	---	---	---	Final	0.004	0.1

TABLE B.1: Proposed SOCs for Regulation (Cont.)

Parameters	Regulatory Status.	MCLG (mg/L)	MCL (mg/L)	Status HA	RID (mg/kg/day)	DWEL (mg/L)
Nitrobenzene	---	---	---	---	---	---
Organotins	---	---	---	---	---	---
Perchlorate	---	---	---	---	---	---
Prometon	Listed	---	---	Final	0.015	0.5
RDX	---	---	---	Final	0.003	0.1
Terbacil	---	---	---	Final	0.013	0.4
Terbufos	---	---	---	Final	0.00013	0.005
Tetrachoroethane (1,1,2,2-)	Listed	---	---	Draft	---	---
Triazine	---	---	---	---	---	---
Trichlorophenol	Listed	---	---	Draft	---	---
Trichloropropane (1,2,3-)	Listed	---	---	Final	0.006	0.2
Trifluralin	Listed	---	---	Final	0.0075	0.3
Trimethylbenzene (1,2,4-)	---	---	---	Draft	---	---

Sources:

1.   US EPA Office of Water, "Drinking Water Regulations and Health Advisories", EPA-822-B-96-002, October 1996.

2.   Federal Register, Volume 62, Number 193, October 6, 1997.

CHAPTER 3

EPA/NSF ETV
EQUIPMENT VERIFICATION TESTING PLAN FOR SOC OXIDATION BY OZONE
AND ADVANCED OXIDATION PROCESSES

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1.0 APPLICATION OF THIS VERIFICATION TESTING PLAN

This document is the ETV Testing Plan for evaluation of water treatment equipment utilizing ozone for oxidation of man-made or synthetic organic chemicals (SOCs). This Testing Plan is to be used as a guide in the development of the Product-Specific Test Plan (PSTP) for testing ozone equipment, within the structure provided by the "EPA/NSF ETV Protocol For Equipment Verification Testing For The Removal Of Synthetic Organic Chemical Contaminants: Requirements For All Studies." This ETV plan is applicable only to treatment systems that rely on ozone to oxidize SOCs in water. Systems using ozone oxidation for reasons other than SOC oxidation (i.e., taste and odor control, disinfection) are not required to conduct the experiments outlined in this ETV plan. Systems may incorporate unique strategies for enhancing the effect of ozone on SOC concentrations, such as the use of ozone/advanced oxidation processes (ozone/AOPs) combining ozone with ultraviolet (UV) light or hydrogen peroxide. All ozone technologies, including ozone/AOPs, may be tested under this plan.

In order to participate in the equipment verification process for SOC oxidation by ozone or ozone/AOPs, the equipment Manufacturer and the designated Field Testing Organization shall use the procedures and methods described in this test plan, and in the "EPA/NSF ETV Protocol For Equipment Verification Testing For The Removal Of Synthetic Organic Chemical Contaminants: Requirements For All Studies" as guidelines for development of the PSTP.

This ETV test plan is applicable to the testing of water treatment equipment utilizing ozone or ozone/AOPs for SOC oxidation in drinking water. This plan is applicable to both surface water and groundwater supplies.

2.0 INTRODUCTION

The organic compounds present in source waters are characterized as either: 1) naturally occurring (e.g., humic acid, fulvic acid); or 2) synthetic (e.g., pesticides, hydrocarbons, phenols, dyes, amines, solvents, and plasticizers, etc.).

Ozone is a powerful oxidant that is applied during water treatment for microbial inactivation as well as oxidation of organic compounds, metals, and taste and odor causing compounds. The use of ozone in potable water treatment in the United States has increased substantially in the last 20 years, due to its superior inactivation of microorganisms (i.e., cysts) relative to chlorine, chloramine, and chlorine dioxide and its ability to reduce the concentrations of certain organics in drinking water.

Ozone is applied to drinking water as a gas, which is generated on-site. The ozone gas is transferred into a dissolved state by either bubbling or injecting ozone gas into the process stream. Ozone can be applied to untreated (raw) or treated (e.g., coagulated/settled or filtered) water. In this ETV plan, the oxidation of SOCs by ozone or ozone/AOPs will be evaluated. Ozone/AOPs, which typically combine ozonation with UV light or hydrogen peroxide, convert dissolved ozone to hydroxyl radicals. In many instances, ozone/AOPs can be more effective than ozone used by itself for oxidation of SOCs.

3.0 GENERAL APPROACH

Testing of equipment covered by this ETV plan will be performed by an NSF-qualified Field Testing Organization (FTO) that is selected by the equipment Manufacturer. Water quality analytical work to be carried out as part of this ETV plan will be contracted with a state-certified or third party- or EPA-accredited qualified analytical laboratory.

4.0 OVERVIEW OF TASKS

4.1 Initial Operations: Overview

The purpose of these tasks is to provide preliminary information which will facilitate final test design and data interpretation.

4.1.1 Task A: Characterization of Feed Water

The objective of this Initial Operations task is to obtain a chemical and physical characterization of the feed water for those systems using ozone or ozone/AOPs for SOC oxidation. Historical records of SOC concentrations in the feed water shall be reviewed to evaluate the use of ozone or ozone/AOPs at the site.

A thorough description of the watershed or aquifer and any pretreatment modules that provide the feed water should be prepared, to aid in interpretation of feed water characterization.

4.1.2 Task B: Initial Test Runs

During Initial Operations, the manufacturer may want to evaluate equipment operation and determine flow rates, hydraulic retention time, ozone dosage, optimum pH, sequencing or timing of UV light and/or hydrogen peroxide addition relative to ozonation, or other factors which provide effective treatment of feed water. This is a recommended Initial Operations task.

The FTO may also want to work with the analytical laboratory to perform blank or preliminary challenges and sampling routines to verify that sampling equipment can perform its required functions. This is also a recommended Initial Operations Task.

4.2 Verification Operations: Overview

The objective of this task is to operate for a minimum of one test period the treatment equipment provided by the FTO and to assess its ability to meet stated water quality goals and any other performance objectives specified by the Manufacturer. The equipment shall be operated to collect data on equipment performance and water quality for purposes of performance verification. The test period selected should represent the worst-case for concentrations of ozone demanding contaminants (e.g.,

iron, organics, hydrogen sulfide, pesticides, or turbidity) and for presence of synthetic organic contaminants.

4.2.1 Task 1: Verification Testing Runs and Routine Equipment Operation

To characterize the technology in terms of efficiency and reliability, water treatment equipment that includes ozone (or ozone/AOPs) shall be operated for Verification Testing purposes with the operational parameters based on the results of the Initial Operations testing.

4.2.2 Task 2: Feed Water and Finished Water Quality

During each Verification Testing period, feed water and treated water samples shall be collected and analyzed for those parameters relevant to oxidation performance and affecting equipment performance, as outlined in Section 10, Table 1.

4.2.3 Task 3: Documentation of Operating Conditions and Treatment Equipment Performance

During each Verification Testing period, operating conditions and performance of water treatment equipment shall be documented. This includes ozone feed gas concentration, gas and liquid pressures, gas and liquid temperatures, gas and liquid flow rates, ozone off-gas concentration, applied and transferred ozone dosage, power usage for the ozone generator, ozone transfer equipment, ozone feed-gas and off-gas monitors (if part of the ozone system) and ozone destruct unit, as well as stability of the electrical power supply (surges, brown-outs, etc.).

If ozone (or an AOP) is used following pretreatment (e.g., coagulation/settling), then a complete description of the pretreatment process shall be provided. For AOP systems, the operating conditions and parameters associated with hydrogen peroxide or UV light equipment must also be documented.

4.2.4 Task 4: SOC Oxidation

The objective of this task is to evaluate SOC oxidation during Verification Testing by measuring the SOCs of interest in the feed water and in the treated water. If the SOC concentration naturally present in the feed water is not sufficiently high for testing, SOC spiking is needed. Another requirement of this task is to provide a gas chromatography/mass spectrometry scan of the organic by-products formed by ozonation of SOCs.

4.2.5 Task 5: Data Management

The objective of this task is to establish an effective field protocol for data management at the field operations site and for data transmission between the FTO and the NSF for data obtained during the Verification Testing. Prior to the beginning of field testing, the database design must

be developed by the FTO and reviewed and approved by NSF. This will ensure that the required data will be collected during the testing, and that it can be effectively transmitted to NSF for review.

4.2.6 Task 6: Quality Assurance/Quality Control (QA/QC)

An important aspect of Verification Testing is the protocol developed for quality assurance and quality control. The objective of this task is to assure accurate measurement of operating and water quality parameters during ozone equipment Verification Testing. Prior to the beginning of field testing, a QA/QC plan must be developed which addresses all aspects of the testing process. Each water quality parameter and operational parameter must have appropriate QA and QC measures in place and documented. For example, the protocol for ozone measurement using a spectrophotometer should describe how the instrument is calibrated, what adjustments are made, and provide a permanent record of all calibrations and maintenance for that instrument.

5.0 TESTING PERIODS

The required tasks in the Verification Testing Plan (Tasks 1 through 6) are designed to be carried out during one or more testing periods, each of which shall provide at least 200 hours of ozone equipment operation. During this time, the performance and reliability of the equipment shall be documented.

Some systems may operate for less than 24 hours per day. Interruptions in ozone production are allowed but the reason for and duration of all interruptions shall be fully described in the Verification Testing report. Any testing conducted at intervals of less than 200 hours is considered a test *run*, whereas the entire 200 hours (either continuous or as the sum of individual test runs) of ozone equipment operation is considered the Verification Test *period*. If ozone production is interrupted during a verification test run, that test run shall be considered to have been concluded at the time of interruption of the ozone feed. After restart, all data collected are to be part of a new verification test run.

6.0 DEFINITION OF OPERATIONAL PARAMETERS

Definitions that apply to ozone and ozone/AOP processes are given below. Refer to Appendix A of *Ozone in Water Treatment, Application and Engineering*, by the American Water Works Association Research Foundation and Compagnie Générale des Eaux, Lewis Publishers, 1991 for a more detailed description of terms.

6.1 Feed Gas or Ozone Production Concentration (% weight or g/m³ NTP)

The feed gas or ozone production concentration (Y_1) is the ozone concentration (in gaseous form) being applied to the water being treated. It is expressed in units of g/m³ normal temperature and pressure

(NTP) or as percent by weight. The temperature and pressure values associated with NTP are 0 °C and one atmosphere (i.e., 14.696 psi, 760 mm Hg, or 101.325 kPa), respectively.

6.2 Off Gas Concentration (% weight or g/m³ NTP)

The off gas concentration (Y_2) is the ozone concentration (in gaseous form) of the gas which is being released (i.e., off gas) from the water being treated. This off gas contains ozone which was not transferred into a dissolved form during treatment. It is expressed in units of g/m³ NTP or as percent by weight.

6.3 Applied Ozone Dosage (mg/L)

The amount of ozone added to the water being treated is the applied ozone dosage. The equation for calculating the applied ozone dosage is as follows:

$$D = P/(8.34*L)$$

where: D = applied ozone dosage (mg/L)
      P = ozone production (lb/day)
      L = water flow rate (MGD, million U.S. gallons per day)

6.4 Transfer Efficiency (percent)

The transfer efficiency is defined as the percentage of ozone that becomes dissolved into the water being treated. The equation for calculating the transfer efficiency is as follows:

$$TE = [(Y_1 - Y_2)/Y_1]*100$$

where: TE = transfer efficiency (percent)
      Y_1 = ozone production concentration (g/m³ NTP or percent by weight)
      Y_2 = off gas ozone concentration (g/m³ NTP or percent by weight)

This calculation assumes that the flow of the feed gas is equal to the flow of the off gas. The transfer efficiency calculation can be refined by measuring both gas flow rates or by monitoring the dissolved gas concentration in the liquid phase if the Manufacturer and their FTO desire.

6.5 Transferred Ozone Dosage (mg/L)

The transferred ozone dosage is the concentration of ozone that becomes dissolved into the water being treated. The equation for calculating the transferred ozone dosage is as follows:

$$T = (D * TE)/100$$

where: T = transferred ozone dosage (mg/L)

D = applied ozone dosage (mg/L)

TE = transfer efficiency (percent, i.e., 95.0 and not 0.95)

6.6 Dissolved Ozone Concentration (mg/L)

The concentration of ozone in solution is the dissolved ozone concentration. It is measured using an indigo bleaching technique (e.g., HACH AccuVac or *Standard Method* 4500-O_3 B) or by inserting a dissolved ozone probe into the process stream (e.g. Orbisphere, Orbisphere Laboratories, Emerson, NJ).

6.7   Ozone Decay Rate (1/min)

After the initial ozone demand has been satisfied, the ozone decay rate is assumed to follow pseudo first-order kinetics. Monitoring the decay rate will provide an indication of the level of ozone demanding substances present in the feed water and the environmental conditions affecting oxidation (e.g., pH and temperature). To calculate the decay rate, the initial ozone concentration (C_o) at time zero and the ozone concentration (C) after time, t, must be known. The equation for calculating the decay rate (k) is as follows:

$$C = C_o e^{-kt}$$

where: C = ozone concentration at time t (mg/L)

Co = ozone concentration at time zero (mg/L)

t = contact time (minutes)

k = decay coefficient (1/minute)

If possible, the ozone residual should be measured after several contact times in the reactor. The best fit line of ln(C/Co) versus t can be used to obtain the decay coefficient, k. If the plot does not fit a straight line, the assumption of pseudo-first order kinetics is not valid.

7.0 TASK A: CHARACTERIZATION OF FEED WATER

7.1 Introduction

This recommended Initial Operations task is performed to determine if the chemical, biological, and physical characteristics of the feed water are appropriate for the water treatment equipment to be tested.

Initial Operations (Tasks A and B) are not mandatory but they are recommended as an aid to successful completion of Verification Testing. If the verification entity conducts a site visit for QA purposes, then Task B would need to be performed.

7.2 Objectives

The objective of this task is to obtain a complete chemical and physical characterization of the source water, or the feed water after pre-treatment, that will be entering the treatment system being tested.

7.3 Work Plan

During this Initial Operations task, the following water quality characteristics of the feed water to the ozone system should be measured and recorded for both ground and surface waters: ozone demand, turbidity, temperature, pH, alkalinity, calcium, total hardness, total sulfides, total organic carbon, dissolved organic carbon, ultraviolet absorbance (at 254 nm), color, bromide, iron, and manganese. Data on SOCs in the feed water (source water) should be obtained from existing databases or by analysis of water samples, so a determination about the need for SOC spiking can be made.

Sufficient information shall be obtained to illustrate the variations expected to occur in these parameters that will be measured during the Verification Testing for a typical annual cycle for the water source. This information will be compiled and shared with NSF so NSF and the FTO can determine the adequacy of the data for use as the basis to make decisions on the testing schedule.

A brief description of the watershed or aquifer source shall be provided, to aid in interpretation of feed water characterization. The watershed description should include a statement of the approximate size of the watershed, a description of the topography (i.e., flat, gently rolling, hilly, mountainous) and a description of the kinds of human activity that take place (i.e., mining, manufacturing, cities or towns, farming, wastewater treatment plants) with special attention to potential sources of pollution that might influence feed water quality. The nature of the water source, such as stream, river, lake or man-made reservoir, should be described as well. Aquifer description should include (if available) the above characterization relative to the recharge zone, a description of the hydrogeology of the water bearing stratum(a), well boring data, and any Microscopic Particulate Analysis data indicating whether the groundwater is under the influence of surface waters.

Any pretreatment, including oxidation, coagulation or pH adjustment, of the water upstream of the ozone equipment shall be completely documented and characterized. Any coagulant or other chemical additions shall be identified and the chemical form and dosage shall be fully described.

7.4 Analytical Schedule

There is no recommended analytical schedule for characterization of the feed water. Any existing water quality data should be reviewed to assess the character of the feed or source water as well as the range of water quality that can be expected during each season. Water quality sampling can be performed if there are data gaps in the existing information.

7.5 Evaluation Criteria

Feed water quality will be evaluated in the context of the Manufacturer's statement of the equipment performance objectives but should not be beyond the range of water quality suitable for treatment for the equipment in question. The device shall be tested using water of the quality for which the equipment was designed.

8.0 TASK B: INITIAL TEST RUNS

8.1 Introduction

During the Initial Operations, a Manufacturer and their FTO may choose to evaluate equipment operations and determine flow rates, hydraulic residence time, ozone production, power supply requirements, or other factors applicable to the technology and related to effective treatment of the feed water, including the weight ratios of hydrogen peroxide to ozone dosages and/or the ratios of UV to ozone dosages. The Manufacturer may also choose to work with the FTO and the analytical laboratory to perform blank or preliminary challenges (if necessary) and sampling routines to verify that sampling equipment can perform the required functions under normal operating conditions. This information may also indicate operating conditions under which the Manufacturer's stated performance objectives are not met. This is a recommended Initial Operations task. An NSF field inspection of equipment operations and sampling and field analysis procedures may be carried out during the initial test runs, and if this occurs, the Initial Operations task must be performed.

8.2 Objectives

The objective of these test runs is to bracket the proper operating parameters for treatment of feed water during Verification Testing. The ability of ozone or ozone/AOP systems to effectively oxidize SOCs and reduce their concentrations will vary depending on the quality of the feed water being treated and the season. Therefore, conducting initial test runs is strongly recommended.

8.3 Work Plan

Because Initial Operations test runs are not a requirement of this ETV plan, the Manufacturer and FTO can decide the duration of Initial Operations. Enough time should be available to establish optimal operating conditions and to ensure that the system will be able to meet any performance objectives.

8.4 Analytical Schedule

Because these Initial Operations are being conducted to define future operating conditions for Verification Testing, a strictly defined schedule for sampling and analysis does not need to be followed. Adhering to the schedule for sampling and analysis to be followed during Verification Testing is recommended, however, so the operator can gain familiarity with the time requirements that will be applicable during Verification Testing. Also, during the Initial Operations phase, the verification

organization may conduct an initial on-site inspection of field operations, sampling activities, and on-site analyses. The sampling and analysis schedule that is to be used during Verification Testing shall be followed during the on-site inspection.

8.5 Evaluation Criteria

The Manufacturer and the FTO should evaluate the data produced during the Initial Operations to determine if the water treatment equipment performed in a manner that will meet or exceed the statement of performance objectives. If performance is not as good as in the statement of performance objectives, the FTO may conduct additional Initial Operations or cancel the remainder of the testing program.

9.0 TASK 1: VERIFICATION TESTING RUNS AND ROUTINE EQUIPMENT OPERATION

9.1 Introduction

Water treatment equipment that includes ozone or ozone/AOPs shall be operated for Verification Testing purposes with operational parameters based on the manufacturer's statement of performance objectives.

9.2 Experimental Objectives

The objective of this task is to operate the ozone or ozone/AOP equipment and characterize the effectiveness and reliability of the equipment.

9.3 Work Plan

9.3.1 Verification Testing Runs

The Verification Testing Runs in this task consist of an evaluation of the treatment system, using the most successful treatment parameters defined during Initial Operations. Performance and reliability of the equipment shall be tested during one or more Verification Testing periods consisting of at least 200 hours of ozone production at the test site.

Verification Testing should be conducted at times when worst-case seasonal water quality conditions exist, including peak concentrations of SOCs or of hydroxyl free radical-demanding contaminants or ozone-demanding contaminants. During each of these testing periods, Tasks 1 through 6 shall be conducted simultaneously.

Factors that can influence SOC oxidation include:

- the presence of ozone demanding substances that may be present in the form of particulate matter, dissolved organic matter, or dissolved inorganic matter; often occurring in the spring, or during reservoir or lake turn-over events, or also encountered in rivers carrying a high sediment load or in surface waters during periods of high runoff resulting from heavy rains or snow melt. Algae also exert an ozone demand as do iron, manganese, and cyanide. The presence of ozone demanding substances will affect the ability of ozone to effectively oxidize SOCs and will react with hydroxyl free radicals needed to destroy the slower-to-oxidize SOCs.

- pH and alkalinity, which can vary seasonally, will affect the decay rate of ozone in natural waters, and may affect the amount of SOC oxidation achieved by the system.

- temperature.

9.3.2 Routine Equipment Operation

If the water treatment equipment is being used for production of potable water during the time intervals between verification runs, routine operation of the equipment will occur. In this situation, the operating and water quality data collected and furnished to the Safe Drinking Water Act (SDWA) primacy agency shall be supplied to the NSF-qualified FTO for use in evaluating conditions during verification testing.

For equipment that is being used to treat water for distribution to customers, it is assumed that the State has already issued a permit (if one is necessary) for installation and operation. If ETV is being conducted to establish the SOC oxidation capabilities of the existing equipment, permission by the State may be required if the system were taken off-line for verification testing.

9.4 Schedule

During Verification Testing, water treatment equipment shall be operated for a minimum of 200 hours. The reason for and duration of any interruptions in ozone production during Verification Testing shall be fully documented.

9.5 Evaluation Criteria

The goal of this task is to operate the equipment for 200 hours during Verification Testing. Data shall be provided to substantiate that 200 hours of operation have been completed.

10.0 TASK 2: FEED WATER AND TREATED WATER QUALITY

10.1 Introduction

Water quality data shall be collected during Verification Testing for the feed water and treated water as shown in Table 1. The Field Test Organization, on behalf of the equipment Manufacturer, shall assure

the sampling or measuring of the water quality parameters in Table 1. The FTO may use local personnel to assist in collection of samples or measurement of test parameters, but is responsible for their training to assure proper techniques are used at all times.

10.2 Experimental Objectives

The objective of this task is to identify the presence and concentration of water quality characteristics that might affect the ability of ozone to oxidize SOCs. This task will also provide data to ensure that the use of ozone does not increase the risk of violating any existing or future SDWA regulations (e.g., THMs, bromate).

10.3 Work Plan

The Manufacturer or FTO will be responsible for establishing the testing operating parameters, on the basis of the Initial Operations testing. Many of the water quality parameters described in this task will be measured on-site by the NSF-qualified FTO or by local community personnel properly trained by the FTO. Analysis of the remaining water quality parameters will be performed by a state-certified or third party- or EPA-accredited analytical laboratory. The methods to be used for measurements of water quality parameters in the field are listed in the Analytical Methods section in Table 2. The analytical methods utilized in this study for on-site monitoring of feed water and treated water qualities are described in Task 6, Quality Assurance/Quality Control (QA/QC). Where appropriate, the *Standard Methods* reference numbers for water quality parameters are provided for both the field and laboratory analytical procedures. EPA Methods for analysis of the parameters listed in Table 2 also may be used.

Samples of the feed water shall be collected and analyzed for background SOC concentrations. Feed water shall also be sent to the state-certified or third party- or EPA- accredited laboratory to conduct spiking QA/QC analysis (see Task 6). The approved analytical methods for SOCs vary, depending on the SOC(s) of interest. A state-certified or third party- or EPA-accredited laboratory should be using an approved EPA or *Standard Method* for SOC analysis. Peer-reviewed and proposed methods for SOC determination are also allowable if approved EPA or *Standard Methods* are not available. The preservatives needed for sample collection also vary for different SOC(s) and the state-certified or third party- or EPA-accredited should fully document sampling requirements for the FTO.

Any disinfectant added upstream of the ozone addition point will affect the ozone demand; therefore, an agreement between NSF, the manufacturer, and the FTO must be made to determine whether or not to allow pre-disinfection prior to ozonation during the Verification Testing Period. If a pre-disinfectant is used, testing shall be conducted to verify that no disinfectant residual exists at the influent of the ozone contactor, or if a disinfectant residual does exist, a quenching solution (e.g., sodium bisulfite or hydrogen peroxide) shall be used. The latter option (quenching) is less desirable because the concentration of the quenching agent will have to be carefully monitored during testing to minimize over-feeding of the quenching agent (which would result in an ozone demand).

10.4 Analytical Schedule

Water quality data shall be collected at the intervals specified in Table 1. Additional sampling and data collection may be performed at the discretion of the Manufacturer and their designated FTO. Sample collection protocol shall be defined by the FTO in the PSTP. Algae sampling is not required for systems using groundwater sources.

For water quality samples that will be shipped to a state-certified or third party- or EPA-accredited laboratory for analysis, the samples shall be collected in appropriate containers (containing preservatives as needed) prepared by the laboratory. These samples shall be preserved, stored, shipped, and analyzed in accordance with appropriate procedures and holding times, as specified by the laboratory. Original field sheets and chain-of-custody forms shall accompany all samples shipped to the laboratory. Copies of field sheets and chain-of custody forms for all samples shall be provided to NSF.

10.5 Evaluation Criteria

The performance of the ozone or ozone/AOP equipment will be compared to the Manufacturer's statement of performance objectives for the equipment being tested.

11.0 TASK 3: DOCUMENTATION OF OPERATING CONDITIONS AND TREATMENT EQUIPMENT PERFORMANCE

11.1 Introduction

Throughout the Verification Testing period, operating conditions shall be documented. This shall include descriptions of pretreatment chemistry and filtration performance for the equipment processes, if used, and their operating conditions. The performance of the ozone equipment (including ozone generator(s), air preparation system(s), off-gas destruct unit(s), injection equipment, ozone monitor(s), and contactor(s)) as well as UV light and hydrogen peroxide equipment shall be documented. The total volume of water treated and the total power usage for all equipment associated with the ozone or ozone/AOP system shall also be recorded.

11.2 Objectives

The objective of this task is to accurately and fully document the operating conditions during treatment, and the performance of the equipment. This task is intended to collect data that describe operation of the equipment and information that can be used to develop cost estimates for operation of the equipment.

11.3 Work Plan

During Verification Testing, treatment equipment operating parameters for both pretreatment and ozonation shall be monitored and recorded on a routine basis by the NSF-qualified FTO or by local community personnel properly trained by the FTO.

Table 3 outlines some of the operating parameters that shall be monitored throughout Verification Testing. Operating parameters, in addition to those listed in Table 3, may be needed to adequately assess the operating conditions of the ozone or ozone/AOP equipment. These additional parameters shall be identified by the Manufacturer and the FTO and agreed upon by the Manufacturer and NSF.

Examples of operational parameters which shall be monitored are:

- water flow rates
- gas flow rates
- water pressures
- gas pressures
- water temperatures
- gas temperatures
- ozone operating voltage
- ozone production power consumption
- air preparation power consumption or other consumables for air preparation
- oxygen feed rate (if applicable) and other pertinent operation information
- performance of oxygen generation or oxygen feed equipment
- ozone electrical frequency, if variable
- amperage of ozone equipment
- weight ratio of hydrogen peroxide (if used) to ozone

On a daily basis, the operator shall note and record whether any visual effects of ozonation are apparent in the treated water or on piping or vessels that convey or hold treated water. This may include surface scum, precipitation of metals, color changes, etc. At the end of the test period if an ozone contact chamber is provided with the equipment and if it is accessible, the contact chamber shall be inspected for deposits of scum, precipitation of metals, or color changes, and this information shall be noted in the Verification Testing report.

11.4 Schedule

Table 3 presents the schedule and recording data required for ozone and AOP systems. The length of time (hours) of operation (during Verification Testing) shall be recorded for all of the ozone and AOP equipment.

11.5 Evaluation Criteria

Where applicable, the data developed from this task will be compared to statements of performance objectives. If no relevant statement of performance capability exists, results of operating and performance data will be tabulated for inclusion in the Verification Report.

12.0 TASK 4: DOCUMENTATION OF EQUIPMENT PERFORMANCE: SOC OXIDATION

12.1 Introduction

The ability of ozone and AOP equipment to oxidize SOCs can be assessed by measuring the initial and final SOC concentrations and computing the change (see Chapter 1 of the Protocol for Equipment Verification Testing of Synthetic Organic Contamination Removal).

12.2 Experimental Objectives

The objective of this task is to determine the effectiveness of ozone or ozone/AOP equipment for SOC oxidation at small systems.

12.3 Work Plan

The FTO shall conduct water quality sampling and calculate the reduction in SOC concentration(s) resulting from ozone or AOP treatment. Task 4 shall be conducted during the Verification Testing runs conducted in Task 1, 2, and 3.

The background or naturally occurring concentration of the SOC(s) of interest shall be determined during either Task A or Task 2 so that the background concentration of SOC(s) in the feed water is known prior to conducting Verification Testing. If the background SOC concentration is too low to adequately show or calculate a percentage removal, spiking of SOC(s) during the 200 hours of Verification Testing will be necessary.

Multiple SOC(s) can be simultaneously evaluated during Verification Testing; however, ozone or AOPs may preferentially react with naturally occurring organics or other SOCs present in solution, thereby reducing its ability to oxidize the SOC(s) of interest. Thus, it is possible that the desired outcome of Verification Testing may not occur during some multiple SOC evaluations.

If the ozone or AOP equipment is already being used at a site and has been approved by the State (if necessary), a manufacturer may want to verify its performance with Verification Testing. This can be accomplished by conducting the tests at the location if naturally occurring or background SOC concentrations are high enough for accurately and precisely calculating reductions. This would not compromise the water quality in any way. However, if SOCs must be spiked for testing, this poses a potential threat to the water quality. In this case, identical equipment would have to be brought on site

and spiked SOC studies would have to be conducted with this additional equipment. The effluent of this spiked SOC testing would be treated as described in Section 12.3.5.

12.3.1 Types of SOCs

This ETV plan is not designed to guide Verification Testing for volatile organic compounds (VOCs). Examples of VOCs include benzene and vinyl chloride, and a list of regulated VOCs (i.e., Phase I) can be found in Pontius (1998).

Oxidation of SOCs by ozone or AOPs can form by-products. The presence and concentration of these by-products is of interest because some of the by-products are considered as potential health concerns as a result of long-term exposure. Therefore, it is necessary that one treated water sample be collected during each Verification Test period, and this sample will be analyzed for the presence and concentration of by-products. This can be accomplished by conducting a scan of semi-volatile organic by-products by using gas chromatography/mass spectrometry by a state-certified or third party- or EPA-accredited analytical laboratory that has scanning and compound library matching capabilities. Some of the common by-products include: aldehydes, ketones, and for atrazine, deethylatrazine and deisopropylatrazine.

12.3.2 Spiking Protocols

Spiking of SOCs shall be used in concentrations sufficient to permit the highest level of stress for the Manufacturer's equipment. Some guidelines for spiking include:

- SOC spiking shall begin at start-up of the treatment equipment and shall continue for the 200 hours of Verification Testing.
- The SOC(s) feed solution shall be prepared by diluting the SOC into dilution water that is distilled or deionized and oxidant demand-free.
- The container used for storing the feed SOC solutions shall be chemically inert (i.e., not reactive or adsorbable with the SOC(s) of interest).
- The feed solution shall be gently and continuously mixed throughout the Verification Test Run.
- The SOC spiked solution shall be fed using an adjustable rate chemical feed pump.
- Use of an in-line static mixer to mix this solution into the feedwater is recommended.
- SOC samples shall be collected in sample bottles prepared (i.e., preservatives added, if necessary) by the analytical laboratory performing the analysis.
- Multiple SOCs can be contained in the same stock feed container (i.e., having only one feed solution).
- The concentration of SOC(s) applied to the feed water shall be agreed upon by the Manufacturer, NSF, and the FTO.

12.3.3 Test Operation and Sample Collection

If spiking is necessary, the SOC(s) of interest shall be continuously applied to the feed water during the 200 hours of Verification Testing. If an ozone or ozone/AOP system is temporarily shut down, then the spiking solution feed equipment should also be shut down and then started again when the ozone or ozone/AOP system is started again.

During the Verification Testing period, SOC samples of the feed water and treated water shall be collected once per 25 hours of operation. If the ozone or ozone/AOP system is not operating continuously, then the SOC samples shall be collected after the mid-point of the run in which the equipment is being operated. For example, if the ozone system is operated in 8 hour shifts, the SOC samples shall be collected after the fourth hour of operation.

During sample collection, minimal sample agitation and exposure to the atmosphere shall occur. An overflowing technique for filling samples bottles is recommended. A piece of Tygon tubing attached to the sample port can be placed such that the unattached end of the tubing rests at the bottom of the sampling container. As the sample fills the bottle, the end of the tubing remains at the bottom of the container. Once the sampling container is overflowing, the tubing can slowly be removed from the container. The lid should be placed on the container immediately after the sample tube is removed from the sample container.

Since some SOC samples require the use of a preservative in the sampling container, the overflowing technique is not applicable to all SOC(s). If this is the case, the Tygon tubing is still recommended (to minimize sample agitation during collection); however, the tubing should be removed prior to the point at which the sample would overflow the container.

Samples shall be delivered to a state-certified or third party- or EPA-accredited analytical laboratory for analysis using approved EPA or *Standard Methods* for measuring the SOC concentrations of interest.

12.3.4 Experimental Quality Control

Duplicates of the feed and treated water samples shall be collected for at least two of the sampling events during a Verification Test Run. A process control and trip control sample shall also be collected as part of Task 6.

The experimental quality control shall be verified by checking the flow rate of the spiked solution once per day. To ensure the proper feed rate of the spiked SOC solution to the ozone or AOP system, use a stopwatch to measure the time required to collect a specified volume of the feed solution from the feed system. This requires that the feed line to the contactor be temporarily disconnected so that the pumping rate of the stock SOC solution can be measured. Typically, a graduated cylinder is used to collect the pumped SOC sample and the size of the graduated cylinder is such that the length of collection time exceeds 10 seconds.

12.3.5 Treatment of Effluent

Treated water resulting from SOC spiking experiments using ozone or ozone/AOP equipment shall not be distributed to the public. The treated water might have to be passed through a granular activated carbon (GAC) filter for removal of residual SOCs during the 200 hours of Verification testing. The size of the GAC filter and the type of carbon would need to be determined by the Manufacturer and FTO and approved by the State's pollution control authority. Since some SOCs are more readily adsorbed than others, and there may be competition between SOCs for adsorption sites on the carbon, GAC filters would have to be designed on a case-by-case basis. The discharge of treated water shall be directed to a location that is approved by the State.

12.4 Analytical Schedule

Feed water and treated water SOC samples shall be collected once per 25 hours of operation. Duplicate sampling is required for two of the samples of Verification Testing.

12.5 Evaluation Criteria

The difference in concentration of the SOC(s) of interest in the feed and treated waters will be compared to the Manufacturer's statement of performance objectives for the equipment being tested. The ozone production and power usage may also be used to evaluate the performance of the equipment.

13.0 TASK 5: DATA MANAGEMENT

13.1 Introduction

The data management system used in the Verification Testing program shall involve the use of computer spreadsheet software and manual recording of the operational parameters for the water treatment equipment on a daily basis.

13.2 Experimental Objectives

The objectives of this task are: 1) to establish a viable structure for the recording and transmission of field testing data so the FTO will provide sufficient and reliable operational data for verification purposes, and 2) to provide the information needed for a statistical analysis of the data, as described in the "EPA/NSF ETV Protocol For Equipment Verification Testing For The Removal Of Synthetic Organic Chemical Contaminants: Requirements For All Studies."

13.3 Work Plan

The following protocol has been developed for data handling and data verification by the FTO. Where possible, a Supervisory Control and Data Acquisition (SCADA) system should be used for automatic entry of testing data into computer databases. Specific parcels of computer databases for operational and water quality parameters should then be downloaded by manual importation into Excel (or similar spreadsheet software) as a comma delimited file. These specific database parcels will be identified based upon discrete time spans and monitoring parameters. In spreadsheet form the data will be manipulated into a convenient framework to allow analysis of water treatment equipment operation. Backup of the computer databases to diskette should be performed on a monthly basis at a minimum. When SCADA systems are not available, direct instrument feed to data loggers and laptop computers shall be used when appropriate.

For parameters for which electronic data acquisition is not possible, field testing operators will record data and calculations by hand in laboratory notebooks (daily measurements will be recorded on specially-prepared data log sheets as appropriate). Each notebook must be permanently bound with consecutively numbered pages. Each notebook must indicate the starting and ending dates that apply to entries in the logbook. All pages will have appropriate headings to avoid entry omissions. All logbook entries must be made in black water insoluble ink. All corrections in any notebook shall be made by placing one line through the erroneous information. Products such as "correction fluids" are never to be utilized for making corrections to notebook entries. Operating logs shall include a description of the water treatment equipment (description of test runs, names of visitors, description of any problems or issues, etc.); such descriptions shall be provided in addition to experimental calculations and other items. The original notebooks will be stored on-site; photocopies will be forwarded to the project engineer of the FTO at an agreed upon schedule. This protocol will not only ease referencing the original data, but will also offer protection of the original record of results.

The database for the project will be set up in custom-designed spreadsheets. The spreadsheets will be capable of storing and manipulating each of the monitored water quality and operational parameters from each task, each sampling location, and each sampling time. All data from the laboratory notebooks and data log sheets will be entered into the appropriate spreadsheets. Data entry will be conducted on-site by the designated field testing operators. All recorded calculations will also be checked at this time. Following data entry, the spreadsheet will be printed out and the print-out will be checked against the handwritten data sheet. Any corrections will be noted on the hard-copies and corrected on the screen, and then a corrected version of the spreadsheet will be printed out. Each step of the verification process will by initialed by the field testing operator or engineer performing the entry or verification step.

Each experiment (e.g. verification run) will be assigned a run number that will then by tied to the data from that experiment through each step of data entry and analysis. As samples are collected and sent to state-certified or third party- or EPA-accredited laboratories, the data will be tracked by use of the same system of run numbers. Data from the outside laboratories will be received and reviewed by the field testing operator. These data will be entered into the data spreadsheets, corrected, and verified in the same manner as the field data.

13.4 Statistical Analysis

Water quality developed from grab samples collected during test runs according to the Analytical Schedule in Task 2 of this Test Plan shall be analyzed for statistical uncertainty. The FTO shall calculate 95% confidence intervals for grab sample data obtained during Verification Testing as described in "EPA/NSF ETV Protocol For Equipment Verification Testing For The Removal Of Synthetic Organic Chemical Contaminants: Requirements For All Studies." Statistical analysis could be carried out for a large variety of testing conditions.

The statistics developed will be helpful in demonstrating the degree of reliability with which water treatment equipment can attain quality goals. Information on the differences in feed water quality variations for entire test runs versus the quality produced during the optimized portions of the runs would be useful in evaluating appropriate operating procedures.

14.0 TASK 6: QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

14.1 Introduction

Quality assurance and quality control of the operation of the water treatment equipment and the measured water quality parameters shall be maintained during the Verification Testing program.

14.2 Experimental Objectives

The objective of this task is to maintain strict QA/QC methods and procedures during the ETV Program. Maintenance of strict QA/QC procedures is important in that if a question arises when analyzing or interpreting data collected for a given experiment, this information will be possible to verify exact conditions at the time of testing.

14.3 Work Plan

Equipment flow rates and associated signals should be verified and verification recorded on a routine basis. Daily routine walk-throughs during the testing program will be used to verify that each piece of equipment or instrumentation is operating properly. Particular care shall be taken to verify that chemicals are being fed at the defined flow rate, and into a flow stream that is operating at the expected flow rate. In addition, the operation of the air preparation equipment or the liquid oxygen supply for the ozone generator, and the ozone generator, shall be checked in each walkthrough and relevant operating data shall be recorded and checked to verify that operating conditions are within the acceptable operating range for the equipment or processes involved. In-line monitoring equipment such as flow meters, etc. will be checked as indicated below to verify that the readout matches with the actual measurement (i.e., flow rate) and that the signal being recorded is correct. The items listed are in addition to any specified checks outlined in the analytical methods.

When collecting water quantity data, all system flow meters will be calibrated using the classic bucket and stopwatch method where appropriate. Hydraulic data collection will include the measurement of the finished water flow rate by the "bucket test" method. This would consist of filling a calibrated vessel to a known volume and measuring the time to fill the vessel with a stopwatch. This will allow for a direct check of the system flow measuring devices.

14.3.1 Daily QA/QC Verifications

- On-line turbidimeter: Clean out reservoirs and recalibrate, check the flow rate (verified volumetrically over a specific time period).
- On-line pH meters (standardize and recalibrate).
- Chemical feed pump flow rates (check and verify components).
- On-line turbidimeter readings checked against a properly calibrated bench model.

14.3.2 QA/QC Verifications Performed Every Two Weeks

- On-line flow meters/rotameters: Clean equipment to remove any debris or biological buildup and verify flow volumetrically to avoid erroneous readings.
- Chemical feed pump flow rates (verify volumetrically over a specific period of time).

14.3.3 QA/QC Verifications Performed Every Testing Period

- Tubing: Verify that all tubing and connections are in good condition and replace if necessary. For surface water systems, microbial growth could occur between seasonal verification test runs, so replacement of tubing prior to each verification test may be necessary.
- Differential pressure transmitters (verify gauge readings and electrical signals using a pressure meter).

14.4 On-Site Analytical Methods

The analytical method utilized in this study for on-site monitoring of raw water and treated water quality are described in the following section. Use of either bench-top or in-line field analytical equipment will be acceptable for the verification testing; however, in-line equipment is recommended for ease of operation.

14.4.1 pH

Analysis for pH shall be performed according to Standard Method 4500-H^+ B or EPA Method 150.1/150.2. A three-point calibration of any pH meter used in this study will be performed once per day when the instrument is in use. Certified pH buffers in the expected range shall be used. The pH probe shall be stored in the appropriate solution defined in the instrument manual. Transport of carbon dioxide across the air-water interface can confound pH measurement in

poorly buffered waters. If this is a problem, measurement of pH in a confined vessel is recommended to minimize the effects of carbon dioxide loss with the atmosphere.

14.4.2 Turbidity Analysis

Turbidity analyses shall be performed according to Standard Method 2130 or EPA Method 180.1 with either a bench-top or in-line turbidimeter. Grab samples shall be analyzed using a bench-top turbidimeter; readings from this instrument will serve as reference measurements throughout the study. The bench-top turbidimeter shall be calibrated within the expected range of sample measurements at the beginning of Verification Testing and on a weekly basis using primary turbidity standards of 0.1, 0.5 and 3.0 NTU. Secondary turbidity standards shall be used on a daily basis to verify calibration of the turbidimeter and to recalibrate when more than one turbidity range is used.

During each verification testing period, the bench-top and in-line turbidimeters will be left on continuously. Once each turbidity measurement is complete, the unit will be switched back to its lowest setting. All glassware used for turbidity measurements will be cleaned and handled using lint-free tissues to prevent scratching. Sample vials will be stored inverted to prevent deposits from forming on the bottom surface of the cell.

The Field Testing Organization shall be required to document any problems experienced with the monitoring turbidity instruments, and shall also be required to document any subsequent modifications or enhancements made to monitoring instruments.

14.4.2.1 Bench-top Turbidimeters. The method for collecting grab samples will consist of running a slow, steady stream from the sample tap, triple-rinsing a dedicated sample beaker in this stream, allowing the sample to flow down the side of the beaker to minimize bubble entrainment, double-rinsing the sample vial with the sample, carefully pouring from the beaker down the side of the sample vial, wiping the sample vial clean, inserting the sample vial into the turbidimeter, and recording the measured turbidity.

When cold water samples cause the vial to fog and prevent accurate readings, allow the vial to warm up by submersing partially into a warm water bath for approximately 30 seconds.

14.4.2.2 In-line Turbidimeters. In-line turbidimeters may be used during verification testing and must be calibrated as specified in the manufacturer's operation and maintenance manual. It will be necessary to periodically verify the in-line readings using a bench-top turbidimeter; although the mechanism of analysis is not identical between the two instruments the readings should be comparable. Should these readings suggest inaccurate readings then all in-line turbidimeters should be recalibrated. In addition to calibration, periodic cleaning of the lens should be conducted using lint-free paper, to prevent any particle or microbiological build-up that could produce inaccurate readings. Periodic verification of the sample flow should also be performed using a volumetric measurement. Instrument bulbs should be replaced on an as-

needed basis. It should also be verified that the LED readout matches the data recorded on the data acquisition system, if the latter is employed.

14.4.3 Dissolved Ozone

The dissolved ozone concentration can be measured using an indigo bleaching technique, such as Standard Method 4500-O_3 B or the HACH Indigo AccuVac method. When sampling for dissolved ozone, it is important to minimize sample agitation and transfer from one container to another. One good sampling technique is to collect the sample directly from the sample tap. If HACH AccuVac vials are used, the tip of the AccuVac can be placed directly into the tap opening where the water is flowing. Apply pressure and snap the tip while it is inside the sample tap opening. The vacuum in the AccuVac vial will draw the water sample into the AccuVac. Once the AccuVac is filled, remove the AccuVac from the sample tap and analyze according the HACH instructions. If necessary, a short piece (i.e., less than 2 feet) of Tygon tubing can be attached to the sample tap for dissolved ozone sampling. If HACH AccuVac vials are not used, use of tubing attached to the sample port for sample collection is recommended to minimize sample agitation and mixing. This tubing should be Tygon and should be no longer than 2 feet in length.

Another method for measuring dissolved ozone is a dissolved ozone probe. These probes can be placed in the process stream to provide continuous measurements of ozone residuals. Check the probe tip daily to ensure that the membrane has been installed properly and that there are no air bubbles underneath the membrane. Also, check that the pressure and flow rate within the contactor are within the appropriate range for the probe being used. The performance of the probe shall be verified on a daily basis by measuring the dissolved ozone concentration with one of the indigo bleaching methods to ensure that the probe is functioning properly.

A third method for measuring dissolved ozone concentrations is an on-line analyzer which uses UV spectrophotometry to measure the gas-phase concentration of ozone which has been stripped from a liquid sample. These analyzers then correlate the gas-phase ozone concentration to the dissolved ozone concentration. These analyzers are calibrated at the factory.

14.4.4 Gas Phase Ozone

Gas phase ozone concentrations can be measured using either UV absorbance ozone monitors or a wet-chemistry test. Ozone monitors are calibrated at the factory and provide a continuous measure of the ozone concentration in gas phase. The wet-chemistry test method of measuring the ozone concentration of a gas stream involves bubbling ozone through a potassium iodide solution, acidification with sulfuric acid, and titration with sodium thiosulfate. This method is described in detail in Gordon *et al*. (1992). During each Verification Test, a wet-chemistry measurement of the ozone feed gas shall be conducted to independently check that the ozone monitor is functioning properly. If ozone monitors are not available, wet-chemistry tests shall be

performed three times per day or three times per shift to measure the ozone concentration in the feed gas and off gas.

14.4.5 Hydrogen Peroxide

The concentration of hydrogen peroxide can be measured using one of two spectrophotometric methods: 1) cobalt-bicarbonate and 2) peroxidase. The cobalt-bicarbonate method, described in Masschelein *et al.* (1977), can be used to measure up to 2 mg/L hydrogen peroxide at 260 nm, whereas the peroxidase method, described in Bader *et al*. (1988), can be used to measure up to 1.7 mg/L hydrogen peroxide at 551 nm.

At low pH, ozone and peroxide can be in solution at the same time, because the reaction rate is slow. The presence of ozone interferes with any hydrogen peroxide analysis; therefore, to measure the amount of hydrogen peroxide in the AOP system, ozone production shall be temporarily terminated while hydrogen peroxide samples are being collected and analyzed.

To ensure the proper feed rate of hydrogen peroxide to the ozone/AOP system, use a stopwatch to measure the time required to collect a specified volume of hydrogen peroxide stock solution from the feed system. This requires that the hydrogen peroxide feed line to the contactor be temporarily disconnected so that the pumping rate of the stock hydrogen peroxide solution can be measured. Typically, a graduated cylinder is used to collect the pumped hydrogen peroxide sample and the size of the graduated cylinder is such that the length of collection time exceeds 10 seconds.

The strength of the peroxide feed solution can also be determined from the peroxide supplier's shipping information, as long as the peroxide being used for testing has not been: 1) diluted by the user; 2) exposed to contamination (which would affect its strength); 3) stored for longer than one year; or, 4) stored at temperatures greater than 77^oF.

14.4.6 Temperature

Readings for temperature shall be conducted in accordance with *Standard Method* 2550. Raw water temperatures shall be obtained at least once daily. The thermometer shall have a scale marked for every 0.1 ^{o}C, as a minimum, and should be calibrated weekly against a precision thermometer certified by the National Institute of Standards and Technology (NIST). (A thermometer having a range of -1^oC to $+51^o$C, subdivided in 0.1^o increments, would be appropriate for this work.)

14.4.7 Color

True color shall be measured with a spectrophotometer at 455 nm, using an adaptation of the *Standard Methods* 2120 procedure. Samples shall be collected in clean plastic or glass bottles and analyzed as soon after collection as possible. If samples can not be analyzed immediately they shall be stored at 4^oC for up to 24 hours, and then warmed to room temperature before

analysis. The filtration system described in *Standard Methods* 2120 C shall be used, and results should be expressed in terms of PtCo color units.

14.4.8 Dissolved Oxygen

Analysis for dissolved oxygen shall be performed according to *Standard Method 4500-O* using an iodometric method or the membrane electrode method. The techniques described for sample collection must be followed very carefully to avoid causing changes in dissolved oxygen during the sampling event. Sampling for dissolved oxygen does not need to be coordinated with sampling for other water quality parameters, so dissolved oxygen samples should be taken at times when immediate analysis is going to be possible. This will eliminate problems that may be associated with holding samples for a period of time before the determination is made.

If the sampling probe is not mounted such that the probe is continuously exposed to the process stream, then care must be taken when measuring the dissolved oxygen concentration. For best results, collect the dissolved oxygen sample with minimal agitation and measure the dissolved oxygen concentration immediately. If possible, measure the dissolved oxygen under a continuous stream of sample by placing the tip of the probe in the sample container, allowing the sample to overflow the container while the probe reaches equilibrium (usually less than 5 minutes).

14.5   Chemical and Biological Samples Shipped Off-Site for Analysis

The analytical methods that shall be used during testing for chemical and biological samples that are shipped off-site for analyses are described in the section below.

14.5.1 Organic Samples

Samples for analysis of total organic carbon (TOC), UV_{254} absorbance, and dissolved organic carbon (DOC) shall be collected in glass bottles supplied by the state-certified or third party- or EPA-accredited laboratory and shipped at 4 °C to the analytical laboratory within 24 hours of sampling. These samples shall be preserved in accordance with Standard Method 5010 B. Storage time before analysis shall be minimized, according to Standard Methods.

14.5.2 Algae

Algae samples shall be preserved with Lugol's solution after collection, stored and shipped in a cooler at a temperature of approximately 2 to 8 °C, and held at that temperature range until counted.

14.5.3 Inorganic Samples

Inorganic chemical samples, including alkalinity, shall be collected and preserved in accordance with Standard Method 2320 B. The samples shall be refrigerated at approximately 2 to 8 °C.

Samples shall be processed for analysis by a state-certified or third party- or EPA-accredited laboratory within 24 hours of collection. The laboratory shall keep the samples at approximately 2 to 8 °C until initiation of analysis.

Bromate samples shall be collected in sampling containers supplied by the state-certified or third party- or EPA-accredited laboratory. Sample collection and storage requirements are outlined in EPA Method 300.1 or shall be provided by the laboratory conducting the analysis.

14.5.4 SOC Analysis

Analysis of SOCs requires a trained analyst using sophisticated instrumentation. Only state-certified or third party- or EPA-accredited laboratories shall analyze SOC samples that are collected during Initial Operations and Verification Testing. As stated in the "EPA/NSF ETV Protocol For Equipment Verification Testing For The Removal Of Synthetic Organic Chemical Contaminants: Requirements For All Studies," approved methods for some SOCs may not be available, and for these SOCs, a proposed, peer-reviewed method may be used.

There are many approved methods for analyzing Phase II and Phase V SOCs. Depending on the laboratory, gas chromatography (GC) or high performance liquid chromatography (HPLC) methods can be used to analyze SOCs. For both methods, the equipment is highly specialized and proper operation of these instruments requires a skilled laboratory technician.

Mass spectrometry is not required for all SOCs, however it is recommended for SOC identification. Retention times relative to the internal standard can also be used to identify SOCs. Either peak height or peak area can be used to determine the SOC concentrations.

SOCs shall be analyzed with an internal standard similar in analytical behavior and not affected by the matrix for QA/QC. An appropriate surrogate standard shall also be used during SOC analysis. Data pertaining to the internal and surrogate standards shall be reported with the SOC concentrations of the samples being analyzed. A method blank shall also be prepared and analyzed by the state-certified or third party- or EPA-accredited laboratory to verify minimal contamination in the laboratory.

At least three standards shall be used to develop the standard curve for SOC quantification and these three standards shall be extracted and analyzed (by GC or HPLC) on the same day as the samples.

During each Verification Test period, one treated water sample shall be analyzed by scanning for the presence and concentration of potential by-products of SOC oxidation by ozone. Gas chromatography followed by mass spectrometry can be used to identify many of the organic by-products formed by ozonation. The spectra obtained by this analysis can be matched to a compound library in a computer database to identify the various byproducts. This analysis shall be performed by a state-certified or third party- or EPA-accredited analytical laboratory. The

scan should be targeted toward the SOC of interest, and the potential by-products associated with ozonation of that SOC.

Spiked samples shall be analyzed once, at the beginning of each Verification Test Run. The laboratory shall spike a feed water sample with a known quantity of the SOC(s) of interest and analyze this spiked sample. SOC analysis of the spiked sample will indicate if there are any interferences present in the feed water. The broad scan can be a performance-based scan (i.e., the scan is not used for compliance, and therefore undergoes less rigorous QA/QC and is less expensive than a compliance based scan analysis.)

14.6 Experimental QA/QC Samples

14.6.1 Process Control

A second round of testing shall be carried out using procedures identical to the steps outlined above, but without operating the ozone or ozone/AOP equipment. The purpose of this testing is to evaluate any cumulative effects produced by the equipment, the spiking and sampling procedures, and the sample handling procedures on SOCs. The process control samples should show minimal loss of SOC(s) relative to the trip control sample. Significant loss of SOC concentrations in the process control sample indicates that some aspect of the process other than ozone oxidation contributes to SOC removal. Re-testing is required when this is shown to occur.

14.6.2 Trip Control

For tests utilizing spiked SOCs, a replicate or subsample of the spiking solution shall accompany the actual spiking solution from the analytical laboratory. This replicate sample shall undergo all of the processes used on the actual solution including dose preparation, shipping, preparation for spiking, and return to the laboratory for analysis. The trip control samples should show minimal loss of SOC(s). Significant decreases in the SOC concentration of the trip control sample indicates that some step in handling the solution contributed to the reduction in the SOC concentration. The seeding tests must be repeated when significant loss of SOCs in the trip control sample is observed.

15.0 OPERATION AND MAINTENANCE

The FTO shall obtain the Manufacturer-supplied Operation and Maintenance (O&M) Manual to evaluate the instructions and procedures for their applicability during the verification testing period. The following are recommendations for criteria for O&M Manuals for drinking water treatment equipment employing ozone treatment.

15.1 Maintenance

The Manufacturer shall provide readily understood information on the recommended or required maintenance schedule for each piece of operating equipment including, but not limited to, the following, where applicable:

- ozone generator (dielectric replacement)
- ozone diffusers or injection port, control valves
- ozone destruct unit (catalyst replacement)
- gas phase ozone monitors (for feed gas and off gas)
- dissolved ozone monitoring equipment
- cooling water equipment
- air preparation unit or oxygen feed system for ozone generation
- gas and liquid rotameters
- UV lamps and other relevant equipment
- peroxide feed equipment
- other equipment such as pumps and valves

The Manufacturer shall also provide readily understood information on the recommended or required maintenance for non-mechanical or non-electrical equipment, including but not limited to, the following, where applicable:

- piping
- contactor chamber

15.2 Operation

The Manufacturer shall provide readily understood recommendations for procedures related to proper operation of all equipment. Among the operating aspects that should be addressed in the O&M manual are:

Ozone Generator

- air preparation or oxygen feed requirements (moisture content, filtration requirements, flow rate)
- cooling water requirements (flow)
- range of variable voltage for adjusting ozone output
- proper sequence of operation for start-up and shut-down
- proper sequence of operation for initial start-up or for re-start after maintenance

Ozone Monitors (Gas Phase)

- temperature and pressure compensation
- zeroing and calibration procedures
- proper sequence of operation for start-up and shut-down

Ozone Destruct Units

- heater and/or blower requirements
- catalyst requirements
- proper sequence of operation for start-up and shut-down

Air Preparation or Oxygen Feed Systems

- desiccant requirements and replacement procedures
- filters (maintenance and replacement schedule)
- proper sequence of operation for start-up and shut-down
- supplemental gas (air or nitrogen) flow rate, pressure, and temperature.

Cooling Water System

- maintenance of proper temperature
- monitoring cooling water flow
- pump maintenance
- proper sequence of operation for start-up and shut-down
- maintenance of recirculation equipment, if cooling water is recirculated

Ozone Contactor Systems

- maintenance schedule and procedures
- replacement procedures

UV lamps

- hours of operation (verification procedures)
- UV irradiance (calibration and verification procedures)
- maintenance schedule and procedures
- replacement procedures
- proper sequence of operation for start-up and shut-down

Hydrogen Peroxide Feed System

- procedures for variable speed adjustments to pump
- information about proper tubing type and size
- anticipated schedule for tubing replacement
- storage information (i.e., safety, container type, container material, temperature, length of storage time) for stock hydrogen peroxide solutions
- proper sequence of operation for start-up and shut-down

Control Valves

- open/close indication
- sequence of operations

The Manufacturer shall provide a troubleshooting guide; a simple checklist of what to do for a variety of problems, including but not limited to:

- no flow to unit
- sudden change in flow to unit
- no electric power
- automatic operation (if provided) not functioning
- valve stuck or will not operate

16.0 REFERENCES

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Table 1. Water Quality Sampling and Measurement Schedule

Parameter	Sampling Location	Mandatory (M) or Optional (O)	Frequency*	
			Surface Water Systems	**Groundwater Systems**
Temperature (°C)	Feed Water, Treated water	M	3/d or 3/shift	3/d or 3/shift
Dissolved Ozone Residual (mg/L)	Treated†	O	3/d or 3/shift	3/d or 3/shift
pH	Feed Water	M	3/d or 3/shift	3/d or 3/shift
Total Alkalinity (mg/L as CaCO$_3$)	Feed Water	O	1/d	1/d
Total Organic Carbon (mg/L)	Feed Water	O	1/25 hours of ozone production	1/50 hours of ozone production
Dissolved Organic Carbon (mg/L)	Feed Water	O	1/25 hours of ozone production	1/50 hours of ozone production
UV absorbance at 254 nm (1/m)	Feed Water, Treated water	O	1/d	1/50 hours of ozone production
Color (Pt-Co)	Feed Water, Treated water	O	1/d	1/50 hours of ozone production
Turbidity (NTU)	Feed Water, treated water	O	3/d or 3/shift	1/d
Bromide (mg/L)	Feed Water	O	1/50 hours of ozone production	1/50 hours of ozone production

Table 1. Water Quality Sampling and Measurement Schedule (continued)

Parameter	Sampling Location	Mandatory (M) or Optional (O)	Frequency*	
			Surface Water Systems	**Groundwater Systems**
Bromate (µg/L)	Treated Water	O	1/50 hours of ozone production	1/50 hours of ozone production
SOCs (µg/L)	Feed Water, Treated water	M	1 per 25 hours of ozone production	1 per 25 hours of ozone production
SOC scan	Feed Water, Treated water	M	1 per Verification test period, after 100th hour of operation	1 per Verification test period, after 100th hour of operation
Total THM (µg/L) (chloroform, bromoform, bromodichloromethane, dibromochloromethane)	Treated Water	O	1/50 hours of ozone production	1/50 hours of ozone production
HAA$_5$ (µg/L) (monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, dibromoacetic acid, trichloroacetic acid)	Treated Water	O	1/50 hours of ozone production	1/50 hours of ozone production
Iron (µg/L)	Feed Water	O	1/50 hours of ozone production	1/50 hours of ozone production
Dissolved Manganese (µg/L) (Manganese concentration passing through 0.2 µm filter)	Feed Water, Treated water	O	1/50 hours of ozone production	1/50 hours of ozone production
Total Manganese (µg/L)	Feed Water, Treated water	O	1/50 hours of ozone production	1/50 hours of ozone production

Table 1. Water Quality Sampling and Measurement Schedule (continued)

Parameter	Sampling Location	Mandatory (M) or Optional (O)	Frequency*	
			Surface Water Systems	**Groundwater Systems**
Total Sulfides	Feed Water	O	1/d	1/d
Dissolved Oxygen	Feed Water, Treated water	O	1/50 hours of ozone production	1/50 hours of ozone production
Hydrogen Peroxide (mg/L)	Stock Solution, Treated Water	M††	1/50 hours of ozone production 1/Verification Test Period	1/50 hours of ozone production 1/Verification Test Period
Quenching Solution (mg/L) (e.g., hydrogen peroxide)	Feed Water	M	1/d	1/d
Algal enumeration and species	Feed Water	O	1 per Verification Test Period	Not Required
Calcium (mg/L as CaCO₃)	Feed Water	O	1/50 hours of ozone production	1/50 hours of ozone production
Total Hardness (mg/L as CaCO₃)	Feed Water	O	1/50 hours of ozone production	1/50 hours of ozone production

* 3/d or 3/shift means that the water quality parameter shall be measured either 3 times per day if ozone production is continuous over the 200 hours of Verification Testing, or 3 times per staffed shift if ozone production is periodically terminated or interrupted, and the length of time of ozone production is less than 24 hours. 1/50 hours of ozone production means that the water quality parameter shall be measured once per each 50 hours of ozone production, regardless of interruptions in ozone production. † The dissolved ozone concentration should be measured at sampling ports within the ozone contactor or immediately at the outlet of the ozone contactor. If the ozone decay coefficient is being determined, at least two sampling ports will need to be sampled. †† The peroxide concentration of the stock solution shall be checked at the prescribed frequency. The peroxide concentration within the contactor shall be checked once during or immediately prior to the verification testing period, while the ozone equipment is not operating. Peroxide monitoring within the contactor will require that samples be withdrawn at appropriate sampling ports at the end or outlet of the contactor.

Table 2. Analytical Methods

Parameter	Facility	*Standard Methods* number or Alternative Reference[1]	EPA Method[2]
Temperature (°C)	On-site	2550 B	
Dissolved Ozone Residual (mg/L)	On-site	4500 O_3 B; HACH Indigo Blue Method*	
pH	On-site	4500 H^+	150.1/150.2
Total Alkalinity (mg/L as $CaCO_3$)	Lab	2320 B	
Phase II and Phase V SOCs	Lab	6252, 6410, 6420, 6431, 6440, 6610, 6630, 6640, 6651	525.2, 505, 515.1, 531.1, 547, 548.1, 549.1, 1613
Total Organic Carbon (mg/L)	Lab	5310 C	
Dissolved Organic Carbon (mg/L)	Lab	5310 C	
UV absorbance at 254 nm (1/m)	Lab	5910 B	
Color (Pt-Co)	Lab	2120 C	110.2
Turbidity (NTU)	On-site	2130 B	180.1
Bromide (mg/L)	Lab	4500-Br^-	300.0
Bromate (µg/L)	Lab		300.1
Total THM (µg/L)	Lab	6232 B	502.2, 524.2, 551
HAA_5 (µg/L)	Lab	6251 B	552.1
Iron (µg/L)	Lab	3111 B, 3113 B, 3120 B	200.7, 200.8, 200.9
Total Manganese (µg/L)	Lab	3111 B, 3113 B, 3120 B	200.7, 200.8, 200.9
Dissolved Manganese (µg/L) (Manganese concentration passing through 0.2 µm filter)	Lab	3500-Mn	3111 B, 3113 B, 3120 B
Total Sulfides	Lab or On-Site	4500-S^{2-} D, E	
Dissolved Oxygen	Lab or On-Site	4500-O	

Table 2. Analytical Methods (continued)

Parameter	Facility	*Standard Methods* number or Alternative Reference[1]	EPA Method[2]
Algal enumeration and speciation	Lab	Part 10000, Biological Examination†	
Parameter	Facility	*Standard Methods* number or Alternative Reference[1]	EPA Method[2]
Calcium (mg/L as $CaCO_3$)	Lab	3500-Ca D, 3111 B, 3120 B	200.7
Total Hardness (mg/L as $CaCO_3$)	Lab	2340 C	
SOC scan	Lab	6410B, 6420C, 6440C	525.2 – Extended for Broad Spectrum

[1] Standard Method Source: 20th Edition of Standard Methods for the Examination of Water and Wastewater, 1999, American Water Works Association.

[2] EPA Methods Source: EPA Office of Ground Water and Drinking Water. EPA Methods are available from the National Technical Information Service (NTIS).

* Dissolved ozone residual measurements can also be from a properly calibrated and installed dissolved ozone monitor or properly calibrated and installed dissolved ozone monitor.

† *Standard Methods* does not contain a method for enumeration and speciation of algae. It does, however, contain methods for laboratory techniques that may need to be performed for proper enumeration and speciation of the algae. Only an experienced and qualified laboratory analyst shall conduct algal enumeration and speciation.

Table 3. System Operating Data

Operational Parameter		Frequency
Water Flow (gpm)	Feed Water	3/d or 3/shift
	Side Stream (if applicable)	3/d or 3/shift
	Cooling Water	3/d or 3/shift
Water Pressure (psig)	Inlet to Ozone System	3/d or 3/shift
	Outlet of Ozone System	3/d or 3/shift
	Side Stream (if applicable)	3/d or 3/shift
	Cooling Water	3/d or 3/shift
Water Temperature (°C)	Inlet to Ozone System	3/d or 3/shift
	Outlet ~~to~~ of Ozone System	3/d or 3/shift
	Side Stream (if applicable)	3/d or 3/shift
Gas Phase Ozone Concentration (% wt)	Feed Gas	3/d or 3/shift
	Off Gas	3/d or 3/shift
Power Usage (kw/hr)	Ozone Generator	3/d or 3/shift
	Air Preparation System or Oxygen System	3/d or 3/shift
	Gas Phase Ozone Feed and Off Gas Monitors	3/d or 3/shift
	Cooling Water System	3/d or 3/shift
	Destruct Units	3/d or 3/shift
	Other pumps or motors	3/d or 3/shift
Ozone Feed Gas Temperature (°C)		3/d or 3/shift
Ozone Feed Gas Pressure (psig)		3/d or 3/shift
Ozone Feed Gas Flow (scfm)		3/d or 3/shift
Atmospheric Pressure (psia)		1/d
Dew Point (if using air feed system)		1/d
Ozone Production (lb/d)		1/d
Ozone Decay Rate (1/minute) (optional)		1/d
If applicable: Peroxide feed concentration (mg/L) Peroxide feed rate (mL/min) Peroxide to Ozone ratio (by weight)		3/d or 3/shift
If applicable: Purity of oxygen supply (%) Supplemental nitrogen flow rate (scfm), pressure (psig), and temperature (°C) Supplemental air flow rate (scfm), pressure (psig), and temperature (°C)		1/d or 1/shift 1/d or 1/shift 1/d or 1/shift
If applicable: Operating parameters for UV-light systems (see ETV Equipment Verification Testing Plan for Microorganism Contaminant Inactivation by Ultraviolet Based Technology)		3/d or 3/shift

CHAPTER 4

EPA/NSF ETV EQUIPMENT VERIFICATION TESTING PLAN
FOR THE REMOVAL OF SYNTHETIC ORGANIC CHEMICAL CONTAMINANTS
BY ADSORPTIVE MEDIA PROCESSES

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1.0 APPLICATION OF THIS EQUIPMENT VERIFICATION TESTING PLAN

This document is the Environmental Technology Verification (ETV) Technology Specific Test Plan (TSTP) for evaluation of drinking water treatment equipment utilizing adsorptive media for synthetic organic chemical (SOC) removal. This TSTP is to be used within the structure provided by *Protocol for Equipment Verification Testing for Removal of Synthetic Organic Chemical Contaminants: Chapter 1 General Requirements.* This TSTP is to be used as a guide in the development of the Product-Specific Test Plan (PSTP) for testing of adsorptive media and related equipment to achieve removal of SOCs.

This document is applicable only to fixed-bed adsorption processes in which adsorption occurs as water flows through a stationary bed of adsorptive media. It is anticipated that most such systems will use granular activated carbon (GAC) as the adsorptive media, but other media types are also acceptable for verification testing. **This document is NOT applicable to slurry systems, such as those using powdered activated carbon (PAC) or other diffuse adsorption processes in which the adsorptive media are added directly to water.**

To participate in the equipment verification process for adsorption processes, the equipment manufacturer and its designated Field Testing Organization (FTO) shall employ the procedures and methods described in this TSTP and in the referenced ETV protocol document as guidelines for the development of the PSTP. The FTO shall clearly specify in the PSTP, the SOCs targeted for removal and the sampling program that shall be followed during verification testing. The PSTP should generally follow those tasks outlined herein, with changes and modifications made for adaptations to specific equipment. At a minimum, the format of the procedures written in the PSTP for each task should consist of the following sections:

- Introduction;
- Objectives;
- Work Plan;
- Analytical Schedule; and
- Evaluation Criteria.

The primary goal of equipment employed in this verification testing program is to remove SOCs present in water supplies, treating water to compliance with Phase II and V Rules of the Safe Drinking Water Act (SDWA). The organic contaminants listed in Phase II (Appendix A, Table A.1) and Phase V (Appendix A, Table A.2) Rules include compounds classified as both SOCs (including pesticides and herbicides) and volatile organic chemicals (VOCs). This document focuses on verification testing of systems for the removal of SOCs (including pesticides and herbicides) as classified in Phase II and V Rules of the SDWA. For verification testing of systems for the removal of VOCs listed in Phase I, II, and V Rules of the SDWA, a companion document should be used: *EPA/NSF ETV Equipment Verification Testing Plan for the Removal of Volatile Organic Chemical Contaminants by Adsorptive Media* (EPA/NSF, 2002). These documents may also be used for verification testing of adsorptive media for the removal of chemicals listed in *Drinking Water Standards and Health Advisories* (USEPA 2000), which are included as Appendix B in this document.

Experimental design of the PSTP shall be developed so that relevant performance specifications for adsorptive media related to SOC removal are addressed. The manufacturer may wish to establish a statement of performance capabilities (see Section 3.0, General Approach) that is based upon removal of target SOCs from influent water sources, or alternatively, one based upon compliance with drinking water standards. For example, the manufacturer could include in the PSTP a statement of performance capabilities that would achieve compliance with maximum contaminant levels (MCLs) stipulated in the National Primary Drinking Water Standards or the EPA National Secondary Drinking Water Regulations for a specific water quality parameter. The experimental design of the PSTP shall be developed to address the specific statement of performance capabilities established by the manufacturer. Each PSTP shall include all of the tasks described in this document, Tasks 1 to 8. An overview of the tasks is given in Section 6.0, Overview of Tasks.

2.0   INTRODUCTION

Fixed-bed adsorptive media processes are currently used for a number of water treatment applications, including removal of color, taste and odor, disinfection byproduct precursors (DBPs), SOCs, VOCs, and inorganic compounds (Snoeyink and Summers 1999). Performance of adsorptive media for SOC removal is highly dependent on a number of factors, including influent SOC concentration; influent water quality, including other SOCs or VOCs, background organic matter (BOM), pH, temperature; and system design, including empty-bed contact time (EBCT) and adsorbent type. Adsorption is not a steady-state process; this TSTP is designed based on a statement of performance capabilities that specifies a run time achievable for a given fixed-bed adsorptive media process under specified influent conditions. The run time is the operation time of the system during which time the removal of SOC(s) meets or exceeds that stated in the manufacturer's statement of performance capabilities. Alternatively, the statement of performance capabilities may specify a maximum adsorbent usage rate (AUR) to be verified.

Standard pretreatment, such as cartridge filtration, included as part of the packaged/modular adsorption treatment equipment is considered an integral part of the treatment system. In such cases, the system shall be considered as a single unit and the pretreatment process shall not be separated for evaluation purposes.

Additional pretreatment processes may be required to reduce particle loading to the adsorption process for surface water applications (and ground waters in which iron and manganese precipitation is an issue). These are considered to constitute a separate treatment module whose performance and operation are outside the scope of this document. Where such pretreatment is required to reduce the fouling potential of the adsorption process feed water, consult the ETV document, *EPA/NSF ETV Protocol for Physical Removal of Microbiological and Particulate Contaminants* (EPA/NSF 2002), for evaluation testing procedures.

Two or more parallel contactors, whose effluents are blended prior to further treatment or distribution, are considered one system for the purposes of verification testing.

3.0   GENERAL APPROACH

Testing of equipment covered by this TSTP shall be conducted by an FTO that is qualified by NSF International (NSF) and selected by the equipment manufacturer. Testing of analytical water quality performed in conjunction with this TSTP shall be contracted with a laboratory that is certified, accredited or approved by a state, a third-party organization (i.e., NSF), or the EPA.

For verification testing, the manufacturer shall identify in a statement of performance capabilities, the specific performance criteria to be verified and the specific operational conditions under which the verification testing shall be performed.   The statement of performance capabilities must be specific and verifiable. Statements should also be made regarding the applications of the equipment, the known limitations of the equipment and under what conditions the equipment is likely to under perform or fail. There are different types of statements of performance capabilities that may be verified. Examples are provided in Table 3.1.

Verification testing shall consist of an evaluation of the fixed-bed adsorptive media treatment system using an influent water containing one SOC at target influent concentrations equal to that stated in the statement of performance capabilities, for a minimum period of 13 days and one 8-hour shift.   Statistical analyses of the data results shall include averages, minimum, and maximum for each analyte. For sample sets of eight or more, the results shall also include the standard deviation and confidence interval for each analyte. A pilot plant representing the package plant shall not be substituted for the actual package treatment system. The 13.3-day minimum testing period is designed to allow for an evaluation of the system's mechanical and hydraulic integrity and operability under field conditions, as well as to assess SOC removal performance for 13.3 days of operation. However, breakthrough of the SOC will often not occur within the first 13.3 days of operation. Consequently, verification testing of the system for longer than 13.3 days may be desirable to achieve breakthrough and will be necessary to verify a manufacturer's statement of performance capabilities of run time greater than 13.3 days. For adsorption systems incorporating in-place media regeneration, the effectiveness of regeneration shall also be assessed.

Table 3.1 Examples of Statements of Performance Capabilities

Testing Mode	Single or Multiple Compounds	Example Statement of Performance Capabilities
Constant influent, low variability	Single	This single-contactor package plant, when operated at a GAC EBCT of 15 minutes or more, is capable of maintaining a treated water endrin concentration below 2 µg/L for up to 60 days (AUR ≤ 0.086 g/L or 0.72 lb/1,000 gal) in GAC influent waters containing mean endrin concentrations at or below 20 µg/L with low variability (RSD ≤ 10%); TOC concentrations at or below 3.0 mg/L; turbidity levels at or below 1.0 Nephlometric Turbidity Units (NTU); and temperature between 20 and 25°C, containing no other SOCs at levels above 1 µg/L.
	Multiple	This single-contactor package plant, when operated at a GAC EBCT of 15 minutes or more, is capable of maintaining a treated water endrin concentration below 2 µg/L for up to 120 days (AUR ≤ 0.043 g/L or 0.36 lb/1,000 gal) in GAC influent waters containing mean endrin concentrations at or below 20 µg/L with low variability (RSD ≤ 10%); TOC concentrations at or below 3.0 mg/L; turbidity levels at or below 1.0 NTU; temperature between 20 and 25°C; containing the following SOCs: dinoseb at 12 µg/L, simazine at 5 µg/L, 2,4-D at 10 µg/L. *A performance statement could also be made for these other compounds.*
Constant influent, high variability	Single	This single-contactor package plant, when operated at a GAC EBCT of 15 minutes or more, is capable of maintaining a treated water endrin concentration below 2 µg/L for up to 60 days (AUR ≤ 0.086 g/L or 0.72 lb/1,000 gal) in GAC influent waters containing mean endrin concentrations at or below 25 µg/L with high variability (ranging from 5 to 40 µg/L, RSD ≥ 30 and ≤ 60%); TOC concentrations at or below 3.0 mg/L; turbidity levels at or below 1.0 NTU; and temperature between 20 and 25°C, containing no other SOCs at levels above 1 µg/L.
	Multiple	This single-contactor package plant, when operated at a GAC EBCT of 15 minutes or more, is capable of maintaining a treated water endrin concentration below 2 µg/L for up to 90 days (AUR ≤ 0.058 g/L or 0.49 lb/1,000 gal) in GAC influent waters containing endrin concentrations at or below 25 µg/L with high variability (ranging from 5 to 40 µg/L, RSD ≥ 30 and ≤ 60%); TOC concentrations at or below 3.0 mg/L; turbidity levels at or below 1.0 NTU; temperature between 20 and 25°C; containing the following SOCs: dinoseb at 12 µg/L, simazine at 5 µg/L, 2,4-D at 10 µg/L. *A performance statement could also be made for these other compounds.*

Table 3.1 Examples of Statements of Performance Capabilities (cont.)

Attenuation of spiked influent	Single	This single-contactor package plant, when operated at a GAC EBCT of 15 minutes or more, is capable of maintaining a treated water endrin concentration below 2 µg/L for up to 60 days (AUR ≤ 0.086 g/L or 0.72 lb/1,000 gal) after the GAC influent water begins receiving a spike of endrin at a mean concentration of 25 µg/L (with low variability, RSD ≤ 10%) for 48 hours; after treating the following water quality with no SOCs present for 120 days or less; TOC concentrations at or below 3.0 mg/L; turbidity levels at or below 1.0 NTU; and temperature between 20 and 25°C, containing no other SOCs at levels above 1 µg/L.
	Multiple	This single-contactor package plant, when operated at a GAC EBCT of 15 minutes or more, is capable of maintaining a treated water endrin concentration below 2 µg/L for up to 90 days (AUR ≤ 0.058 g/L or 0.49 lb/1,000 gal) after the GAC influent water begins receiving a spike of endrin at a mean concentration of 25 µg/L (with low variability, RSD ≤ 10%) for 48 hours; after treating the following water quality with no SOCs present for 120 days or less; TOC concentrations at or below 3.0 mg/L; turbidity levels at or below 1.0 NTU; temperature between 20 and 25°C; with the following SOCs also contained in the 48-hour spiked influent: dinoseb at 12 µg/L, simazine at 5 µg/L, 2,4-D at 10 µg/L. *A performance statement could also be made for these other compounds.*

The design and duration of the equipment verification testing is based on the overall equipment performance demonstration goal of the test. At a minimum, verification testing must accomplish a demonstration of system integrity and initial performance by operating the system for a minimum of 13.3 days [System Integrity Verification Testing (SIVT)]. Equipment verification testing for a time period exceeding 13.3 days may have two objectives. Objective A includes completing the requirements of SIVT, and then evaluating adsorption capacity by testing until breakthrough of the SOC. Objective B also includes completing the requirements of SIVT, and then evaluating adsorption capacity to a run time greater than 13.3 days, but prior to breakthrough of the SOC. Testing under Objective B will result in termination of testing prior to breakthrough, yielding an AUR higher than that potentially achievable by the system. However, due to long run times to breakthrough for highly adsorbable SOCs, it may be preferable to terminate the test prior to breakthrough, still showing that run times substantially greater than 13.3 days are achievable by the system for the SOC tested. For both SIVT and both optional objectives, the AUR shall be determined by the run time of the last effluent sample taken during testing (if testing is terminated prior to breakthrough), or the run time to breakthrough, whichever occurs first.

During verification testing, the target SOC may already be present in the source water used. However, the manufacturer may wish to perform verification testing at an influent concentration higher than that of the SOC normally present in the source water, or the manufacturer may wish to test for a compound not detected in the source water to be tested. In these cases, the adsorption influent water may be spiked to the target concentration with the SOC to be tested.

If a manufacturer's statement of performance capabilities bases performance on simultaneous treatment of multiple SOCs, verification testing shall be performed with an equivalent mixture of multiple SOCs (specific SOCs and influent concentrations targeted based on the statement of performance capabilities). Although testing with multiple influent SOCs is allowable, this TSTP is designed to verify performance of a single SOC influent. However, standard verification testing of a multiple-compound manufacturer's statement of performance capabilities can be conducted using this TSTP. For verification testing of an AUR by testing until breakthrough of the SOC (Objective A), this document provides guidance for estimating the usage rate. This guidance, however, is based on a single compound influent, and is not directly applicable to multiple-compound influents, due to the impact of competitive adsorption. The manufacturer's statement of performance capabilities may be based on a run time for a single compound within the mixture of compounds, or it may be based on multiple run times for each of multiple compounds. For regulated SOCs, the AUR will be based on the first compound to exceed the MCL in the system effluent.

Verification testing of three modes of operation are possible under this TSTP: (1) constant influent with low variability, (2) constant influent with high variability about a target mean concentration, and (3) attenuation of a spiked influent. Most statements of performance capabilities will be based on the presence of a single influent SOC at a constant concentration with low variability, and this TSTP has been designed to verify these types of manufacturer's statements of performance capabilities. However, this TSTP may also be used to perform verification testing under conditions of highly variable influent SOC concentrations about a target mean concentration and attenuation of a spiked influent. For verification testing of attenuation of a spiked influent, the statement of performance capabilities must state the amount of time the system was in operation receiving influent water without the SOC to be spiked before spiking begins, as in the example given in Table 3.1.

Package plants that operate by blending the effluents of more than one contactor in parallel prior to further treatment and distribution shall be evaluated by assessing the water quality of the blended effluent from all contactors. If contactors are operated in staggered operation cycles to improve the overall efficiency of the process, then effluent testing will still be performed on the blended effluent of all contactors. The statement of performance capabilities shall clearly state the number of contactors operated and clearly describe the mode of operation (parallel or parallel-staggered) so that package plant performance can be evaluated in terms of the mode of operation employed.

For verification testing of Objective A (testing until breakthrough is reached), breakthrough is defined as reaching an effluent concentration of the SOC tested. This concentration can be chosen by the manufacturer or it can be a level equal to a regulated or proposed MCL, in which case the statement of performance capabilities should designate it as such. Depending on the quality and amount of data gathered to characterize the breakthrough curve, the AUR can be calculated by different methods, as described in Section 11.5.

4.0   BACKGROUND

This section provides a brief overview of SOC regulations, SOC health effects, SOC removal by fixed-bed adsorptive systems, and adsorption system design. This information should assist in

providing a background on SOC removal by adsorption processes and on the applicability of fixed-bed adsorption processes to treatment of SOCs. Due to the predominance of the use of GAC media for adsorption, the information presented in this section will focus on adsorption using GAC. The term SOC as used in this section includes volatile, semi volatile, and nonvolatile compounds.

4.1 SOC Health Effects and Regulations

Three general types of organic compounds found in water are (1) compounds resulting from the breakdown of naturally-occurring organic material, such as humic materials from plants and algae, microorganisms and their metabolites, and high molecular weight aliphatic and aromatic hydrocarbons; (2) compounds formed due to domestic and commercial activities (SOCs); and (3) compounds formed by chemical reactions during water treatment and transmission (Cohn, Cox, and Berger 1999). SOCs include pesticides, solvents, metal degreasers, and polychlorinated biphenyls.

The 1974 SDWA specified the process by which EPA adopted national drinking water regulations, including the establishment and publication of recommended maximum contaminant levels (RMCLs), set at levels at which no known or anticipated health effects would occur (Pontius and Clark 1999). RMCLs were followed by the establishment of MCLs, set as close to the RMCL as economically and technically feasible. Currently, 56 organic contaminants are regulated under Phase I Rule Volatile Organic Contaminants, Phase II Rule Contaminants, and Phase V Rule Contaminants. Appendix A lists currently regulated organic contaminants, including MCL goal (MCLG), MCL, potential health effects and sources of drinking water contamination. Appendix B contains the most recent *Drinking Water Standards and Health Advisories* tables available (USEPA 2000), listing 172 SOCs, and describing the status of their legislation, MCLGs, MCLs, health advisory document status, and available health effects data. These tables are revised periodically by EPA and can be accessed on the Internet at www.epa.gov/ost/drinking/standards/summary.html or a copy may be ordered by calling the Safe Drinking Water Hotline (1-800-426-4791).

The SDWA also requires that EPA establish a list of contaminants that serves as the primary source for priority contaminants considered for regulation. The list is divided into contaminants that are priorities for future research, those that need additional occurrence data, and those that are priorities for future rulemaking. The final Drinking Water Contaminant Candidate List (CCL) was published in 1998. The CCL can be accessed on the Internet at www.epa.gov/safewater/ccl/cclfs.html.

4.2 SOC Removal by Adsorption Processes

Removal of organic compounds by adsorption occurs through several steps: external diffusion, internal diffusion, and adsorption. First, organic compounds are transported from the bulk solution to the boundary layer of water surrounding the adsorbent particle. Second, organic compounds are transported by molecular diffusion through the external boundary layer (film diffusion). Third, organic compounds are transported through the adsorbent's pores to an available internal adsorption site. The transport mechanism for internal diffusion can be pore diffusion, molecular diffusion through the solution within the pores, or surface diffusion

(diffusion along the adsorbent surface after adsorption has occurred). The final step is physical adsorption of the organic compound to the adsorbent. The slowest step of these four is the rate-limiting step, and it will control the rate of organic compound removal. In adsorption by GAC, the rate-limiting step is usually film diffusion or pore diffusion (Snoeyink and Summers 1999).

4.3   Application of Adsorptive Media

In a GAC fixed-bed adsorption system, the mass transfer zone (MTZ) is the region in which adsorption is taking place. The activated carbon behind the MTZ is completely saturated with the adsorbate, while that ahead of the MTZ has not been exposed. Within the MTZ, the degree of saturation varies from zero to complete saturation. The length of the MTZ can vary (see Snoeyink and Summers 1999 for more information on factors affecting the MTZ length) and in some cases, the MTZ is very short and an ideal plug-flow behavior can be assumed. This assumption simplifies analysis and prediction of run time to breakthrough for adsorption of a single compound. Breakthrough is defined as the point when the contactor effluent concentration reaches the maximum acceptable effluent concentration, which is also referred to as the treatment objective. The breakthrough curve is a plot of column effluent concentration as a function of operation time or throughput in bed volumes (BV) treated. Throughput is related to operation time by EBCT, as presented in Equation 1:

$$\text{Throughput}\ \ (\text{BV}) = \frac{\text{Operation time (days)} \cdot 1{,}440 \text{ min/day}}{\text{EBCT (min)}} \tag{1}$$

EBCT is the hydraulic retention time of an empty contactor. The EBCT parameter normalizes bed depths at different loading rates and it is calculated as the volume of the contactor occupied by the adsorbent divided by the flow rate.

The performance of adsorptive media for removal of SOCs varies widely. In large part, performance is dependent on the influent concentration and adsorbability of the compound studied. For a 6-minute EBCT adsorber with bituminous coal-based GAC, breakthrough of trichloroethene to 50% of its influent concentration (310 µg/L) occurred after 25,000 BV (104 days).   Breakthrough of cis-1,2 dichloroethene to 50% of its influent concentration (70 µg/L) occurred after 17,000 BV (59 days) in a 5-minute EBCT contactor, also using bituminous coal-based GAC (Sontheimer, Crittenden, and Summers 1988).

The equilibrium relationship between the solid phase concentration (quantity of adsorbate per unit adsorbent), q_E, and the equilibrium solution concentration, C_E, is the adsorption isotherm. This relationship can be described by the Freundlich equation, as presented in Equation 2:

$$q_E = K C_E^{1/n} \tag{2}$$

where K and $1/n$ are constants. The constant K is related to the capacity of the adsorbent for the adsorbate, and $1/n$ is a function of the strength of adsorption (Snoeyink and Summers 1999). Values for K and $1/n$ have been tabulated for many SOCs in the literature (Snoeyink and Summers 1999; Sontheimer, Crittenden, and Summers 1988; Faust and Aly 1998; Speth and Miltner 1990, 1998). The value and units of K are dependent on the units of C_E and q_E.

Many researchers have shown that the presence of BOM can have a negative impact on the adsorption capacity of an adsorbent for SOCs. Relative to the SOC targeted for removal by adsorption, BOM will move more rapidly through the contactor and adsorb onto adsorbent sites. As more adsorption sites are taken by preloading with BOM, the capacity of the adsorbent for the SOC is reduced (Crittenden et al. 1985; Sontheimer, Crittenden, and Summers, 1988; Speth and Adams 1993; Snoeyink and Summers 1999). In one study, the capacity of activated carbon for trichloroethene (TCE) was reduced by 50% when the carbon was preloaded with BOM, as compared to adsorption in distilled water (Summers et al. 1989).

Competitive adsorption can also impact performance. In many cases, other SOCs will be in solution in the source water to be treated for removal of a specific SOC. The amount of adsorbent required for the same removal of a specific SOC within a mixture of SOCs will be greater than that for adsorption of the SOC in a single solute system. SOCs will compete for adsorption sites on the adsorbent surface (Snoeyink and Summers 1999). In addition, displacement of adsorbed compounds from the surface of the adsorbent can result in an effluent concentration greater than the influent concentration. More information on competitive effects can be found in the literature (Sontheimer, Crittenden, and Summers 1988; Speth and Adams 1993; Snoeyink and Summers 1999).

Adsorptive media designed for the removal of SOCs can be used to remove a SOC present in the source water at a constant concentration, yielding an effluent concentration below the treatment objective; when the treatment objective is reached, the media is replaced or regenerated in-place. The influent SOC concentration may be fairly constant, or highly variable. In another application, adsorptive media can attenuate a SOC spike event, such as a spill, lowering the effluent concentration of the SOC to a level that is below the treatment objective. This TSTP can be used to evaluate adsorptive media as treatment to constant SOC influent concentration (low or high variability) and to attenuate a short-duration spike of an SOC.

During operation of an adsorbent contactor subjected to a constant influent SOC concentration, the concentration of the SOC in the influent and effluent can be monitored and plotted. A plot of the effluent concentration as a function of operation time or throughput in BV treated is a breakthrough curve. Breakthrough curves are often generated by pilot-scale contactors to develop design criteria for full-scale systems. As defined in this document, breakthrough is reached when the concentration of the target compound in the adsorbent contactor effluent reaches the treatment objective, often the MCL. Immediate breakthrough is the level of adsorbate present in the adsorbent contactor effluent at the start of operation. For many highly-adsorbable SOCs, this level will not be detectable. Initial breakthrough is the point at which effluent concentrations begin to rise above immediate breakthrough levels.

The breakthrough curve is often used to determine the AUR. The AUR is the mass of adsorbent required to treat a specific volume of water to a predetermined quality. High AUR values result in increased operation and maintenance (O&M) costs caused by more frequent adsorbent replacement. The AUR can be calculated by the formula presented as Equation 3:

$$AUR = \frac{r}{BV_{bt}} \tag{3}$$

where r is the apparent density of the adsorbent and BV_{bt} is the BV to breakthrough. The AUR commonly has units of lbs/1,000 gal or g/L. The AUR can be converted from g/L to lbs/1,000 gal by multiplying the value in g/L by 8.35 lb-L/g-1,000 gal.

At an influent concentration, C_0, assuming a symmetrical breakthrough curve, the adsorbent capacity q can be estimated for a specific compound from the breakthrough curve by the formula presented as Equation 4:

$$q = \frac{C_0}{AUR_{bt=50\%}} \qquad (4)$$

where $AUR_{bt=50\%}$ is the AUR calculated at 50% breakthrough of the compound. This approximation of adsorbent capacity is only valid at the influent concentration (C_0) of the compound. It is not valid at other influent concentrations; capacity is highly dependent on influent concentration.

4.4 Adsorption System Design Considerations

4.4.1 Contactor Configuration and Operation

An important contactor design parameter is the EBCT. The EBCT has a large impact on cost and performance of an adsorbent system. In general, systems with shorter EBCTs have lower capital costs, but higher O&M costs due to more frequent adsorbent replacement. Large EBCTs will result in lower O&M costs, but higher capital costs. Most GAC system EBCTs range from 5 to 20 minutes. The EBCT can be calculated by the following equations, presented as Equation 5:

$$EBCT = \frac{V}{Q} = \frac{L}{Q/A_c} = \frac{L}{HLR} \qquad (5)$$

where V is the volume of bed occupied by the adsorbent, Q is the flow rate, L is the adsorbent bed length, A_c is the cross-sectional adsorbent bed area, and HLR is the hydraulic loading rate.

In some cases, it is advantageous to operate two contactors in series, where half of the required adsorbent media (and therefore EBCT) is contained in each. A sampling port between the two contactors allows for monitoring of breakthrough of the compound being treated. The spent adsorbent in the upper half of the system can be replaced or regenerated, and the flow of water rerouted so the contactor containing fresh adsorbent is downstream. See Sontheimer, Crittenden, and Summers (1988) and Snoeyink and Summers (1999) for more information on contactor configuration.

Package plants that contain more than one adsorbent contactor in parallel operation can achieve more efficient AURs by staggering the operation of parallel contactors (at the expense of higher capital costs). When multiple contactors are operated in parallel and staggered with respect to their operation cycles (Figure 4.1), the blended effluent of all contactors constitutes the water quality treated by the system. Under this mode of

operation, poorer water quality of older contactors is blended with high quality water from contactors containing fresh adsorbent. The water quality of each contactor may exceed the treatment objective, but the blended water quality is maintained below the treatment objective. Thus, each contactor can be operated for a longer period of time as compared to single contactor operation (USEPA 1999).

For small package plants, this mode of operation may not always be feasible since the logistics of staggering the operation of a very small number of contactors (e.g., two), due to the characteristics of the breakthrough curve of the SOC being treated could lead to an increase in capital costs. A very sharp breakthrough curve could lead to difficulties in scheduling contactors for replacement. However, O&M costs may be lowered substantially when contactors are operated in parallel-staggered mode, especially if the package plant is comprised of several contactors, or if several package plants are operated in parallel. Based on a modeling analysis of multiple contactor operation presented by the USEPA (1999), operation times for two contactors operated in parallel-staggered mode are estimated as 29 to 50% longer than that for a single contactor, assuming a treatment objective of 40 to 60% breakthrough. For the same treatment objective, the gain in individual contactor operation time is estimated as 43 to 67% for three contactors, and 55 to 83% for four contactors. The range in estimates is a function of the shape of the breakthrough curve and the relative treatment objective. These estimates may not be applicable to extremely sharp breakthrough curves.
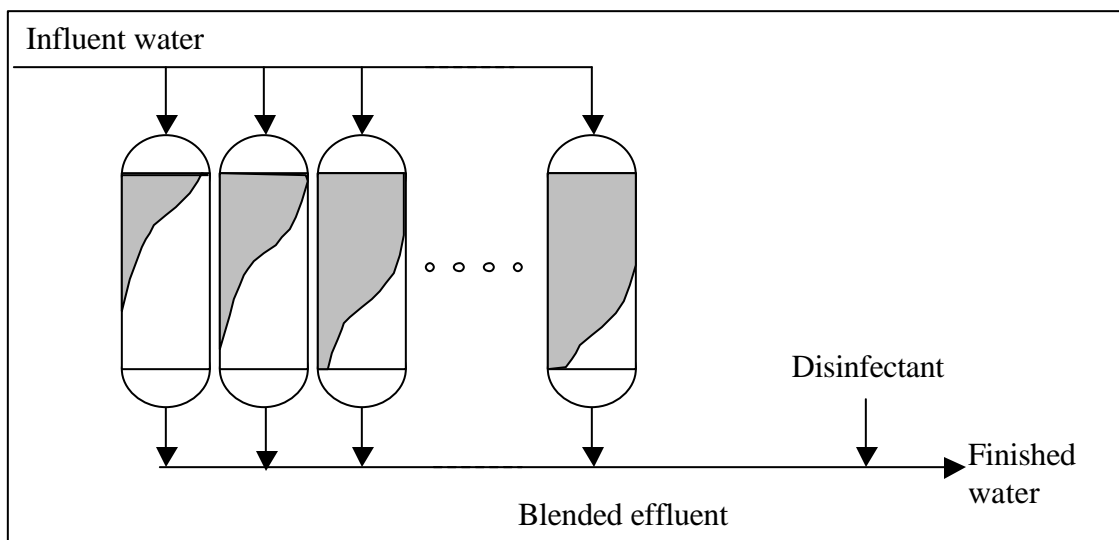
Figure 4.1 Multiple Adsorbent Contactors Operated in Parallel-Staggered Mode
(*Adapted from USEPA 1999*)

4.4.2 Types of Adsorbents

The most widely used adsorbent is activated carbon. The most commonly used raw materials for producing activated carbon used in water treatment are bituminous coal, peat, lignite, petrol coke, wood, and coconut shells. The pore structure and adsorbent properties of activated carbon are a function of the raw material used and the activation

process—activating agent, length of activation and temperature of activation. The surface area of activated carbon used for water treatment ranges from 600 to 1,500 m^2/g (Sontheimer, Crittenden, and Summers 1988).

Many types of synthetic resins have been used for adsorption of organic compounds from water. Synthetic resins vary in both the functional groups and the matrices that support functional groups (Snoeyink and Summers 1999). More information on types of ion exchange resins can be found in Clifford (1999) and Snoeyink and Summers (1999).

4.5   In-Place Regeneration

Once the effluent concentration of the SOC treated exceeds the treatment objective, the adsorbent is taken off-line and regenerated or replaced with fresh adsorbent. Some adsorption systems, especially resins, are designed for in-place regeneration. Normally, in-place reactivation is produced by addition of a strong base solution or a solvent such as acetone or isopropanol to the adsorbent bed. The ability of the regeneration step to restore the resin's capacity is important and is included as part of the verification testing.

5.0   DEFINITION OF OPERATIONAL PARAMETERS AND ABBREVIATIONS

Definitions and abbreviations that may apply to adsorptive media processes for SOC include:

1/n: Freundlich exponent constant.

Adsorbate: the molecule adsorbed on to the surface of the adsorbent.

Adsorbent: the solid material onto which molecules adsorb, such as GAC or synthetic resins.

Adsorbent capacity: mass of solute adsorbed per unit mass of adsorbent at a given point of operation, commonly equilibrium.

A_c: cross-section area of adsorbent bed.

Adsorption capacity: see adsorbent capacity.

Adsorbent usage rate (AUR): the mass of adsorbent required to treat a specific volume of water to a predetermined quality, in units of g/L or lb/1,000 gal (1 g/L = 8.35 lb/1,000 gal).

$AUR_{bt=50\%}$: AUR calculated at 50% breakthrough of the compound.

AUR_{DW}: AUR for a compound in distilled water.

AUR_{NW}: AUR for a compound in natural water (in the presence of BOM).

Bed volumes (BV): a normalized unit of throughput, defined as operation time divided by EBCT.

BOM: background organic matter. Measurement of the source water total organic carbon (TOC) concentration will provide an indicator of the level of BOM present.

Breakthrough: the point when the concentration of a target compound in the adsorbent contactor effluent reaches the treatment objective.

Breakthrough curve: a plot of effluent adsorbate concentration as a function of operation time or throughput in BV, usually extending past the breakthrough point to exhaustion. The curve is characteristic of the adsorbent, adsorbate, system parameters, and influent water quality.

BV_{bt}: BV to breakthrough.

CCL: Drinking Water Contaminant Candidate List.

C_E: equilibrium solution concentration.

C_e: concentration in the adsorbent contactor effluent.

C_0: concentration in the adsorbent contactor influent.

$\overline{C_e}$: average contactor effluent concentration for a GAC breakthrough curve operated until exhaustion.

d_{10}: effective size, defined as the sieve opening size (mm) at which 10% of the sample passes.

d_{50}: mean particle diameter, defined as the sieve opening size (mm) at which 50% of the sample passes.

Empty-bed contact time (EBCT): the hydraulic retention time of an empty contactor, defined as volume of the contactor occupied by the adsorbent divided by the flow rate, *Q*.

E_R: the regeneration efficiency (percent).

Exhaustion or saturation: the point in the breakthrough curve when the effluent concentration reaches its influent concentration, indicating that no adsorption is occurring. In practice, effluent concentrations may reach a plateau below the influent concentration because the adsorbate is removed by other mechanisms, such as biodegradation or slow adsorption kinetics.

GAC: granular activated carbon.

gpm: gallons per minute.

HLR: hydraulic loading rate.

Hydraulic loading rate: the velocity or flow rate per area at which water is loaded to the contactor (Q/A_c or L/EBCT), usually in units of gpm/ft^2 or m/hr.

K: Freundlich constant.

L: length of contactor, usually in units of meters.

Loading rate: see hydraulic loading rate.

m: meters.

m_A: mass of adsorbent.

MCL: maximum contaminant level.

MCLG: maximum contaminant level goal.

m_R: mass SOC recovered in the regeneration stream.

MRL: minimum reporting level.

min: minutes.

N_S: minimum number of paired influent and effluent samples required to be taken.

Q: volumetric flow rate.

q: adsorbent capacity, in units of mass of adsorbate/mass of adsorbent (also moles of adsorbate/mass of adsorbent).

q_E: equilibrium adsorbent solid phase concentration of the adsorbate.

$(q)_0$: mass of adsorbate adsorbed (mg/g) when the contactor effluent concentration is equal to the influent concentration.

r: apparent bed density of the adsorbent, in units of g/L, kg/m^3, or lb/ft^3.

r_{GAC}: apparent bed density of the adsorbent, in units of g/L, kg/m^3, or lb/ft^3.

RSD: relative standard deviation, calculated as the standard deviation (s) divided by the mean ($\bar{y}$).

s: standard deviation.

SCADA: Supervisory Control and Data Acquisition System.

SOC: synthetic organic chemical.

t: operation time, usually in units of days or hours.

t_{bt}: operation time to breakthrough, usually in units of days or hours.

Throughput: dimensionless time of operation in BV.

TOC: total organic carbon.

UV-254: ultraviolet absorbance at 254 nm.

V: contactor volume.

VOC: volatile organic chemical.

$\overline{\mathbf{y}}$: mean.

Y_{bt}: adsorbent throughput to breakthrough, in units of BV.

6.0   OVERVIEW OF TASKS

6.1   Task 1: Characterization of Source Water Quality

This task includes an analysis of available historic data for the source water to be treated, including the concentrations of SOCs and water quality parameters, as well as seasonal variability in concentrations. SOCs (including VOCs) already present in the source water can impact the performance of the adsorptive media for SOC removal depending on the concentration of the background SOCs and their adsorbability relative to the SOC to be tested. Furthermore, BOM can also reduce the capacity of the adsorbent for SOCs, and this "fouling" tends to be greater at higher BOM concentrations. Finally, an assessment of the need for pretreatment or the appropriateness of currently planned pretreatment must be made based on source water quality.

If sufficient historic data is not available to properly evaluate the source water quality, additional monitoring of the source water shall be performed to adequately assess source water quality.

6.2   Task 2: System Design and Operation

This task involves procedures for determining the design and operating parameters of the adsorptive media treatment system. The following tasks shall be performed or documented: the experimental mode of operation, treatment system design parameters, start-up and O&M procedures, an operations monitoring plan, and an estimate of the run time to SOC breakthrough (for verification testing beyond the minimal 13.3-day period).

6.3   Task 3: System Integrity Verification Testing (SIVT)

The objectives of this task are to demonstrate that the equipment is (1) able to initially produce a finished water as described in the manufacturer's statement of performance capabilities and (2) able to reliably operate under field conditions. The equipment is operated, monitored, and sampled for approximately two weeks. This task evaluates the short-term ability of the equipment to produce water of acceptable quality. SIVT is not designed to evaluate the long-term ability of the equipment to treat water containing SOCs. SIVT must be performed at least once for each system evaluated under this TSTP.

6.4   Task 4: Adsorption Capacity Verification Testing (ACVT)

After Task 3 has been performed, the long-term effectiveness of the treatment system to remove SOCs shall be evaluated by Task 4. The main purpose of Adsorption Capacity Verification Testing (ACVT) is to evaluate the capability of the adsorptive media treatment system for removal of SOCs. Specifically, the AUR will be determined for the SOC tested. The AUR will be assessed under the design and operation conditions of the treatment system, as well as influent water quality conditions of the source water after pretreatment, if any. Influent and effluent sampling guidelines are described based on the experimental design (constant influent with low variability, constant influent with high variability, or attenuation of a spiked influent).

6.5   Task 5: In-Place Regeneration

Some treatment systems may use adsorptive resins that can be regenerated in-place, and may incorporate regeneration capability as an integral part of the equipment. In such cases, the objective of this task is to evaluate regeneration effectiveness and the impact of regeneration of performance.

6.6   Task 6: Operation and Maintenance Manual

The FTO shall obtain the manufacturer-supplied O&M manual(s) to evaluate the instructions and procedures for their applicability during the verification testing period. Recommendations for criteria for the evaluation of O&M manuals for package plants employing adsorptive media for SOC removal are given in this section.

6.7   Task 7: Data Management

The objective of this task is to establish an effective field procedure for data management at the field operations site and for transmission of data obtained during the verification testing from the FTO to NSF.

6.8   Task 8: Quality Assurance/Quality Control

The objective of this task is to develop a Quality Assurance/Quality Control (QA/QC) plan for verification testing. This important item will assist in obtaining an accurate measurement of operational and water quality parameters during adsorptive media system verification testing.

7.0   TESTING PERIOD

Guidelines for adsorptive media equipment verification testing frequency and duration are given in this section. To some extent, the number and length of test runs conducted will depend on how rigorous a demonstration the equipment manufacturer wishes to perform, and how strong a statement of performance capabilities the manufacturer would like to be able to make about equipment performance.

During initial operations, a manufacturer shall evaluate equipment operation and determine the appropriate conditions that result in effective treatment of the feed water.   After an initial

operations step, a test run shall consist of operating the treatment equipment for 13 days and one 8-hour shift of actual run time, the minimum required testing duration to satisfy the requirements of this TSTP. Although 13.3 days of operation are adequate to verify system integrity (e.g., mechanical and hydraulic functioning, excessive headloss, channeling, etc.), SOCs at levels typically found in natural source waters will not achieve breakthrough within 13.3 days of operation. Equipment manufacturers should recognize that a statement of performance capabilities that their adsorption system could treat a natural source water effectively for 13.3 days without exhibiting SOC breakthrough would not be impressive. For this reason, it is expected that the test will be made more rigorous (strengthening the statement of performance capabilities a manufacturer could make) by operating the test equipment for a longer period or until breakthrough of SOCs is achieved. Task 3 shall consist of 13.3 days of testing for verification of system integrity. Task 4, adsorption capacity verification testing, shall verify the long-term effectiveness of the treatment system to remove SOCs.

For tests not running until breakthrough, the AUR reported can be based on no greater a run time than the total operation time during which the equipment was operated as of the last pair of SOC influent and effluent samples taken. To verify a minimum AUR, or longest possible run time while maintaining the target SOC concentration below the treatment objective as stipulated in the manufacturer's statement of performance capabilities, the system must be operated until breakthrough is achieved. Once breakthrough occurs, and the effluent SOC concentration is greater than the treatment objective stated in the manufacturer's statement of performance capabilities, it is no longer necessary to continue operation of the system, unless a complete breakthrough curve is desired. It may be desirable to capture the complete breakthrough curve, however, as the AUR can be calculated based on the last effluent sample with concentration lower than the treatment objective, or by an interpolation of a best-fit curve approach to a complete breakthrough curve data set. These options are described in Section 11.5.

Definition of *target treatment objective exceeded*. Due to analytical and experimental variability, the concentration of the SOC in the contactor may increase above the treatment objective, only to fall below it on a subsequent sampling. Therefore, it is recommended that verification testing be designed to produce the best possible quality data set, one that clearly shows the breakthrough curve trend and minimizes scatter in the data caused by analytical and experimental variability. If the data set clearly shows a breakthrough trend, with some variability, a best-fit curve may be used to fit the data, and the point at which the effluent SOC concentration exceeds the treatment objective can be interpolated. Otherwise, the *last* sample taken (with concentration below the treatment objective) prior to the *first* point at which the effluent equals or exceeds the treatment objective shall designate the run time for purposes of calculation of the AUR. It is worthwhile to develop a very good quality data set that can be fit to a curve. Utilizing the run time of the last data point prior to the first data point with a concentration above the treatment objective will yield a conservative estimate of the run time to breakthrough.

The duration of verification testing to determine the AUR based on operation until the SOC tested reaches breakthrough for many SOCs will be longer than 13.3 days. The length of the testing period will depend on the adsorbability and concentration of the compound tested. Highly adsorbable compounds may yield operation times greater than one year in length prior to breakthrough. The run termination criteria can be based on achieving breakthrough (as defined

by an effluent SOC concentration exceeding the MCL or other treatment objective). In this case, the testing period would be the shortest time necessary to verify the AUR. The AUR will be determined for a test regardless of the operation time; when the test is terminated prior to breakthrough, the AUR will be calculated based on the total run time for which the SOC was treated while effluent levels were maintained below treatment objective. For verification testing operating until breakthrough or beyond, a best-fit curve of the data set can be used to interpolate the run time used for the AUR calculation. In addition, a full breakthrough curve is information that may be of benefit to the manufacturer. Determining the AUR is explained in more detail in Task 2, System Design and Operation.

For ACVT of attenuation of a spiked SOC compound, the testing period shall begin when the application of the spike ends (see examples in Table 3.1). The amount of time the system is operated prior to, during, and after the application of the spike shall be specified by the manufacturer. Ideally, the time period during which the system is operated after the application of the spike shall be long enough to demonstrate effective attenuation of the influent pulse.

8.0   TASK 1: CHARACTERIZATION OF SOURCE WATER QUALITY

8.1   Introduction

A characterization of the source water quality is necessary to identify SOCs present in the source water and to evaluate the impact of other water quality parameters or contaminants on adsorption of SOCs. The presence of other SOCs at detectable concentrations (e.g., > 1 µg/L) can negatively impact the adsorption of the SOC being tested due to competitive adsorption. The significance of the effect will depend on the concentration of background SOCs and their adsorbability relative to the SOC being tested. For studies evaluating AURs at breakthrough, estimates of run times to breakthrough must be examined together with existing water quality to determine the potential reliability of the estimates.

BOM in water can reduce the adsorption capacity of SOCs. Since all source waters contain organic matter, some impact is expected. Higher levels of BOM will typically have an increased impact on adsorption of SOCs, but characteristics of the organic matter are important and the adsorbability of the SOC is also a factor. Measurement of the source water TOC concentration will provide an indicator of the level of BOM present. Pretreatment prior to the adsorption process may reduce TOC levels. Other water quality indicators such as pH, temperature, and conductivity may impact adsorption and should be quantified.

Seasonal variability in water quality may impact the results of equipment verification testing since testing duration often spans several months. Assessment of seasonal variability in water quality prior to equipment verification testing will help in evaluating whether the proposed water source is appropriate, what type of pretreatment might be necessary, or the appropriateness of pretreatment that is already in place. Source water variability should be evaluated in relation to the expected length of the testing period

8.2   Objectives

The objectives of this task are to:

- Identify SOCs known to occur in the proposed source water;
- Determine typical values for concentrations of other water quality parameters;
- Identify any characteristic seasonal trends in concentrations of SOCs and other water quality parameters;
- Determine the level of BOM present in the source water; and
- Assess the need for pretreatment prior to adsorption, or assess the appropriateness of designed pretreatment.

If historic water quality data is not available for one or more parameters, an analysis of the proposed source water shall be performed for these parameters.

8.3   Work Plan

A combination of laboratory analysis and review of historic data should provide the needed data to evaluate source water quality. Sources for historic data include municipalities, laboratories, United States Geographical Survey (USGS), EPA, and local regulatory agencies. Analysis of the proposed source water prior to verification testing shall be performed for those parameters for which no historic data can be located. Ideally, 2 to 5 years of historic water quality data for each parameter will be available for the proposed source water. At a minimum, 1 year of data sampled at no greater than 3-month intervals, may constitute historic data.

The FTO shall prepare a Source Water Quality Evaluation Report containing the historic and monitored data obtained, a statistical evaluation of the data, and graphical summaries for all parameters. This report shall be shared with NSF so that NSF and the FTO can determine the significance of the data for use in developing a PSTP. If the source water quality data is not obtained or analyzed properly, the verification test may fail or the results of the test may not be considered acceptable.

The report shall list all SOCs previously identified in the source water, emphasizing those encountered most recently and those that show a seasonal reoccurrence that might impact equipment verification testing.

A description of the source water should also be included in the Source Water Quality Evaluation Report including, but not limited to, the following items:

- Nature of water source (i.e., ground water or surface water);
- Location of water source;
- Size of watershed;
- Brief description of land use; and
- Potential sources of pollution.

If the SOC concentrations in the source water are below that described by the manufacturer's statement of performance capabilities, higher SOC concentrations can be obtained during verification testing by spiking.

8.4 Analytical Schedule

When historic data are not available, it is recommended that at least 12 months of monthly (or more frequent) monitoring be performed prior to verification testing. At a minimum, 2 samples, spaced by a minimum of 4 weeks and a maximum of 12 months, shall be obtained for the parameters listed in Table 8.1.

Table 8.1 Source Water Sampling Requirements*

Parameter	Notes
Alkalinity	
Ammonia	Optional
Calcium hardness	
Conductivity	Optional
Dissolved oxygen	Required for groundwater sources only.
Hydrogen sulfide	Required for groundwater sources only.
pH	
SOC scan	*Standard Method*s 6410B, 6420C, 6431C, 6440C, 6630D. EPA Method 525.2 (extended for broad spectrum)
Temperature	
Total chlorine	Total chlorine residual must be < 0.1 mg/L during verification testing.
Total dissolved solids (TDS)	Optional
Total hardness	
TOC	
Total suspended solids (TSS)	
Turbidity	
UV-254	

*See Table 10.1 for analytical methods.

All data collected, whether from historic records or sampled directly and analyzed, shall be summarized in conjunction with the sampling date. Results shall include the average, minimum, maximum, and number of data points in the data set. For sample sets of eight or more, the results shall also include the standard deviation and confidence interval for each analyte. When summarizing SOC data of sample sets of eight or more, the 10th, 25th, 50th, 75th, and 90th percentiles shall also be reported.

For each water quality parameter, a graph of concentration vs. sampling date shall be constructed. This type of graph aids in the interpretation of seasonal trends that may impact

equipment verification testing. Where convenient (e.g., calcium and total hardness) more than one parameter may be combined in one graph. The concentration of each parameter shall be plotted against actual sampling date. A box-and-whisker style plot to demonstrate the distribution of each parameter is also recommended.

8.5   Evaluation Criteria

The source water quality shall be evaluated in the context of the manufacturer's statement of performance capabilities for the removal of SOCs. The source water quality shall also be evaluated with regards to the appropriateness of pretreatment in place prior to adsorption or the need for pretreatment. The source water quality should challenge the capabilities of the equipment, but should not be beyond the range of water quality suitable for treatment by the equipment. Other evaluation criteria are given below:

- Pretreatment for particle removal may be required if the source water turbidity is greater than 5 to 10 NTU or if the source water TSS exceeds 5 mg/L. Manufacturer specifications regarding pretreatment for particle removal should be followed.
- Pretreatment for hardness may be required if the source water hardness is greater than the manufacturer's recommendations or if the pH, alkalinity, and hardness analyses indicate that the water is unstable.
- Adjustment of source water pH may be required if the source water pH is outside the manufacturer's specifications. Water pH can impact adsorption efficiency and, at extremes, may pose a corrosion hazard to the equipment.

9.0   TASK 2: SYSTEM DESIGN AND OPERATION

9.1   Introduction

This task involves procedures for determining the design and operating parameters of the adsorptive media treatment system.

9.2   Objectives

The objectives of this task are to:

- Establish the experimental design (mode of operation: constant, spike, or variable influent; SOC spiking);
- Document treatment system design parameters;
- Describe system start-up and O&M procedures;
- Develop an operations monitoring plan; and
- Estimate the run time to SOC breakthrough (for verification testing beyond the minimal 13.3-day period).

Documentation of the treatment system design parameters shall be provided to EPA, NSF, and peer reviewers for evaluation.

Each PSTP will include a list of criteria for evaluating O&M information. This shall be compiled and submitted for evaluation by EPA, NSF and technical peer reviewers. An example is provided in Table 9.1. The purpose of this O&M information is to allow utilities to effectively choose a technology that their operators are capable of operating, and to provide information on how many hours the operators can be expected to work on the system. Information about obtaining replacement parts and ease of operation of the system would also be valuable.

Table 9.1 Maintenance and Operability Information for Adsorptive Media Package Plants

Maintenance Information

Equipment	Maintenance frequency	Replacement frequency
Pumps		
Valves		
Motors		
Mixers		
Chemical mixers		
Water meters		
Pressure gauges		
Cartridge filters		
Seals		
Piping		

Operability Information: Rank 1 (easy) to 3 (difficult) or N/A (not applicable)

Operation aspect	Rank
Chemical feed pumps calibration	
Flow meters calibration	
Pressure gauges calibration	
pH meters calibration	
TDS or conductivity meters calibration	

9.3 Work Plan

The PSTP shall specify information on the design and operation of the adsorption system being evaluated. The work activities of this task are described below.

Experimental design. Three types of experimental designs are allowable under this TSTP: (1) constant influent with low variability, (2) constant influent with high variability, and (3) attenuation of a spiked influent. In general, this TSTP is designed for verification testing of a

system treating a single SOC at a constant influent concentration with low variability. In some cases, the manufacturer's statement of performance capabilities may be based on a system treating a water with high variability in SOC concentration, or it may be based on attenuation of a spiked influent. In these cases, the experimental design will be based on testing under the influent conditions to be verified.

If the SOC to be tested for removal by adsorptive media is not present in the influent to the adsorptive media, it shall be spiked into the influent water so that the resulting concentration is equal to the targeted concentration. A sampling point shall be located downstream of the spike location, but prior to the adsorption media, to confirm the influent concentration during testing. All influent samples shall be taken from this sampling point. For testing of highly variable influent conditions or attenuation of a spike influent, spiking shall simulate the conditions of high variability or a spiked influent. For example, a spike concentration of 50 µg/L diquat for a duration of 3 days could simulate a spike influent for an attenuation study. In all cases, spiking of the SOC shall match as closely as possible the influent conditions described in the manufacturer's statement of performance capabilities.

This TSTP is designed to assess the removal of only one SOC in the adsorptive system influent. If a manufacturer's statement of performance capabilities is based on simultaneous treatment of multiple compounds, this should be simulated in the adsorption influent by spiking additional compounds as necessary. Some sections in this document, such as the estimation of run time to breakthrough, are designed based on a single compound influent and are not directly applicable to simultaneous treatment of multiple compounds. In general, run times will be lower (AURs will be higher) for systems subjected to multiple influent compounds as compared to those treating an influent water with a single compound, due to the effects of competitive adsorption.

System design parameters. The FTO shall document the adsorption system design parameters listed in Table 9.2. The PSTP shall contain a simple schematic of the entire treatment system, including any pretreatment processes, showing sampling points, spike location, valves, pumps, etc. An example of this schematic is shown in Figure 9.1.

Start-up and O&M procedures. System start-up and O&M procedures based on manufacturer specifications shall be described by the FTO in the PSTP. Specific procedures for backwashing and regeneration shall be included. Start-up procedures may include bed preparation such as pre-wetting, degassing, and fines removal. Start-up itself will involve setting valves to the correct run status, starting the feed pump to deliver test water to the system, adjusting the flow rate to the target value, and other procedures as required by the manufacturer. Assuming continuous operation, the system shall be operated for 24 hours before sampling commences. For purposes of calculating run times, the start of operation shall constitute the beginning of the run.

Table 9.2 Adsorption System Design Parameters

Parameter	Units	Notes
General		
Test type		Constant influent with low variability, constant influent with high variability, or attenuation of spiked influent
Test location		
Utility name		
Water source		Surface or ground water
Water source name		
Water source type (surface water only)		Reservoir, lake, river, etc.
Feed mode (semi-batch or continuous)		Describe
Spiked SOC compound(s), if any		
Target spike concentration(s)	µg/L	
Spiking method		Describe
Pretreatment processes		Describe
Adsorptive Media		
Media manufacturer		
Media type		Bituminous, lignite, etc.
Media trade name		
Mesh size	US std mesh sizes	Upper x lower
Effective size, d_{10}	mm	Indicate whether measured in field or as reported by manufacturer
Mean particle diameter, d_{50}	mm	Indicate whether measured in field or as reported by manufacturer
Apparent bed density, r_{GAC}	g/L, kg/m^3, lb/ft^3	Indicate whether measured in field or as reported by manufacturer
Adsorption System		
Contactor configuration		Describe
Number of adsorbers in series		
Adsorber dimensions	m	Diameter, depth and any other appropriate dimensions
BV per adsorber	L	
Bed depth for each adsorber	m	
Volumetric flow rate	mL/min	
EBCT	min	Clearly report total EBCT if more than one contactor in series
Hydraulic loading rate (or superficial velocity)	m/hr	
Mass of dry media per adsorber	kg	
Regeneration system, regenerant fluid, and regeneration procedure		Describe, if system has in-place regeneration capacity
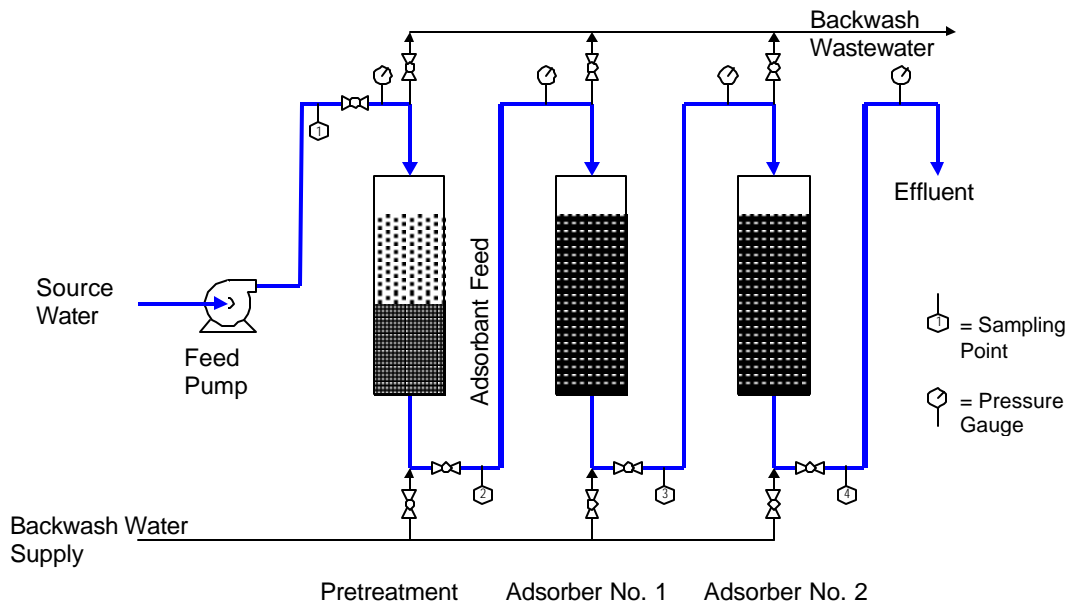
Figure 9.1 Example of an Adsorption Treatment System Schematic

Operation with a continuous flow of test water from the source is preferable, but continuous feeding from a batch-filled feed tank is acceptable. If a batch feed tank is used, the residence time in the feed tank should be minimized to avoid volatilization losses of SOCs. (Although the SOC to be tested may be considered nonvolatile, other SOCs present in the source water that may impact adsorption performance may be semi-volatile or volatile.) The system flow rate should be adjusted as necessary during operation to maintain the system flow rate within 5% of the target flow. The system should be operated continuously to the extent possible, and only shut down for backwashing, necessary maintenance, or regeneration (for in-place regenerable media). Any down time shall be recorded and not included in the cumulative run time or throughput volume calculations. The reason for each shutdown shall be documented. Adsorbers using non-disposable media should be backwashed at least once during the test period. The manufacturer shall specify backwash parameters including, but not limited to, flow rate, percent bed expansion, and duration of expansion.

If the system is designed for continuous operation, then the system should be evaluated under continuous operation for verification testing. If the system is designed for intermittent or continuous operation, than either mode of operation during verification testing is acceptable. It is preferable that the system be operated continuously. As with down time, total operation time under intermittent operation constitutes the sum of the amount of time the system is in operation providing treated water.

Operations monitoring plan. The FTO shall provide an operations monitoring plan in the PSTP, including operational parameters to be monitored, monitoring points, and monitoring frequencies. At a minimum, flow rate, pressure before and after each adsorption or filtration bed and headloss (differential pressure) across each bed, influent temperature, and influent pH should be monitored routinely. Other parameters recommended by the equipment manufacturer should

also be included. Influent and effluent sampling times should also be specified in the monitoring plan.

Estimation of throughput to breakthrough. For systems evaluating single SOC adsorption under constant influent conditions with low variability, the following section provides a methodology for estimating the run time to breakthrough. This step should still be followed if verification testing is planned for the minimum 13.3-day period, to confirm that breakthrough will most likely not occur within the 13.3-day run time. If the objective of verification testing is to achieve breakthrough of the compound treated, an estimation of throughput to breakthrough is critical for purposes of estimating the duration of the operation cycle, and for purposes of designing a sampling plan to effectively capture the breakthrough curve and/or the breakthrough point (point at which the effluent concentration exceeds the treatment objective).

If the run time estimate to breakthrough is lower than 13.3 days, then effluent sampling during verification testing should be designed assuming that the AUR will be based on operation of the system to breakthrough. This should be done even if verification testing is planned for only 13.3 days: breakthrough may occur earlier than 13.3 days, and sampling guidelines should be followed to best capture the point of breakthrough for use in the AUR calculation. The system must be operated for a minimum 13.3-day period regardless of when the treatment objective is exceeded. If it is very likely that the treatment objective will be exceeded during the 13.3-day minimum verification period, then it is recommended that the manufacturer evaluate modifications to the system design, such as an increase in the adsorber EBCT.

This method of estimating adsorbent bed life to breakthrough is based on a methodology described in Snoeyink and Summers (1999). It is assumed that all the adsorbent in the adsorber will reach equilibrium with the influent concentration, that isotherm data can be successfully extrapolated to the influent concentration to estimate the capacity, and that the length of the mass transfer zone is negligible (a very sharp breakthrough curve is assumed).

This method is based on isotherm data using the Freundlich equation, presented as Equation 6:

$$(q)_0 = K C_0^{1/n} \tag{6}$$

where $(q)_0$ is the mass adsorbed (mg/g) when the effluent concentration, C_e, is equal to the influent concentration, C_0; and K and $1/n$ are constants. Literature sources should be consulted for appropriate values of K and $1/n$ (Snoeyink and Summers 1999; Sontheimer, Crittenden, and Summers 1988; Faust and Aly 1998; Speth and Miltner 1990, 1998).

The AUR (mass of adsorbent in the column divided by the volume treated to breakthrough) is then estimated from isotherm data in the formula presented as Equation 7:

$$\text{AUR(g/L)} = \frac{(C_0 - \overline{C_e})\,\text{mg/L}}{(q)_0\,(\text{mg/g})} \tag{7}$$

where $\overline{C_e}$ is the average effluent concentration during the entire run.

Using this estimate of the AUR, the volume of water that can be treated per unit volume of carbon is estimated by Equation 8:

$$Y_{bt} = \frac{r_{GAC}}{AUR} \tag{8}$$

where Y_{bt} is the throughput in BV and r_{GAC} is the apparent density of the adsorbent.

Finally, the operation time to breakthrough, t_{bt}, in days can be calculated from the throughput by Equation 9:

$$t_{bt} = \frac{Y_{bt} \cdot EBCT(min)}{1,440(min/\ day)} \tag{9}$$

The value of t_{bt} estimated by Equation 9 is a rough estimate of the time to breakthrough, based on several assumptions noted above. It should be used with care, and a generous safety factor should be included, as breakthrough may occur much earlier or later than this run time estimate due to several factors described previously.

Several limitations of this method exist and should be noted. First, it is only valid for a single long contactor, or for columns in series in which all of the adsorbent in the column is in equilibrium with the compound at the influent concentration. Second, this method does not account for the potential impact of biodegradation of the compound during treatment or slow adsorption kinetics. Finally, the impact of competition for adsorption sites on adsorption equilibrium in a batch is not necessarily the same as that on adsorption in a column. Competitive effects may have a larger impact on adsorption in a column than in a batch study (Snoeyink and Summers 1999).

Another limitation of the AUR estimated by this method is that adsorption capacity is based on experiments performed in distilled water, in the absence of BOM that may have a significant impact on adsorption capacity in the field. A natural water correction factor has been proposed, whereby the distilled water AUR (AUR_{DW}) is adjusted, yielding a better estimate of the natural water AUR, AUR_{NW} (Ford et al., 1989; USEPA 1990). For this relationship, the units of AUR are lb/1,000 gal. The correlation described by Equation 10a is valid for values of $AUR_{DW} = 0.564$ lbs/1,000 gal. For values of $AUR_{DW} > 0.564$ lbs/1,000 gal, the value for AUR_{NW} used is equal to AUR_{DW}, as described in Equation 10b.

$$AUR_{NW} = 0.7443 \cdot (AUR_{DW})^{0.4835} \qquad AUR_{DW} = 0.564 \text{ lbs/1,000 gal} \tag{10a}$$

$$AUR_{NW} = AUR_{DW} \qquad AUR_{DW} > 0.564 \text{ lbs/1,000 gal} \tag{10b}$$

Example. To estimate the adsorbent bed life of a 10 minute EBCT GAC ($r_{GAC} = 500$ g/L) contactor treating dalapon at a constant influent concentration of 300 µg/L, first look up the Freundlich K and $1/n$ values for dalapon, as shown in Equations 11 and 12:

$$K = 23 \ (\text{mg/g})(\text{L/mg})^{1/n} \tag{11}$$

$$1/n = 0.224 \tag{12}$$

Use Equation 6 to calculate $(q_e)_0 = 17.6$ mg/g. Assuming $\overline{C_e} = 0$, use Equation 7 to estimate the AUR_{DW}, 0.0171 g/L (0.142 lb/1,000 gal). Correcting this value using Equation 10a, gives $AUR_{NW} = 0.290$ lb/1,000 gal or 0.0348 g/L. The throughput, Y_{bt}, is 14,400 BV, calculated by Equation 8. Finally, the estimate of operation time to breakthrough, t_{bt}, is calculated by Equation 9 , which is 99.8 days.

Although Equation 10a includes a correction factor for the impact of BOM on adsorption, it does not account for the impacts of biodegradation or competitive effects due to the possible presence of other SOCs. The BOM correction is only an estimate; the actual impact of BOM on performance will vary, depending on the characteristics of BOM, concentration, and the amount of time the adsorbent has been preloaded with BOM prior to verification testing of SOC adsorption.

The above analysis is applicable to single contactor operation. For package plants that operate two or more contactors in parallel, with staggered operation cycles, longer run times are expected for a given treatment objective maintained in the blended effluent of all contactors. Depending on the shape of the breakthrough curve, and the operation time to initial breakthrough for a single contactor, the run time of each of two to four contactors operated in parallel-staggered mode may be increased by 30 to 80%. For extremely sharp breakthrough curves, this mode of operation may not yield any significant benefit, depending on the ratio of the treatment objective to the influent concentration, in relation to the number of parallel contactors. It is recommended that parallel operation of adsorbent contactors be modeled to yield the best estimate of operation times based on maintaining a treatment objective in the blended effluent. See USEPA (1999) for an analysis of multiple contactor effluent blending for GAC. Alternatively, the effluents of each contactor can be monitored, with the experimental results of breakthrough in the first adsorber used to refine the run time estimate based on the blended effluent.

9.4   Analytical Schedule

System flow rate, pressures and headloss across each contactor, and other operational parameters should be measured at the frequencies indicated in Table 9.3. Ideally, flow rate and headloss are measured on a continuous basis. The headloss before and after backwashing should be recorded as a measure of backwash effectiveness. A record of backwashing frequency and backwash water volume produced should also be maintained. See Table 9.3 for further details. Stoppage time should be recorded, including the exact times of stoppage and restart, as well as the reason for the stoppage. This will allow for an accurate assessment and adjustment for the impact of stoppage time on the effective operation time. The cumulative amount of stoppage time that must be taken into account in calculating the total run time of verification testing should be continuously updated.

Table 9.3 Schedule for Observing and Recording Package Plant Operating and Performance Data

Operational Parameter	Action
Feed water and adsorbent contactor volumetric flow rate	When staffed, check and record every 2 hours; adjust when >5% above or below target. Record before and after adjustment.
GAC contactor headloss	Record initial clean bed total headloss at start of run and record total headloss every 2 hours, when staffed.
Filter backwash	Record time and duration of each filter washing. Record volume used to wash filter. Record headloss before and after backwashing.
Electric power	Record meter daily.
Chemicals used	Record name of chemical, supplier, commercial strength, and dilution used for stock solution to be fed (if diluted) for all chemicals fed during treatment.
Chemical feed volume and dosage	Check and record every 2 hours. Refill as needed and note volumes and times of refill.
RPM of rapid mix and flocculator (if applicable)	Check daily and record.
Hours operated per day	Record in logbook at end of day or at beginning of first shift on the following work day. Any stoppage of flow to the contactors shall be recorded. Flow stoppage that exceeds 2 hours per a 24-hour period or 7 hours per week shall be accounted for by not including it in the cumulative operation time.

9.5   Evaluation Criteria

The contactor flow rate should be maintained within 5% of the target value. The flow rate should be adjusted when it is outside of this range. Criteria for backwashing are usually based on a headloss threshold and should be provided by the equipment manufacturer. The criteria will likely vary depending on EBCT on adsorbent media size.

10.0 TASK 3: SYSTEM INTEGRITY VERIFICATION TESTING

10.1 Introduction

This task will evaluate the short-term ability of the equipment to produce water of acceptable quality. SIVT is not designed to evaluate the long-term ability of the equipment to treat water containing SOCs. SIVT must be performed at least once for each system evaluated under this TSTP.

10.2 Objectives

The objectives of this task are to demonstrate that the equipment is (1) able to produce a treated water within performance objectives, and (2) able to operate reliably under field conditions.

Specific objectives include:

- Characterization of the influent SOC concentration and variability and
- Evaluation of the concentrations during testing of other water quality parameters that impact SOC adsorption, including TOC, UV-254, pH, temperature, and other background SOCs.

10.3 Work Plan

The manufacturer and its designated FTO shall specify in the PSTP the operating conditions to be evaluated during verification testing and shall supply written procedures on the O&M of the treatment system.   For applications where the treatment system is expected to operate continuously, the equipment shall be operated continuously for a minimum of 320 hours (13 full days plus one 8-hour work shift) to complete SIVT. For applications where the treatment system is expected to operate intermittently, such as for very small systems, the equipment shall be operated for a minimum of 2 hours continuously each day for a total minimum operation time of 320 hours. For adsorptive media vessels operated as post-filter adsorbers, the media filters on-line upstream of the adsorptive media vessels shall be operated from start-up until turbidity breakthrough or terminal headloss is attained, at which time the media filters shall be backwashed and operation shall resume.

For adsorptive media filters that are not operated as post-filter adsorbers, but that specify a backwash cycle as part of normal operation, at least one backwashing event, located between day 3 and 10 of SIVT, shall be included in the test. This backwash shall be performed even if the backwash criteria (e.g., volume treated, headloss, pressure drop) are not experienced or met. Backwashing the adsorber a few days prior to the end of the SIVT allows for an evaluation of system performance after backwashing. For systems that are backwashed more often (e.g., every 3 to 4 days), at least one backwashing event shall occur between days 3 and 10 of SIVT.

Interruptions in the treatment system shall be documented and are allowed only for backwashing events and required equipment maintenance. Since adsorptive media performance is a function of EBCT, which is dependent on the volumetric flow rate, it is critical that verification testing be conducted at a set flow rate that is maintained within 5% of the design value.

Any influent spiking irregularities that occur during the study must be reported by the FTO. This includes, but is not limited to, events such as a period of time when the contaminant feed pump is not pumping at the correct flow rate, a period of time when the contaminant stock solution runs out, or a period of time when volatile losses may have occurred from the stock solution. The FTO must document the occurrence of these events, including a clear description, corrective actions taken, the length of time during which the irregularity occurred (this may have to be estimated), and the approximate dates and times when the event began and ended. The description should include the FTO's opinion as to the severity of the irregularity, in terms of its impact on testing results.

Package plants that contain multiple adsorbent contactors to be operated in parallel should follow manufacturer's guidelines for system start-up. If the contactors are to be operated in a staggered format, then each contactor should be brought on-line sequentially, as designated by the manufacturer's instructions. If the SOC to be treated is already present in the influent water, then the start of verification testing should take place when the first contactor is brought on-line. Alternatively, each contactor can be brought on-line sequentially until all contactors are in operation prior to the start of verification testing if the SOC to be tested is not present in the source water. Spiking of the SOC to be tested would begin when all contactors are operational. The FTO shall provide the details for spiking in the PSTP, such as materials for preparation of the spike solution, details about feed pumps, reservoirs and mixers, and sampling to confirm influent concentrations.

Water Quality Sample Collection. Water quality data shall be collected at regular intervals as described in the analytical schedule (see Table 10.1). Additional or more frequent analyses may be stipulated at the discretion of the FTO. Sample collection frequency and procedure shall be defined by the FTO in the PSTP.

The PSTP shall identify the treated water data quality objectives (DQOs) to be achieved in the statement of performance capabilities of the equipment to be evaluated in the verification test. The PSTP shall also identify in the statement of performance capabilities the specific SOCs that shall be monitored during equipment testing. The statement of performance capabilities prepared by the FTO shall indicate the range of water qualities and operating conditions under which the equipment can be challenged while successfully treating the contaminated water supply.

It should be noted that many of the packaged and/or modular drinking water treatment systems participating in an SOC removal verification test will be capable of achieving multiple water treatment objectives. Although the SOC TSTP is designed for the removal of SOCs, the manufacturer may want to examine the capabilities of the treatment system for removal of additional water quality parameters. Appropriate EPA/NSF ETV protocol(s) and TSTP(s) should be consulted.

Many of the water quality parameters described in this task shall be measured on-site by the NSF-qualified FTO. For the water quality parameters requiring analysis at an off-site laboratory, water samples shall be collected in appropriate containers (containing necessary preservatives as applicable) prepared by a laboratory that is certified, accredited or approved by a state, a third-party organization (i.e., NSF), or the EPA. Representative methods to be used for

measurement of water quality parameters in the field and lab are identified in Table 10.1. If new methods are published and approved or current methods updated, the most current methods shall be used.

Sample collection procedures for intermittent flow systems must ensure that freshly treated water is collected and not water that was stagnant in the bed. For intermittent flow systems, sample collection should occur during a continuous flow period, after a minimum of 10 BV has passed through the system or after 1 hour of continuous flow.

Table 10.1 Required Water Quality Analyses and Minimum Sampling Frequencies for SIVT

Parameter	Frequency	Sampling Location[1]	Standard Method	EPA Method	Analysis Location[2]
SOCs	Daily	INF, EFF	See Table 10.2	See Table 10.2	2
Alkalinity	Weekly	INF	2320 B		3
Ammonia	Weekly	INF	4500-NH$_3$ D, G	350.1	3
Calcium hardness	Weekly	INF	3111 D; 3120 B; 3500-Ca D	200.7	3
Chlorine, free	Daily[3]	INF	4500-Cl D, F, G, H		1
Chlorine, total	Daily[3]	INF	4500-Cl D, E, F, G, I		1
Conductivity	Weekly	INF	2510 B	120.1	3
Dissolved oxygen	Weekly	INF	4500-O B, G		1
Hydrogen sulfide	Weekly	INF	4500-S^{2-} D, E, F, G		3
pH	Daily	INF, EFF	4500-H$^+$ B	150.1; 150.2	1
Temperature	Daily	INF	2550 B		1
TDS	Weekly	INF	2540 C		3
Total hardness	Twice weekly	INF	2340 B, C		3
TOC	Daily	INF, EFF	5310 B, C, D		2
Total suspended solids (TSS)	Weekly	INF	2540 D		3
Turbidity	See note[4]	INF, EFF	2130 B	180.1	1
UV-254	Twice weekly	INF, EFF	5910 B		3

[1] INF: Influent; EFF: Effluent. Where both influent and effluent sampling is required, samples should be paired (taken at approximately the same time).

[2] Analysis location: 1-Must be analyzed on-site; 2-Must be analyzed by a laboratory that is certified, accredited or approved by a state, a third party organization (i.e., NSF), or the EPA; 3-Can be analyzed either on-site or by a laboratory that is certified, accredited or approved by a state, a third party organization (i.e., NSF), or the EPA.

[3] Free and total chlorine should be analyzed daily to ensure the absence of chlorine in the influent water. The FTO may require less frequent monitoring if there is no reason to expect free or total chlorine in the influent water. This will depend on the water source.

[4] For contactors operated in filter-adsorber mode, a continuous turbidimeter should be used. Daily samples should be analyzed using a bench-top turbidimeter to confirm the continuous turbidimeter readings. For contactors operated in post-filter adsorber mode, the minimum sampling frequency for turbidity is weekly.

In the case of water quality samples to be shipped to the laboratory that is certified, accredited or approved by a state, a third party organization (i.e., NSF), or the EPA for analysis, the samples shall be collected in appropriate containers (containing preservatives as applicable) prepared by the laboratory. These samples shall be preserved, stored, shipped, and analyzed in accordance with appropriate procedures and holding times, as specified by the analytical laboratory. Acceptable methods for the required analytical procedures are described in Task 8, Quality Assurance/Quality Control. At a minimum, all PSTPs shall include a table(s) showing all parameters to be analyzed, the analytical methods, the laboratory reporting limits or quantitation limits, sample volume, bottle type, preservation method, and holding time.

If the known or expected concentration of the SOC or SOCs to be tested in the influent water is lower than desired for verification testing, then the influent water should be spiked to achieve the desired concentration. The FTO shall stipulate in the PSTP procedures to be followed for influent spiking. These should be based on information reported in the literature and the experience of the FTO and manufacturer with the compound or compounds to be tested.

In general, three types of experimental designs for ACVT are allowable under this TSTP (as described in Section 9.3). SIVT should be conducted following the procedures applicable to the experimental design to be tested during ACVT. Furthermore, once the SIVT phase is complete, testing may continue under the guidelines and procedures described for ACVT. It is expected that SIVT will be performed with a constant influent concentration of the SOCs to be tested.

10.4   Analytical Schedule

10.4.1 Operational Data Collection

The FTO shall provide written procedures describing the operational parameters that should be monitored, the monitoring points, and the frequency of monitoring. At a minimum, such operational parameters shall include system flow rates and headloss or pressure. The FTO shall include acceptable values and ranges for all operational parameters monitored.

10.4.2 Water Quality Data Collection

During SIVT, the GAC influent and effluent water quality shall be characterized by analysis of the water quality parameters listed in Table 10.1. The first sampling for each required analyte shall be performed 1 day after plant operation start-up and then by the given frequency. Although many parameters may be analyzed off site, free and total chlorine residual, dissolved oxygen, pH, temperature, and turbidity must be analyzed on-site. It is recommended that UV-254 be also analyzed on-site.

The required water quality parameters listed in Table 10.1 are selected to provide state drinking water regulatory agencies with background data on the quality of the GAC influent water being treated and the quality of the treated water. Collection of these data will enhance the acceptability of the SIVT to a wide range of drinking water regulatory agencies.

Acceptable analytical methods for Phase II and V Rule SOCs are listed in Table 10.2. References to both *Standard Method* and EPA Method procedures for sample analysis are given. If new methods are published and approved or current methods updated, the most current methods shall be used.

For the water quality parameters requiring analysis at an off-site laboratory, water samples shall be collected in appropriate containers (containing necessary preservatives as applicable) prepared by a laboratory that is certified, accredited or approved by a state, a third-party organization (i.e., NSF), or the EPA. These samples shall be preserved, stored, shipped and analyzed in accordance with appropriate procedures and holding times, including chain of custody requirements, as specified by the analytical lab.

Table 10.2 Analytical Methods for Phase II and V Rule SOCs

Parameter	Standard Method	EPA Method
Alachlor		505; 507; 525.2; 508.1; 551.1
Aldicarb	6610 B	531.1
Aldicarb sulfone	6610 B	531.1
Aldicarb sulfoxide	6610 B	531.1
Atrazine		505; 507; 508.1; 525.2; 551.1
Benzo(a)pyrene (PAHs)	6410 B; 6440 B	525.2; 550; 550.1
Carbofuran	6610 B	531.1
Chlordane	6410 B; 6630 B,C	505; 508; 508.1; 525.2
2,4-D	6640 B	515.1; 515.2; 555
Dalapon	6640 B	515.1; 515.3; 552.1; 552.2
Di (2-ethylhexyl) adipate		506; 525.2
Di (2-ethylhexyl) phthalate		506; 525.2
Dibromochloropropane (DBCP)	6200 B, C; 6231 B	504.1; 551
Dinoseb	6640 B	515.1; 515.2; 515.3; 555
Diquat		549.2
Endothall		548.1
Endrin	6410 B; 6630 B, C	505; 508; 508.1; 525.2; 551.1
Ethylene dibromide (EDB)	6040 B; 6200 B, C; 6231 B	504.1; 551
Glyphosate	6651 B	547
Heptachlor	6410 B; 6630 B, C	505; 508; 508.1; 525.2; 551.1
Heptachlor epoxide	6410 B; 6630 B, C	505; 508; 508.1; 525.2; 551.1
Hexachlorobenzene	6040 B; 6410 B	505; 508; 508.1; 525.2; 551.1
Hexachlorocyclopentadiene	6410 B	505; 508; 508.1; 525.2; 551.1
Lindane	6630 B	505; 508; 508.1; 525.2; 551.1
Methoxychlor	6630 B	505; 508; 508.1; 525.2; 551.1

Table 10.2 Analytical Methods for Phase II and V Rule SOCs (cont.)

Parameter	Standard Method	EPA Method
Oxamyl (vydate)	6610 B	531.1
Pentachlorophenol	6410 B; 6420 B; 6640 B	515.1; 515.2; 515.3; 525.2; 555
Picloram	6640 B	515.1; 515.2; 515.3; 555
Polychlorinated biphenyls (PCBs)	6410 B; 6630 C	505; 508; 508A; 508.1; 515.2
Simazine		505; 507; 508.1; 525.2; 551.1
2,3,7,8-TCDD (Dioxin)		1613
Toxaphene	6410 B; 6630 B, C	505; 508; 508.1; 525.2
2,4,5-TP (Silvex)	6640 B	515.1; 515.2; 515.3; 555

10.5   Evaluation Criteria

The results of SIVT shall be evaluated based on removal of SOCs. For filter-adsorbers, turbidity removal shall also be evaluated. The *EPA/NSF Equipment Verification Testing Plan for Coagulation and Filtration* within the *EPA/NSF ETV Protocol for Physical Removal of Microbiological and Particulate Contaminants* (EPA/NSF 2002) shall be followed if the filter-adsorber is to be verified as a filter of particulate matter. Time series plots shall be generated describing GAC influent and effluent SOC concentration, TOC concentration, UV-254, and turbidity. The other parameters analyzed should be tabulated. Statistical analyses of the data results shall include averages, minimum, and maximum for each analyte. For sample sets of eight or more, the results shall also include the standard deviation and confidence interval for each analyte. When summarizing SOC data of sample sets of eight or more, the 10th, 25th, 50th, 75th, and 90th percentiles shall also be reported. The length of the study, after taking into account all stoppage time, must be clearly reported.

The SIVT should yield high percent removals (low immediate breakthrough) of SOCs, TOC, and UV-254, demonstrating the initial very effective ability of GAC to remove natural and synthetic organic compounds. High levels of immediate breakthrough of SOCs are indicative of failure of the treatment system to initially adsorb SOCs, possibly due to hydraulic channeling, insufficient media, very low GAC adsorption capacity, or inappropriate GAC contactor design for the water quality tested (concentration of SOC combined with concentrations of other water quality parameters). Long-term SOC control will be evaluated during Task 4, Adsorption Capacity Verification Testing.

The mean and variability of the influent SOC concentration during testing shall be reported by the FTO. A target concentration value may be reported as the mean concentration during testing if it is within 5% of the actual measured mean concentration.

11.0 TASK 4: ADSORPTION CAPACITY VERIFICATION TESTING

11.1 Introduction

Removal of SOCs by adsorptive media is an unsteady-state process. The ability of an adsorptive media treatment system to remove SOCs in most cases will initially be excellent, but will diminish over time as breakthrough of the SOC occurs. The breakthrough of a given SOC is characteristic of the SOC and of the treatment system: breakthrough is dependent on design, EBCT, type of adsorptive media used, influent SOC concentration, SOC adsorbability, and influent water quality. Breakthrough behavior is highly dependent on the concentration and adsorbability of SOCs.

The main purpose of ACVT is to evaluate the capability of the adsorptive media treatment system for removal of SOCs. Specifically, the AUR will be determined for the SOC tested. The AUR will be assessed under the design and operation conditions of the treatment system, as well as influent water quality conditions of the source water after pretreatment, if any. Accurate characterization of influent water quality is important because the AUR, as a function of influent water quality, needs to be evaluated in that context. The "influent" is defined as water entering the adsorber after all pretreatment steps. The breakthrough of the SOC must be captured by a sufficient amount of data (number and scheduling of effluent samples) to allow for an accurate determination of the AUR under the conditions of the verification test.

ACVT shall be performed at least once for a system, but may be performed multiple times on different water qualities to verify the manufacturer's objectives made on the ability of the equipment to remove SOCs under various influent water quality conditions. ACVT may also be performed multiple times to evaluate different levels of influent SOCs (treatment challenge levels) and different modes of testing (constant influent with low or high variability, and attenuation of a spike SOC).

For standard testing (single compound at constant target influent concentration with low variability), it is critical to accurately determine the average influent concentration during testing of a system. Furthermore, variability of the influent concentration above and below the mean must be minimized. Excessive variability may impact the AUR and diminish the validity of the test and, therefore, is not acceptable. The maximum allowable influent concentration variability is defined in this section. The mean and variability of the influent SOC concentration during testing shall be reported by the FTO. A target concentration value may be reported as the mean concentration during testing if it is within 5% of the actual measured mean concentration.

Systems evaluating adsorbent performance under non-standard modes (attenuation of a spiked influent SOC and treatment of a highly variable influent concentration) will not target a constant influent concentration with low variability; restrictions on the variability of the influent concentration do not apply. Separate influent variability guidelines for non-standard modes of operation are described in this section.

Adsorption will also be affected by the concentrations of other water quality parameters and SOCs. Characterization of the influent water quality to the adsorption process is needed so that system performance can be assessed properly and to ensure that influent water quality conditions

match those targeted for equipment verification testing. The adsorption process influent water and the source water may or may not be identical, depending on whether the treatment equipment incorporates pretreatment (such as filtration).

Package plants that contain multiple contactors operated in parallel and staggered with respect to operation cycles shall be considered a single adsorptive media system: the influent water as applied in this section relates to the influent to all parallel contactors. The effluent as applied in this section relates to the blended effluent of all contactors in operation. It is assumed that the contactors in a multiple contactor package plant each contain the same EBCT. If the EBCT varies between contactors, then an average EBCT should be reported, as well as the actual EBCTs of each adsorber and an explanation of the system setup and operation.

11.2   Objectives

The objective of this task is to verify the manufacturer's statement of performance capability regarding the operation time and AUR of the adsorptive media treatment system for removal of one or more SOCs to levels below the treatment objective.

Specific objectives include:

- Characterization of the influent SOC concentration and variability;
- Evaluation of the concentrations during testing of other water quality parameters that impact SOC adsorption including TOC, UV-254, pH, temperature, and other background SOCs;
- Evaluation of the breakthrough of SOC to determine the AUR; and
- Evaluation of the breakthrough of other water quality parameters.

11.3   Work Plan

For ACVT, the FTO shall specify a run time criterion. A run time criterion can be set based on treated water quality conditions (such as exceeding the MCL for the SOC tested), or set to a specific maximum run time. A combination of treated water quality and maximum run time criteria may also be utilized. Since the duration of SIVT is 13 days plus one 8-hour shift, the minimum duration of ACVT shall also be 13 days plus one 8-hour shift. However, it is expected that all ACVT runs will be longer than 2 weeks in duration.

The PSTP shall identify the treated water DQOs to be achieved in the statement of performance capabilities of the equipment to be evaluated in the verification test. The PSTP shall also identify in the statement of performance capabilities the specific SOCs that shall be monitored during equipment testing. The statement of performance capabilities prepared by the FTO shall indicate the range of water qualities and operating conditions under which the equipment can be challenged while successfully treating the contaminated water supply.

It should be noted that many of the packaged and/or modular drinking water treatment systems participating in an SOC removal verification test will be capable of achieving multiple water treatment objectives. Although the SOC TSTP is designed for the removal of SOCs, the manufacturer may want to examine the capabilities of the treatment system for removal of

additional water quality parameters. Appropriate EPA/NSF ETV protocol(s) and TSTP(s) should be consulted.

Some of the water quality parameters described in this task shall be measured on-site by the NSF-qualified FTO. For the water quality parameters requiring analysis off site, water samples shall be analyzed by a laboratory that is certified, accredited or approved by a state, a third-party organization (i.e., NSF), or the EPA. Representative methods to be used for measurement of water quality parameters in the field and lab are identified in Table 10.2. The analytical methods utilized for on-site monitoring of raw and finished water qualities are described in Task 8, Quality Assurance/Quality Control.

For the water quality parameters requiring analysis at an off-site laboratory, water samples shall be collected in appropriate containers (containing necessary preservatives as applicable) prepared by a laboratory that is certified, accredited or approved by a state, a third-party organization (i.e., NSF), or the EPA. These samples shall be preserved, stored, shipped and analyzed in accordance with appropriate procedures and holding times, including chain of custody requirements, as specified by the analytical lab.

Package plants that contain multiple adsorbent contactors to be operated in parallel should follow manufacturer's guidelines for system start-up. If the contactors are to be operated in a staggered format, then each contactor should be brought on-line sequentially, as designated by the manufacturer's instructions. If the SOC to be treated is already present in the influent water, then the start of verification testing should take place when the first contactor is brought on-line. Alternatively, each contactor can be brought on-line sequentially until all contactors are in operation prior to the start of verification testing if the SOC to be tested is not present in the source water. Spiking of the SOC to be tested would begin when all contactors are operational.

For multiple contactor verification testing of attenuation of a spiked compound, all contactors should be brought on-line sequentially as designated by the manufacturer prior to spiking the compound.

Any influent spiking irregularities that occur during the study must be reported by the FTO. This includes, but is not limited to, events such as a period of time when the contaminant feed pump is not pumping at the correct flow rate, a period of time when the contaminant stock solution runs out, or a period of time when volatile losses may have occurred from the stock solution. The FTO must document the occurrence of these events including a clear description, corrective actions taken, the length of time during which the irregularity occurred (this may have to be estimated), and the known or estimated dates and times when the event began and ended. The description should include the FTO's opinion as to the severity of the irregularity in terms of its impact on testing results.

11.4   Analytical Schedule

11.4.1 Influent Sampling Requirements

Standard testing. All SOCs named in the manufacturer's statement of performance capabilities or analyzed in the adsorptive system effluent shall be sampled in the influent water. Influent SOC samples shall be taken at a sampling port located prior to the

adsorptive media, after all pretreatment steps. During the first 2 weeks of testing, systems being tested for the first time should follow the influent sampling guidelines specified under Task 3, System Integrity Verification Testing. These systems should then follow the requirements specified in this section for influent sampling after the first 2 weeks. Systems that have already completed SIVT requirements can follow the influent sampling guidelines specified in this section for the entire study.

"Standard testing" applies to systems expected to be tested with a constant SOC influent concentration study with a low amount of influent variability. Standard testing also applies to studies in which the influent SOC is spiked to a constant level into a source water in which the influent SOC is either not present or is present at a lower, constant concentration. For standard testing, influent SOC concentration variability should not exceed the guidelines summarized in Table 10.2.

Since variability of source water SOC concentration may be higher than expected during any study, about twice as many influent samples are required to be taken as are analyzed. Equation 13 defines the total number of influent samples that must be taken (this number will be greater than the number analyzed, as long as variability is shown to be within the guidelines summarized in Table 11.1).

$$N_S = \frac{63.7 + t_{bt}}{8.24} \tag{13}$$

where N_S is the required minimum number of samples taken (but not necessarily analyzed) for low-variable influent studies and t_{bt} is the operation time to breakthrough in days.

The result of this formula should be rounded to the nearest whole integer. Of the total number of samples taken (as given by Equation 13), every second sample must be analyzed, beginning with the first sample taken. By using this formula, the minimum frequency of influent sampling is gradually reduced: for a 1-year study, a minimum of 26 samples must be analyzed, or 1 sample every 2 weeks. This compares to 8 analyzed samples required for a 60-day study, or approximately 1 every week. The intent of this minimum influent sampling schedule is to reduce the sampling burden on more lengthy studies. The equation is not valid for run times shorter than 60 days. Assuming SIVT is not applicable to the study, the frequency of sampling between day 1 and 60 should be 3 samples per week. As before, every second sample should be analyzed. When SIVT is performed for the first 2 weeks of operation, then the sampling guidelines given in Task 3, System Integrity Verification Testing, must be followed for the first 2 weeks. Between 14 and 60 days, 3 samples per week are required, with every second sample analyzed.

If the data resulting from the analysis of every second influent sample confirms that the variability of the influent SOC concentration is low, then the samples taken but not analyzed can be discarded. However, if the data shows that the influent variability is unexpectedly high, then the "skipped" samples must be analyzed for a more accurate assessment of influent SOC concentration variability. The breakpoint between low and high variability is defined in Table 11.1.

For purposes of determining the minimum influent sampling rate, the testing period is defined as the operation time between start-up and breakthrough. If the SOC being tested reaches breakthrough (as defined in this document) on day 100, but the system is operated for an additional 150 days (for a total of 150 days since startup), the minimum number of influent samples taken between day 1 and day 100 should be 10, as defined by Equation 13. Influent samples taken after breakthrough occurs should not be used to determine the mean influent concentration and influent concentration variability statistics. As stated earlier, breakthrough is defined in this document as the point during the run when the SOC concentration in the adsorber effluent exceeds the treatment objective.

In addition to the minimum frequency of influent sampling requirement, studies performed on a source water with low SOC variability (or studies in which the SOC is spiked to a constant concentration) must maintain an influent SOC concentration variability below the maximum allowable, as defined by the relative standard deviation (RSD), Equation 14:

$$RSD = s / \bar{y} \tag{14}$$

where σ is the standard deviation and $\bar{y}$ is the mean. Since low-level SOC concentrations [in relation to the method minimum reporting level (MRL)] will likely result in higher analytical variability as compared to measured SOC concentration at higher levels, the maximum RSD is set based on the average concentration expressed as a multiple of the MRL, as shown in Table 11.1.

Table 11.1 Influent Concentration Variability Requirements for Standard Testing During ACVT

Average concentration (expressed as a multiple of the method MRL)	Maximum RSD of all influent samples (between $t=0$ and $t=t_{bt}$)
1.0 - 1.5	50.0
>1.5 – 3.0	40.0
>3.0 – 10.0	30.0
>10.0	20.0

For example, if the method MRL for trichloroethylene is 1.0 µg/L, and the average measured influent trichloroethylene concentration of all samples analyzed between day 1 and t_{bt} is 5.0 µg/L, then the maximum RSD allowable is 30.0%. If the MRL was 2.0 µg/L for the same average influent SOC concentration, then the maximum RSD allowable would be 40.0%. Studies that exceed this maximum RSD must be classified as adsorptive systems treating an influent water with a highly variable SOC concentration: the "skipped" samples taken, but not analyzed, must now be analyzed. Additional sampling requirements are stipulated for highly variable influent SOC concentration studies as detailed below. Since the sampling rate required for studies conducted with highly variable influent SOC concentration is more stringent than that for studies conducted on influent SOCs with low variability, steps should be taken to minimize variability of the influent SOC during low-variability studies. If variability is higher than anticipated, the number of influent and effluent samples analyzed will be greater.

Highly variable influent concentration. For studies designed to test adsorptive media performance at a constant target influent concentration for a water source where a high amount of variability is expected, a higher number of samples is necessary to capture the variability of the influent SOC concentration. This higher sampling frequency is also required for studies in which the influent SOC concentration varies over time, resulting in an increasing or decreasing concentration over the course of the study, or other long-term trends that will impact the calculated RSD. The influent SOC concentration in such a study may not be extremely variable on a day-to-day basis, but the long-term trend must be characterized with the increased sampling frequency. Such a study is not ideal as the long-term change in influent concentration hampers data interpretation. This higher influent sampling frequency is also recommended when the expected SOC influent concentration variability is unknown.

The minimum number of influent samples for high-variability studies is also determined by Equation 13. Every sample taken must be analyzed. By using this formula, the minimum frequency of influent sampling is gradually reduced: for a 1-year study, a minimum of 52 samples must be taken and analyzed, or 1 sample every week. This compares to 15 samples required for a 60-day study, or approximately 2 every week. The intent of this minimum influent sampling schedule is to reduce the sampling burden on more lengthy studies. The equation is not valid for run times lower than 60 days. Assuming SIVT is not applicable to the study, the frequency of sampling between day 1 and 60 should be 3 samples per week. Again, every sample should be analyzed. When SIVT is performed for the first 2 weeks of operation, then the sampling guidelines given in Task 3, System Integrity Verification Testing, must be followed for the first 2 weeks. Between 14 and 60 days, 3 samples per week are required, with every second sample analyzed.

For purposes of determining the minimum influent sampling rate, the testing period is defined as the operation time between start-up and breakthrough. Therefore, if the SOC being tested reaches breakthrough (as defined in this document) on day 100, but the system is operated for an additional 50 days (for a total of 150 days since start-up), the minimum number of influent samples taken between day 1 and day 100 should be 20, as defined by Equation 13. Influent samples taken after breakthrough occurs should not be used to determine the mean influent concentration and influent concentration variability statistics. As stated earlier, breakthrough is defined in this document as the point during the run when the adsorber effluent reaches or exceeds the treatment objective.

No maximum measure of variability shall be set for these highly variable influent studies, but the variability in SOC influent concentration shall be summarized statistically by calculating the mean, standard deviation, 10th, 25th, 50th, 75th, and 90th percentiles, minimum, and maximum. In addition, a statement shall be included describing the variability observed in the influent SOC concentration over the course of the study.

SOC spike attenuation. For spike attenuation studies, the sampling frequency required for low-variability studies (standard testing) shall be followed. The purpose of sampling will be mainly to demonstrate the absence of significant levels of the SOC before and after the spike. During the spike, the influent shall be sampled more often, at a rate

sufficient to capture the spike and confirm the accuracy of the spike concentration for purposes of data interpretation. During the spike, at least 2 samples per day are required, and a minimum total of 6 samples is required. Samples should be taken daily for at least 2 days before the spike and for at least 3 days after the spike.

Multiple SOC testing. Sampling requirements for verification testing of multiple SOCs should follow the guidelines set forth above. Each SOC tested shall be sampled at the minimum specified frequency.

Influent sampling requirements for other water quality parameters. Regardless of the type of study performed (low SOC variability, high SOC variability, or SOC spike attenuation), the sampling frequency for water quality parameters summarized in Table 11.2 shall be followed.

Table 11.2 Minimum Influent Sampling Frequency Requirements for Water Quality Parameters

Parameter	Frequency
Alkalinity	Monthly
Ammonia (optional)	Monthly
Calcium hardness	Monthly
pH	Weekly
TDS or conductivity	Monthly
Temperature	Weekly
TOC	Monthly
Total hardness	Monthly
TSS	Monthly
Turbidity	See note[1]
UV-254	Monthly

[1] For contactors operated in filter-adsorber mode, a continuous turbidimeter should be used. Daily samples should be analyzed using a bench-top turbidimeter to confirm the continuous turbidimeter readings. For contactors operated in post-filter adsorber mode, the minimum sampling frequency for turbidity is weekly.

Multiple contactor operation influent sampling requirements. Ideally, water quality parameter samples should be taken from an influent line that is then split to each contactor. If this is not possible, then the influent to each contactor should be sampled at the required sampling frequency. For studies in which the SOC is spiked into the influent water, the spike should be located at an influent line or batch container that is then split to each contactor in service.

11.4.2 Effluent Sampling Requirements

To verify the manufacturer's run time or AUR statement of performance capability, an accurate determination of the run time to breakthrough of the SOC must be obtained during ACVT. Due to the unsteady-state nature of breakthrough, the uncertain impact of BOM and other SOCs on adsorption capacity, and the potential for lengthy analysis

turnaround time, it is difficult to design a sampling plan that will always capture the complete breakthrough curve, especially when it is very sharp. A few strategies for sampling designed to improve the chances of collecting samples at critical points (during breakthrough) while minimizing the analytical cost are presented in this section.

The minimum effluent sampling requirements (N_S) are identical to those defined for the influent, described in Section 11.4.1, Influent Sampling Requirements. Samples should be paired: influent and effluent samples should always be taken at the same time, regardless of study design. If the influent SOC concentration variability is higher than expected, requiring the "skipped" samples to be run, then the paired effluent for each additional influent sample analyzed must also be analyzed.

For purposes of determining the minimum effluent sampling rate, the testing period is defined as the operation time between start-up and breakthrough. Thus, if the SOC being tested reaches breakthrough (as defined in this document) on day 100, but the system is operated for an additional 150 days (for a total of 150 days since start-up), the minimum number of effluent samples taken between day 1 and day 100 should be 20, as defined by Equation 13. As stated earlier, breakthrough is defined in this document as the point during the run when the adsorber effluent concentration exceeds the treatment objective.

A conservative sampling schedule approach is recommended, since breakthrough could occur earlier than expected. Care exercised in establishing the sampling plan will improve the potential of the data generated to verify the AUR for the SOC tested. This includes, but is not limited to, an increase in the sampling rate when breakthrough is expected. Guidance follows on developing a conservative sampling plan.

If prior experience with breakthrough of the target SOC under similar BOM conditions is identified, the results of previous experiments can be used to improve the run time estimate obtained during Task 2 using Equations 6 through 9. For example, if prior experience with adsorption of the same compound on the same water source indicates a run time to breakthrough 50% shorter than that predicted assuming the absence of BOM, then the run time estimated in Task 2 should be adjusted accordingly. Prior experience with other SOCs on the same water source can be used in the same manner, assuming similar adsorption characteristics to the present compound of interest. Differences in adsorbent type, temperature, EBCT, pH, etc. should be taken into account when applying the results of previous studies to the current verification testing.

If no prior experience with SOC adsorption on the water source to be used for verification testing is available, then two approaches can be followed: a) isotherm tests with the SOC and adsorbent preloaded with the BOM and b) literature isotherm values for the SOC and adsorbent can be used with, and adjusted for, non-distilled water conditions. Isotherm testing can be used to determine the Freundlich adsorption constant values under preloaded conditions. To do so, adsorbent that has been preloaded with BOM should be used for isotherm testing. Details on performing isotherm tests can be found in the literature (Randtke and Snoeyink 1983; Sontheimer, Crittenden, and Summers 1988; Snoeyink and Summers 1999). Literature Freundlich isotherm constant

values from the literature can be modified by using Equations 6 and 10a to yield an estimate of the breakthrough time (see example in Section 9.3).

Once the best possible estimate of run time to breakthrough is determined, a sampling plan that adequately captures the breakthrough curve must be used. It is recommended that the rate of effluent sampling for the SOC be increased before, during and after the expected breakthrough point. It is extremely difficult to estimate run time to breakthrough accurately. Therefore, a safety factor should be placed around the estimate of run time in case the compound breaks through earlier than expected. This safety factor should be as large as feasible. This scenario assumes that all samples taken are subsequently analyzed.

Another method is to collect many more samples than will be analyzed, such as 5 times as many samples. Only every 10th sample is analyzed, while the rest are stored appropriately. When the zone in which breakthrough occurs is known, selected reserve samples that will fill in the breakthrough curve are analyzed. Only samples that capture the breakthrough curve are analyzed, thus minimizing the number of samples analyzed. This method requires that results for the initial samples analyzed are received before the holding times for the stored samples are exceeded. Overall, the sampling frequency should be equal to or greater than the minimum described in this section.

Special care should be exercised when evaluating the breakthrough of a SOC in the presence of other SOCs at significant concentrations. Due to competitive adsorption effects, breakthrough of the SOC tested may occur earlier than expected.

Effluent sample requirements for the water quality parameters summarized in Table 11.3 should be evenly spaced over the course of the run. These requirements should be followed for all types of studies, including low and high variability, spike attenuation, and multiple parallel contactors.

Table 11.3 Minimum Effluent Sampling Frequency Requirements for Other Water Quality Parameters

Parameter	Frequency
TOC	Monthly
UV-254	Monthly
Turbidity	See note[1]

[1] For contactors operated in filter-adsorber mode, a continuous turbidimeter should be used. Daily samples should be analyzed using a bench-top turbidimeter to confirm the continuous turbidimeter readings. For contactors operated in post-filter adsorber mode, the minimum sampling frequency for turbidity is weekly.

The effluent sampling requirements outlined in this section apply also to package plants that blend the effluents of multiple parallel adsorbers prior to further treatment and distribution. For purposes of sampling, the set of multiple parallel contactors constitutes the adsorption treatment system evaluated.

11.5 Evaluation Criteria

Data analysis and interpretation for this task includes:

- Effluent SOC data collected and analyzed as described in Section 11.4.2, Effluent Sampling Requirements, shall be evaluated on a continuous basis to determine whether breakthrough is occurring or has occurred. A fast turnaround time for sample analysis is preferable.

- The effluent SOC data shall be used in conjunction with the run time estimate described in Section 9.3 to determine when to terminate test runs. Due to the turnaround time required for SOC analysis, it may take time to establish when breakthrough has occurred and that the test can be terminated. It is not recommended that the test be terminated on the basis of the run time estimate alone. The length of the study, after taking into account all stoppage time, must be clearly reported.

- Plots of effluent concentration against operation time or throughput shall be prepared for all SOCs evaluated. Breakthrough curves should be prepared on a continuous basis, as data is available, to aid in evaluating the status of SOC breakthrough. Similar plots should be prepared for all other water quality analyses conducted.

- The AUR shall be determined based on data obtained during verification testing that shows effluent concentrations lower than the effluent criteria specified in the manufacturer's statement of performance capabilities. The run time will be shorter than the maximum testing run time if breakthrough of the SOC evaluated occurs prior to the end of the run.

- The mean and variability of the influent VOC concentration during testing shall be reported by the FTO. Results shall include the average, minimum, maximum, and number of data points in the data set. For sample sets of eight or more, the results shall also include the standard deviation and confidence interval for each analyte. When summarizing VOC data of sample sets of eight or more, the 10th, 25th, 50th, 75th, and 90th percentiles shall also be reported. A target concentration value may be reported as the mean concentration during testing if it is within 5% of the actual measured mean concentration.

- Based on t_{bt}, the AUR is calculated using the following equation, Equation 15:

$$AUR(g/L) = \frac{r(g/L)}{Y_{bt}} \tag{15}$$

where r is the apparent media density and Y_{bt} is the number of BV to breakthrough. The value for Y_{bt} is calculated from t_{bt} by Equation 16:

$$Y_{bt} = \frac{t_{bt}(\text{days}) \cdot 1{,}440\text{min/d ay}}{\text{EBCT(min)}} \tag{16}$$

- For spike attenuation studies, the influent data should be evaluated to determine if influent SOC concentration matches that described by the manufacturer's statement of performance capabilities. Effluent data should be evaluated to determine if effluent SOC levels exceed the MCL as stated in the manufacturer's statement of performance capabilities. If effluent data exceed the MCL, the operation time at which it exceeded the MCL should be determined (relative to when the spike occurred) the same way that the operation time is determined for constant influent studies. Thus the effective AUR may also be determined for spike attenuation studies.

Constant influent studies: determination of run time to breakthrough. For manufacturers wishing to make a stronger performance capabilities statement and operate their adsorptive media system for run times long enough to observe breakthrough of the SOC(s) tested, an evaluation of the influent and effluent data on which the AUR is based must be performed. This section provides some guidance on performing this evaluation, which will help with experimental design and data analysis.

As stated previously, it is difficult to predict when breakthrough will occur for a given SOC during removal by adsorptive media. After appropriate influent and effluent sampling that provides the best possible evaluation of the manufacturer's statement of performance capabilities (described previously in this section), the data analyzed should be evaluated to determine the run time to breakthrough. Run time to breakthrough can be determined from the data in two ways, depending on the quality of the data.

Basic quality data is best described as effluent data that is not evenly spaced, that fails to capture the shape of the breakthrough curve (i.e., an effluent data point below detection limits is followed by one that approximates influent concentrations), or that is so variable that a best-fit breakthrough curve would contain excessive uncertainty. Examples of these are shown in Figure 11.1. One or more of these conditions may result in a data set that is difficult to interpret in determining when breakthrough occurred. Therefore, a conservative approach to determining the operation time to breakthrough for basic quality data must be utilized: the operation time of the last sample taken prior to a sample that exceeds the treatment objective is the run time used for the AUR calculation. Sub-optimal quality data is a result of a variety of factors, including insufficient or poorly-spaced sampling, variability in system flow rate, analytical variability, excessive influent SOC concentration variability, or variability of other water quality parameters, such as pH, TOC, turbidity, or other SOCs. A poor quality data set may result in an effective AUR much higher than that actually achievable by the treatment system evaluated. Therefore, it is in the manufacturer's best interest that the data generated during verification testing be of the highest quality possible.

The operation time to breakthrough and AUR can be calculated from good quality data using the same method described for basic quality data. Alternatively, a curve fit of a good quality data set can be performed to determine the operation time to breakthrough by interpolation. In many cases, good quality data will allow for a straightforward evaluation of the breakthrough curve, from the point of initial breakthrough to column exhaustion. Evenly spaced data points will be located throughout the breakthrough curve. Data will often be collected at operation times well beyond the point of breakthrough (the point at which the effluent concentration reaches the treatment objective). Examples of good quality data are also given in Figure 11.1.

The FTO shall assess the quality of the data generated by the study. Based on this analysis, the FTO shall determine which method of calculating the run time to breakthrough should be employed. In either case, a graph of the data must be included in the report. If a curve fit is performed to determine the operation time to breakthrough, a graph of the data and the curve fit should be included, along with the curve fit type or method, and relevant statistical information on the goodness of fit (e.g., r^2), and confidence intervals. A confidence interval on the calculated AUR should be reported.

Again, since basic quality data will yield a conservative estimate of the run time to breakthrough, it is advantageous for the study to be designed and performed so that the best possible quality data is obtained.

The methods for estimating the operation time to breakthrough described in this section apply to both low variability and high variability constant influent studies.
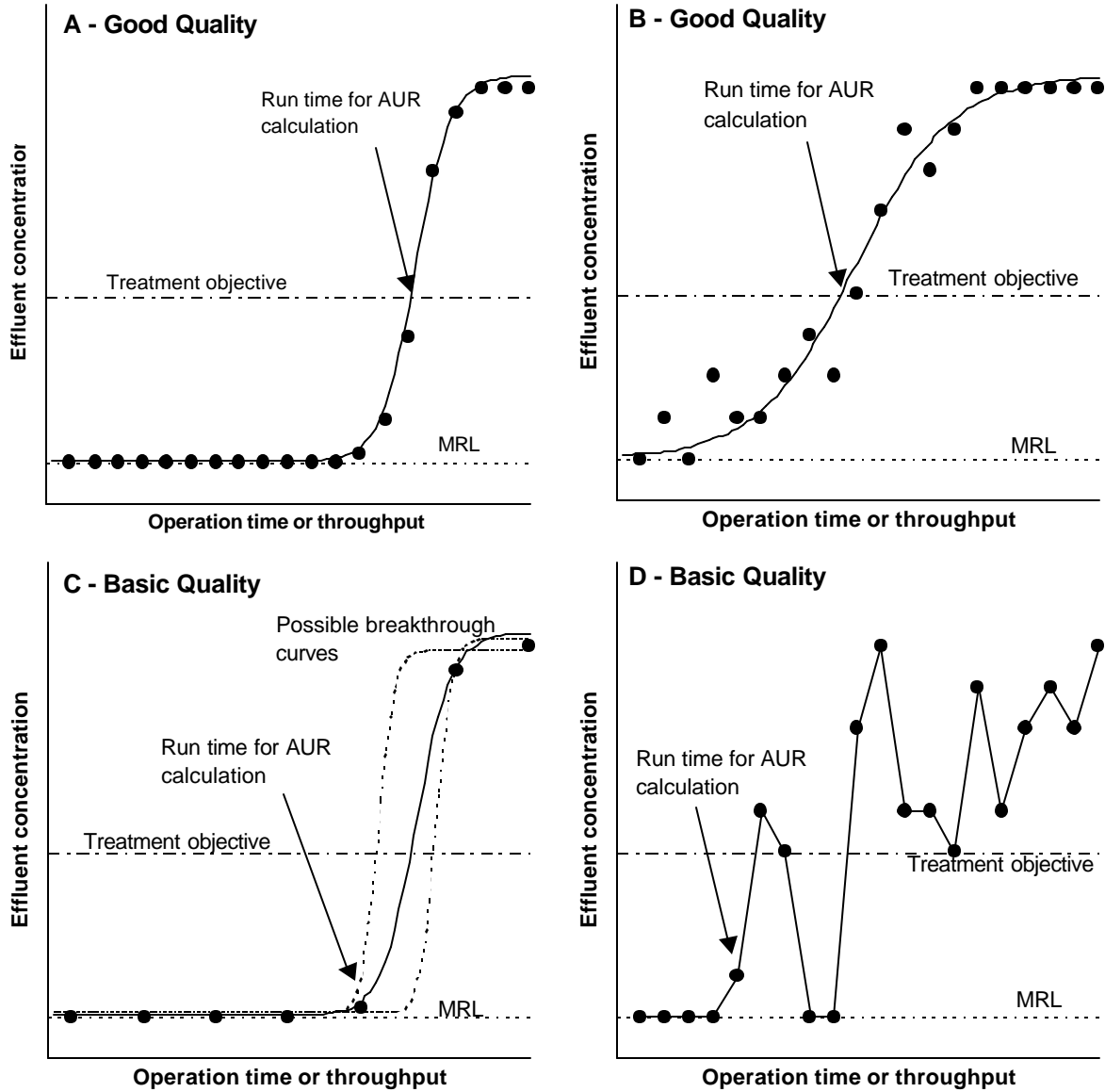
Figure 11.1 Examples of Good and Basic Quality Breakthrough Curves

Attenuation of spiked influent. For studies designed to assess the ability of the adsorptive media to attenuate a spiked influent, the FTO shall analyze the data obtained to assess that effluent concentrations were reduced and did not exceed the treatment objective. If effluent concentrations exceeded the treatment objective, then the AUR should be calculated based on the point of breakthrough. Based on the data quality, the methods described above for constant influent studies should be applied.

12.0   TASK 5: IN-PLACE REGENERATION

12.1   Introduction

This task is applicable only to adsorption treatment systems that use adsorptive media that can be regenerated in-place and that incorporate regeneration capability as an integral part of the equipment being tested. If the manufacturer wishes to make a statement of performance capabilities about the in-place regeneration capability of the equipment, verification testing must include, as a minimum, two complete cycles: an initial loading cycle, followed by a regeneration cycle, and then a second loading cycle, followed by a second regeneration cycle. This additional requirement allows for a comparison of adsorptive media performance before and after regeneration. Furthermore, the regeneration efficiency shall be determined based on the second regeneration cycle.

Verification of in-place regeneration based on two complete loading/regeneration cycles is limited, and additional cycles are recommended if possible. However, the guidelines for modified testing to verify an in-place regeneration statement of performance capabilities are described under this task. The regeneration system, regenerant fluids used, and regeneration procedure shall be documented as part of Task 2, System Design and Operation.

12.2   Objectives

The objectives of this task are to:

- Describe operation and sampling requirements for systems in which in-place regeneration will be verified;
- Evaluate adsorptive media performance before and after in-place regeneration;
- Characterize any residuals produced during regeneration; and
- Evaluate regeneration efficiency.

12.3   Work Plan

To verify a manufacturer's statement of performance capabilities regarding the in-place regeneration capability of adsorption equipment, verification testing shall be conducted as described in Section 10.0 (Task 3, System Integrity Verification Testing) and Section 11.0 (Task 4, Adsorption Capacity Verification Testing), combined with the additional requirements or modifications as described in this task.

The testing period shall include, as a minimum, two complete cycles: an initial loading cycle, followed by a regeneration cycle, and then a second loading cycle, followed by a second regeneration cycle. During each loading period, the adsorptive media system must be operated at least until breakthrough of the SOC occurs, based on the treatment objective defined in the manufacturer's statement of performance capabilities.

The SOC influent target concentration shall be the same during both loading cycles. The mode of testing (low-variability constant influent, high-variability constant influent, or attenuation of a spiked influent SOC) shall also be identical during both loading cycles. All other experimental parameters, such as water source, pretreatment, and presence of background SOCs, shall be as

similar as possible during the two (or more, if necessary) loading cycles. If the four-step cycle is completed in less than 60 days, additional loading/regeneration cycles shall be performed until the total run time is at least 60 days.

If possible, incorporation of additional cycles into the verification test would increase the amount of data on regeneration effectiveness and retention of adsorption capacity over time. Whether or not additional cycles are completed, the FTO must make a statement about the long-term efficiency of regeneration for the adsorptive media tested. If the long-term efficiency of regeneration is not studied as part of this verification test, or available from other studies, a statement by the FTO is required indicating that the long-term regeneration efficiency is unknown. For adsorptive media that has been well studied, a statement on the long-term regeneration efficiency can be based on the results of previous peer-reviewed published studies.

Any residuals produced during in-place regeneration of the adsorptive media shall be fully characterized and documented with respect to quantity and SOC composition. For example, if an off-gas stream is produced by a high temperature gas purge of the media, the off-gas flow rate, duration, and total off-gas volume emitted should be measured, and sampling and analysis should be conducted to determine SOC concentrations and total SOC mass emissions. Likewise, if a solvent solution is used for regeneration, the quantity and characteristics of the regenerant before and after use (including SOC concentrations) should be measured and reported. The information from this residuals characterization task shall be used to determine the efficiency of regeneration. A mass balance approach shall be used to determine whether all the SOCs were removed during the regeneration process. The regeneration efficiency and the AUR for each cycle shall be reported.

12.4   Analytical Schedule

Influent and effluent sampling requirements described in Section 10.0 and Section 11.4, shall be applied to *each* loading cycle to assess SOC breakthrough and other water quality parameters. For characterization of regeneration residuals, a sampling and analytical plan shall be developed by the FTO in the PSTP to thoroughly characterize the VOC content of the residual stream.

12.5   Evaluation Criteria

Verification testing of adsorption treatment systems with in-place regeneration includes the same types of data analysis and interpretation as described previously for standard adsorption systems in Section 11.5. In addition, a comparative analysis of adsorption characteristics before and after media regeneration shall be performed. The purpose of the comparative analysis is to assess and quantify whether any reduction in adsorptive media service life or adsorption capacity occurs as a result of in-place regeneration. This shall be evaluated by determining the media service life (operation time, throughput in BV of water treated, and AUR until breakthrough) for the initial and subsequent loading periods, and by quantitatively comparing the results. Similarly, the adsorption capacity before and after regeneration can be determined and compared. In addition, a mass balance should be developed for the SOC tested to evaluate the regeneration efficiency using Equation 17:

$$E_R = \frac{q \cdot m_A}{m_R} \tag{17}$$

where E_R is the regeneration efficiency, q is the adsorption capacity estimated using Equation 4 (and subject to the limitations noted earlier), m_A is the mass of adsorbent, and m_R is the mass SOC recovered in the regeneration stream. The regeneration efficiency shall be calculated after both regeneration cycles.

13.0   TASK 6: OPERATION AND MAINTENANCE MANUAL

13.1   Objectives

The FTO shall obtain the manufacturer-supplied O&M manual(s) to evaluate the instructions and procedures for their applicability during the verification testing period.   Below are recommendations for criteria to evaluate O&M manuals for package plants employing adsorptive media for SOC removal.

13.2   Operation

The manufacturer shall provide readily understood information on the required or recommended procedures related to the proper operation of the package plant equipment including, but not limited to, the following.

Monitoring of Preconditioning of Adsorptive Media:

- Utilize manufacturer's procedure, which may vary depending upon adsorptive media selected;
- Backwash parameters (flow rate, time, backwash water turbidity, etc.);
- Pretreatment chemical application (chemical concentration, time, and flow rate);
- Volume of wastewater; and
- Wastewater disposal requirements (see Regeneration Wastewater Disposal below).

Monitoring Operation:

The feed water is the untreated or pretreated water that serves as influent to the package plant, prior to any treatment processes preceding adsorption in the package plant. Treated water is the adsorptive media effluent water and is blended if multiple contactors are operated in parallel.

- Feed water SOC concentration;
- Feed water pH;
- Feed water adjusted pH (if applicable);
- Feed water flow rate;
- Feed water pressure;
- Treated water SOC concentration;
- Treated water pH;
- Treated water adjusted pH;

- Treated water pressure;
- Chemical feed rates;
- Chemical consumption;
- Maintenance and operator labor requirements; and
- Spare parts requirements.

Monitoring Regeneration of Adsorptive Media:

- Utilize manufacturer's procedure for regeneration which shall vary depending upon selected adsorptive media, equipment, and process variables;
- Backwash parameters (flow rate, time, backwash water turbidity, etc.);
- Regeneration parameters (flow rate, time, regeneration chemical concentration and flow rate, effluent concentration, effluent pH, etc.);
- Neutralization parameters (flow rate, time, neutralization chemical concentration); and
- Adsorptive media makeup requirement.

Monitoring Regeneration Wastewater Disposal:

- Utilize manufacturer's procedure for processing, reclaiming, and/or disposing of regeneration wastewater, adsorptive media preconditioning wastewater, and waste solids, which shall vary depending upon selected adsorptive media, equipment, treatment chemicals and process variables;
- pH adjustment parameters (flow rate, pH, time, pH adjustment chemical consumption, etc.);
- Flocculation/coagulation parameters (flow rate, time, flocculation/coagulation chemical consumption, etc.);
- Liquid/solid separation parameters (flow rate, time, etc.);
- Solids dewatering parameters (flow rate, time, sludge conditioning chemical consumption, dewatered sludge solids, content, toxicity of dewatered solids, etc.);
- Solids disposal parameters (volume, toxicity, permits, transportation of solids to disposal site, cost factors of transportation and disposal, etc.); and
- Liquid disposal parameters (volume, toxicity, pH, permits, adjustment requirements, cost factors of disposal, etc.).

13.3   Maintenance

The manufacturer shall provide readily understood information on the required or recommended maintenance schedule for each piece of operating equipment including, but not limited to:

- Pumps;
- Valves;
- All chemical feed and storage equipment; and
- All instruments.

The manufacturer shall provide readily understood information on the required or recommended maintenance schedule for non-mechanical or non-electrical equipment including, but not limited to:

- Adsorptive media vessels;
- Feed lines; and
- Manual valves.

14.0   TASK 7: DATA MANAGEMENT

14.1   Introduction

The data management system used in the verification test shall involve the use of computer spreadsheets, manual recording methods, or both, for recording operational parameters for the adsorptive media treatment equipment on a daily basis.

14.2   Objectives

The objective of this task is to establish a viable structure for the recording and transmission of field testing data to ensure that the FTO provides sufficient and reliable operational data to NSF for verification purposes.

14.3   Work Plan

The following procedure has been developed for data handling and data verification to be used by the FTO. Where possible, a Supervisory Control and Data Acquisition (SCADA) system should be used for automatic entry of testing data into computer databases. Specific parcels of the computer databases for operational and water quality parameters should then be downloaded by manual importation into Microsoft Excel or similar spreadsheet software. These specific database parcels shall be identified based upon discrete time spans and monitoring parameters. In spreadsheet form, the data shall be manipulated into a convenient framework to allow analysis of equipment operation. Backup of the computer databases to diskette should be performed on a weekly basis at a minimum.

In the case that a SCADA system is not available, field testing operators shall record data and calculations by hand in laboratory notebooks (daily measurements shall be recorded on specially-prepared data log sheets as appropriate). The laboratory notebook shall provide carbon copies of each page. The original notebooks shall be stored on-site; the carbon copy sheets shall be forwarded to the project engineer of the FTO at least once per week. This procedure shall not only ease referencing the original data, but offer protection of the original record of results. Pilot operating logs shall include a description of the adsorptive media treatment equipment (description of test runs, names of visitors, description of any problems or issues, etc.); such descriptions shall be provided in addition to experimental calculations and other items.

The database for the project shall be set up in the form of custom-designed spreadsheets. The spreadsheets shall be capable of storing and manipulating each monitored water quality and operational parameter from each task, each sampling location, and each sampling time. All data

from the laboratory notebooks and data log sheets shall be entered into the appropriate spreadsheet. Data entry shall be conducted on-site by the designated field testing operators. All recorded calculations shall also be checked at this time. Following data entry, the spreadsheet shall be printed out and the printout shall be checked against the handwritten data sheet. Any corrections shall be noted on the hard copies and corrected on the screen, and then a corrected version of the spreadsheet shall be printed out. Each step of the verification process shall be initialed by the field testing operator or engineer performing the entry or verification step.

Each sample shall be assigned a unique identification (ID) number that shall then be tied to the data from that experiment through each step of data entry and analysis. As samples are collected and sent to NSF-qualified analytical laboratories, the data shall be tracked by use of the same system ID numbers. Data from the outside laboratories shall be received and reviewed by the field testing operator. These data shall be entered into the data spreadsheets, corrected, and checked in the same manner as the field data.

15.0   TASK 8: QUALITY ASSURANCE/QUALITY CONTROL

15.1   Introduction

QA/QC for the operation of the adsorptive media treatment equipment and the measured water quality parameters shall be maintained during the verification test.

15.2   Objectives

The objective of this task is to maintain strict QA/QC methods and procedures during the equipment verification test. Maintenance of strict QA/QC procedures is important, in that if a question arises when analyzing or interpreting data collected for a given experiment, it will be possible to determine the exact conditions at the time of testing.

15.3   Work Plan

When developing the Quality Assurance Project Plan (QAPP) within the PSTP, the FTO should refer to Chapter 1, Section 6.0 Quality Assurance Project Plan, in addition to the information provided herein. All of the requirements and guidelines described in Chapter 1 shall be included in the development of the PSTP. In addition to the general ETV Program QA/QC described in Chapter 1, the PSTP shall incorporate the specific adsorptive media QA items detailed in this section.

Equipment flow rates and associated signals should be checked and must be recorded on a routine basis. A routine daily visual check during testing shall be established to confirm that each piece of equipment or instrumentation is operating properly. Particular care shall be taken to confirm that chemicals are being fed at the defined flow rate into a flow stream that is operating at the expected flow rate and that the chemical concentrations are correct. In-line monitoring equipment, such as flow meters, shall be checked to confirm that the readout matches with the actual measurement (i.e., flow rate) and that the signal being recorded is correct. The items listed in this task are in addition to any specified checks outlined in the analytical methods.

It is extremely important that system flow rates be maintained at set values and monitored frequently. Doing so allows a constant and known EBCT to be maintained in the adsorbent contactor. Adsorbent performance is directly affected by the EBCT, which in turn is proportional to the volumetric flow rate through the contactor. Therefore, an important QA/QC objective shall be the maintenance of a constant volumetric flow rate through the adsorbent contactor by means of frequent monitoring and documentation. Documentation shall include an average and standard deviation of recorded flow rates through the adsorbent contactor.

15.3.1 Daily QA/QC Checks

- Chemical feed pump flow rates (checked volumetrically; more frequent monitoring, such as every 8 hours, is recommended);
- In-line turbidimeter flow rates (checked volumetrically, if employed);
- Adsorbent contactor(s) flow rate(s) (checked volumetrically every 2 hours when staffed; at least twice daily. The flow rate should be adjusted to maintain its value within 5% of the design flow rate); and
- Recalibration of in-line pH meters (if used).

15.3.2 Weekly QA/QC Checks

- Recalibration of conductivity meters, and/or turbidimeters (if used). If less frequent recalibration of conductivity meters and turbidimeters is recommended by manufacturer, then follow manufacturer's recommendation;
- In-line flow meters/rotameters (confirm flow rate volumetrically over a specific period of time to confirm instrument reading and, if necessary, clean equipment to remove any foulant buildup); and
- Tubing (check condition of all tubing and connections and replace if necessary).

15.3.3 Monthly QA/QC Checks

- In-line turbidimeters (clean out reservoirs and recalibrate, if employed) and
- Differential pressure transmitters (confirm gauge readings and electrical signal using a pressure meter).

15.4 Analytical Methods

On-Site Analyses. The analytical methods utilized in this study for on-site monitoring of feed and effluent water quality are described below. Use of either bench-top or in-line field analytical equipment will be acceptable for the verification testing; however, in-line equipment is recommended for ease of operation. Use of in-line equipment is also preferable because it reduces the introduction of error and the variability of analytical results generated by inconsistent sampling techniques.

> **pH.** Analyses for pH shall be performed according to *Standard Method* 4500-H$^+$ (APHA, AWWA, and WEF 1998). A 3-point calibration of the pH meter used in this study shall be performed once per day when the instrument is in use. Certified pH buffers in the expected range shall be used. The pH probe shall be stored in the appropriate solution

defined in the instrument manual. Transport of carbon dioxide across the air-water interface can confound pH measurement in poorly buffered waters. If this is a problem, measurement of pH in a confined vessel is recommended to minimize the effects of carbon dioxide loss to the atmosphere.

Temperature. Temperature measurements shall be made in accordance with *Standard Method* 2550. The thermometer used should be a high quality, mercury-filled, Celsius thermometer with a scale marked for every 0.1°C that covers the range of expected temperatures with markings etched in the glass. The thermometer should be checked periodically against a precision thermometer certified by the National Institute of Standards and Technology (NIST). An in-line thermometer is acceptable for this work.

Turbidity. Turbidity analyses shall be performed according to *Standard Method* 2130 with either an in-line or bench-top turbidimeter. During verification testing, the in-line and bench-top turbidimeters shall be left on continuously. Once each turbidity measurement is complete, the unit shall be switched back to its lowest setting. All glassware used for turbidity measurements shall be cleaned and handled using lint-free tissues to prevent scratching. Sample vials shall be stored inverted to prevent deposits from forming on the bottom surface of the cell.

The FTO shall document any problems experienced with the monitoring turbidity instruments during testing, and shall also document any subsequent modifications or enhancements made to monitoring instruments.

Bench-top Turbidimeters. Grab samples shall be analyzed using a bench-top turbidimeter. Readings from this instrument shall serve as reference measurements throughout the study. The bench-top turbidimeter shall be calibrated within the expected range of sample measurements at the beginning of verification testing and on a weekly basis using primary turbidity standards of 0.1, 0.5, and 3.0 NTU. Secondary turbidity standards shall be obtained and checked against the primary standards. Secondary standards shall be used on a daily basis to check the calibration of the turbidimeter and to recalibrate when more than one turbidity range is used.

The method for collecting grab samples shall consist of running a slow, steady stream from the sample tap, triple-rinsing a dedicated sample beaker in this stream, allowing the sample to flow down the side of the beaker to minimize bubble entrainment, double-rinsing the sample vial with the sample, carefully pouring from the beaker down the side of the sample vial, wiping the sample vial clean, inserting the sample vial into the turbidimeter, and recording the measured turbidity. In the case of cold water samples that cause the vial to fog preventing accurate readings, the vial shall be allowed to warm up by partial submersion in a warm water bath for approximately 30 seconds.

In-line Turbidimeters. In-line turbidimeters shall be used for measurement of turbidity in the filtrate water during verification testing and must be calibrated and maintained as specified in the manufacturer's O&M manual. It will be necessary to check the in-line readings using a bench-top turbidimeter at least daily; although the mechanism of analysis is not identical between the two instruments, the readings should be comparable.

If the comparison suggests inaccurate readings, then all in-line turbidimeters should be recalibrated. In addition to calibration, periodic cleaning of the lens should be conducted using lint-free paper to prevent any particle or microbiological build-up that could produce inaccurate readings. Periodic checks of the sample flow should also be performed using a volumetric measurement. Instrument bulbs should be replaced on an as-needed basis. The LED readout should also be checked to ensure that it matches the data recorded on the data acquisition system, if the latter is employed.

Off-Site Analyses. All off-site analytical work associated with equipment verification testing shall be performed by a laboratory that is certified, accredited or approved by a state, a third-party organization (i.e., NSF), or the EPA. Sampling for off-site analyses shall be conducted using proper sampling techniques and samples shall be collected in appropriate volumes and containers provided by the laboratory. These samples shall be preserved, stored, shipped, and analyzed in accordance with appropriate procedures and holding times, as specified by the analytical lab.

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APPENDIX A: REGULATED SOCS

Table A.1 Phase II Rule SOCs

Contaminant	MCLG (mg/L)	MCL (mg/L)	Status	Potential health effects from ingestion of water	Sources of contaminant in drinking water	BAT
Acrylamide	Zero	TT[1]	Final	Nervous system or blood problems; increased risk of cancer	Added to water during sewage/wastewater treatment	PAP
Alachlor	Zero	0.002	Final	Eye, liver, kidney or spleen problems; anemia; increased risk of cancer	Runoff from herbicide used on row crops	GAC
Aldicarb	0.001	0.003	Delayed	Nervous system effects	Insecticide on cotton, potatoes, other crops; widely restricted	GAC
Aldicarb sulfone	0.001	0.002	Delayed	Nervous system effects	Biodegradation of aldicarb	GAC
Aldicarb sulfoxide	0.001	0.004	Delayed	Nervous system effects	Biodegradation of aldicarb	GAC
Atrazine	0.003	0.003	Final	Cardiovascular system or reproductive problems	Runoff from herbicide used on row crops	GAC
Carbofuran	0.04	0.04	Final	Problems with blood, nervous system, or reproductive system	Leaching of soil fumigant used on rice and alfalfa	GAC
Chlordane	Zero	0.002	Final	Liver or nervous system problems; increased risk of cancer	Residue of banned termiticide	GAC
2,4-D	0.07	0.07	Final	Kidney, liver, or adrenal gland problems	Runoff from herbicide used on row crops	GAC
1,2-Dibromo-3-chloropropane (DBCP)	Zero	0.0002	Final	Reproductive difficulties; increased risk of cancer	Runoff/leaching from soil fumigant used on soybeans, cotton, pineapples, and orchards	GAC, PTA
Epichlorohydrin	Zero	TT[1]	Final	Increased cancer risk, and over a long period of time, stomach problems	Discharge from industrial chemical factories; an impurity of some water treatment chemicals	PAP
Ethylene dibromide (EDB)	Zero	0.00005	Final	Problems with liver, stomach, reproductive system, or kidneys; increased risk of cancer	Discharge from petroleum refineries	GAC, PTA
Heptachlor	Zero	0.0004	Final	Liver damage; increased risk of cancer	Residue of banned termiticide	GAC
Heptachlor epoxide	Zero	0.0002	Final	Liver damage; increased risk of cancer	Breakdown of heptachlor	GAC

Table A.1 Phase II Rule SOCs (continued)

Contaminant	MCLG (mg/L)	MCL (mg/L)	Status	Potential health effects from ingestion of water	Sources of contaminant in drinking water	BAT
Lindane	0.0002	0.0002	Final	Liver or kidney problems	Runoff/leaching from insecticide used on cattle, lumber, gardens	GAC
Methoxychlor	0.04	0.04	Final	Reproductive difficulties	Runoff/leaching from insecticide used on fruits, vegetables, alfalfa, livestock	GAC
Pentachlorophenol	Zero	0.001	Final	Liver or kidney problems; increased cancer risk	Discharge from wood preserving factories	GAC
Polychlorinated biphenyls (PCBs)	Zero	0.0005	Final	Skin changes; thymus gland problems; immune deficiencies; reproductive or nervous system difficulties; increased risk of cancer	Runoff from landfills; discharge of waste chemicals	GAC
2,4,5-TP (silvex)	0.05	0.05	Final	Liver problems	Residue of banned herbicide	GAC
Toxaphene	Zero	0.003	Final	Kidney, liver, or thyroid problems; increased risk of cancer	Runoff/leaching from insecticide used on cotton and cattle	GAC

[1]Each water system must certify, in writing, to the state (using third-party or manufacturer's certification) that when acrylamide and epichlorohydrin are used in drinking water systems, the combination (or product) of dose and monomer level does not exceed the levels specified, as follows:

    Acrylamide = 0.05% dosed at 1 mg/L (or equivalent)

    Epichlorohydrin = 0.01% dosed at 20 mg/L (or equivalent)

Abbreviations: **MCL:** maximum contaminant level   **GAC:** granular activated carbon
                 MCLG: maximum contaminant level goal   **PTA:** packed tower aeration
                 BAT: best available technology   **PAP:** polymer addition practices

Sources: USEPA, 2002; adapted from Pontius and Clark (1999) and Faust and Aly (1998)

Table A.2 Phase V Rule SOCs

Contaminant	MCLG (mg/L)	MCL (mg/L)	Status	Potential health effects	Sources of contaminant in drinking water	BAT
Benzo(a)pyrene (PAHs)	Zero	0.0002	Final	Reproductive difficulties; increased risk of cancer	Leaching from linings of water storage tanks and distribution lines	GAC
Dalapon	0.2	0.2	Final	Minor kidney changes	Runoff from herbicide used on rights of way	GAC
Di (2-ethylhexyl) adipate	0.4	0.4	Final	Weight loss, liver problems, or possible reproductive difficulties.	Discharge from chemical factories	GAC, PTA
Di (2-ethylhexyl) phthalate	Zero	0.006	Final	Reproductive difficulties; liver problems; increased risk of cancer	Discharge from rubber and chemical factories	GAC
Dinoseb	0.007	0.007	Final	Reproductive difficulties	Runoff from herbicide used on soybeans and vegetables	GAC
Diquat	0.02	0.02	Final	Cataracts	Runoff from herbicide use	GAC
Endothall	0.1	0.1	Final	Stomach and intestinal problems	Runoff from herbicide use	GAC
Endrin	0.002	0.002	Final	Liver problems	Residue of banned insecticide	GAC
Glyphosate	0.7	0.7	Final	Kidney problems; reproductive difficulties	Runoff from herbicide use	OX
Hexachlorobenzene	Zero	0.001	Final	Liver or kidney problems; reproductive difficulties; increased risk of cancer	Discharge from metal refineries and agricultural chemical factories	GAC
Hexachlorocyclo-pentadiene	0.05	0.05	Final	Kidney or stomach problems	Discharge from chemical factories	GAC, PTA
Oxamyl (vydate)	0.2	0.2	Final	Slight nervous system effects	Runoff/leaching from insecticide used on apples, potatoes, and tomatoes	GAC
Picloram	0.5	0.5	Final	Liver problems	Herbicide runoff	GAC
Simazine	0.004	0.004	Final	Problems with blood	Herbicide runoff	GAC
2,3,7,8-TCDD (Dioxin)	Zero	3×10^{-8}	Final	Reproductive difficulties; increased risk of cancer	Emissions from waste incineration and other combustion; discharge from chemical factories	GAC

Abbreviations: **MCL:** maximum contaminant level **GAC:** granular activated carbon
MCLG: maximum contaminant level goal **OX:** oxidation
BAT: best available technology **PTA:** packed tower aeration

Sources: USEPA, 2002; adapted from Pontius and Clark (1999) and Faust and Aly (1998)

APPENDIX B: DRINKING WATER STANDARDS AND HEALTH ADVISORIES

Table B.1 Drinking Water Standards and Health Advisories

| Chemicals | Standards | | | Status HA Document | Health Advisories | | | | | | Cancer Group |
| | Status Reg. | MCLG (mg/L) | MCL (mg/L) | | 10-kg child | | RfD (mg/kg/day) | DWEL (mg/L) | Lifetime (mg/L) | mg/L at 10^{-4} Cancer Risk | |
					One-day (mg/L)	Ten-day (mg/L)					
Acenaphthene	-	-	-	-	-	-	0.06	2	-	-	-
Acifluorfen (sodium)		-	-	F '88	2	2	0.01	0.4	-	0.1	B2
Acrylamide	F	zero	TT[1]	F '87	1.5	0.3	0.0002	0.007	-	0.001	B2
Acrylonitrile		-	-	-	-	-	-	-	-	0.006	B1
Alachlor	F	zero	0.002	F '88	0.1	0.1	0.01	0.4	-	0.04[2]	B2
Aldicarb[3]	F[4]	0.007	0.007	F '95	0.01	0.01	0.001	0.04	0.007	-	D
Aldicarb sulfone[3]	F[4]	0.007	0.007	F '95	0.01	0.01	0.001	0.04	0.007	-	D
Aldicarb sulfoxide[3]	F[4]	0.007	0.007	F '95	0.01	0.01	0.001	0.04	0.007	-	D
Aldrin	-	-	-	F '92	0.0003	0.0003	0.00003	0.001	-	0.0002	B2
Ametryn	-	-	-	F '88	9	9	0.009	0.3	0.06	-	D
Ammonium sulfamate	-	-	-	F '88	20	20	0.2	8	2	-	D
Anthracene (PAH)[5]	-	-	-	-	-	-	0.3	10	-	-	D
Atrazine[6]	F	0.003	0.003	F '88	-	-	0.035	1	0.2	-	C
Baygon	-	-	-	F '88	0.04	0.04	0.004	0.1	0.003	-	C
Bentazon	-	-	-	F '99	0.3	0.3	0.03	1	0.2	-	E
Benz[a]anthracene (PAH)	-	-	-	-	-	-	-	-	-	-	B2
Benzene	F	zero	0.005	F '87	0.2	0.2	-	-	-	0.1	A
Benzo[a]pyrene (PAH)	F	zero	0.0002	-	-	-	-	-	-	0.002	B2
Benzo[b]fluoranthene (PAH)	-	-	-	-	-	-	-	-	-	-	B2
Benzo[g,h,i]perylene (PAH)	-	-	-	-	-	-	-	-	-	-	D
Benzo[k]fluoranthene (PAH)	-	-	-	-	-	-	-	-	-	-	B2
bis-2-Chloroisopropyl ether	-	-	-	F '89	4	4	0.04	1	0.3	-	D
Bromacil	-	-	-	F '88	5	5	0.1	5	0.09	-	C
Bromobenzene	-	-	-	D '86	4	4	-	-	-	-	D

[1] When acrylamide is used in drinking water systems, the combination (or product) of dose and monomer level shall not exceed that equivalent to a polyacrylamide polymer containing 0.05% monomer dosed at 1 mg/L.

[2] Determined not to be carcinogenic at low doses by OPP.

[3] The lifetime HA value or the MCLG/MCL value for any combination of two or more of these three chemicals should remain at 0.007 mg/L because of similar mode of action.

[4] Administrative stay of the effective date.

[5] PAH = Polycyclic aromatic hydrocarbon

[6] Under review

Table B.1 Drinking Water Standards and Health Advisories (Cont.)

Chemicals	Standards			Status HA Document	Health Advisories						Cancer Group
					10-kg child		RfD			mg/L at	
	Status Reg.	MCLG (mg/L)	MCL (mg/L)		One-day (mg/L)	Ten-day (mg/L)	(mg/kg/ day)	DWEL (mg/L)	Lifetime (mg/L)	10^{-4} Cancer Risk	
Bromochloromethane	-	-	-	F '89	50	1	0.01	0.5	0.09	-	D
Bromodichloromethane (THM)	F	zero	0.08[1]	D '93	6	6	0.02	0.7	-	0.06	B2
Bromoform (THM)	F	zero	0.08[1]	D '93	5	2	0.02	0.7	-	0.4	B2
Bromomethane	-	-	-	D '89	0.1	0.1	0.001	0.05	0.01	-	D
Butyl benzyl phthalate (PAE)[2]	-	-	-	-	-	-	0.2	7	-	-	C
Butylate	-	-	-	F '89	2	2	0.05	2	0.4	-	D
Carbaryl	-	-	-	F '88	1	1	0.1	4	0.7	-	D
Carbofuran[3]	F	0.04	0.04	F '87	0.05	0.05	0.005	0.2	0.04	-	E
Carbon tetrachloride	F	zero	0.005	F '87	4	0.2	0.0007	0.03	-	0.03	B2
Carboxin	-	-	-	F '88	1	1	0.1	4	0.7	-	D
Chloramben	-	-	-	F '88	3	3	0.015	0.5	0.1	-	D
Chlordane	F	zero	0.002	F '87	0.06	0.06	0.0005	0.02	-	0.001	B2
Chloroform (THM)	F	zero	0.08[1]	D '93	4	4	0.01	0.4	-	0.6	B2
Chloromethane	-	-	-	F '89	9	0.4	0.004	0.1	0.003	-	C
Chlorophenol (2-)	-	-	-	D '94	0.5	0.5	0.005	0.2	0.04	-	D
p-Chlorophenyl methyl sulfide/sulfone/sulfoxide	-	-	-	-	-	-	-	-	-	-	D
Chlorothalonil	-	-	-	F '88	0.2	0.2	0.015	0.5	-	0.15	B2
Chlorotoluene o-	-	-	-	F '89	2	2	0.02	0.7	0.1	-	D
Chlorotoluene p-	-	-	-	F '89	2	2	0.02	0.7	0.1	-	D
Chlorpyrifos	-	-	-	F '92	0.03	0.03	0.003	0.1	0.02	-	D
Chrysene (PAH)	-	-	-	-	-	-	-	-	-	-	B2
Cyanazine	-	-	-	D '96	0.1	0.1	0.002	0.07	0.001	-	-

[1] 1998 Final Rule for Disinfectants and Disinfection By-products: The total for trihalomethanes is 0.08 mg/L.

[2] PAE = phthalate acid ester

[3] Under review

Table B.1 Drinking Water Standards and Health Advisories (Cont.)

Chemicals	Status Reg.	MCLG (mg/L)	MCL (mg/L)	Status HA Document	One-day (mg/L)	Ten-day (mg/L)	RfD (mg/kg/day)	DWEL (mg/L)	Lifetime (mg/L)	mg/L at 10^{-4} Cancer Risk	Cancer Group
		Standards			10-kg child			Health Advisories			
Cyanogen chloride[1]	-	-	-	-	0.05	0.05	0.05	2	-	-	D
2,4-D (2,4-dichlorophenoxyacetic acid)	F	0.07	0.07	F '87	1	0.3	0.01	0.4	0.07	-	D
DCPA (Dacthal)	-	-	-	F '88	80	80	0.01	0.4	0.07	-	D
Dalapon (sodium salt)	F	0.2	0.2	F '89	3	3	0.03	0.9	0.2	-	D
Di(2-ethylhexyl)adipate	F	0.4	0.4	-	20	20	0.6	20	0.4	3	C
Di(2-ethylhexyl)phthalate (PAE)	F	zero	0.006	-	-	-	0.02	0.7	-	0.3	B2
Diazinon	-	-	-	F '88	0.02	0.02	0.00009	0.003	0.0006	-	E
Dibromochloromomethane (THM)	F	0.06	0.08[2]	D '93	6	6	0.02	0.7	0.06	0.04	C
Dibromochloropropane (DBCP)	F	zero	0.0002	F '87	0.2	0.05	-	-	-	0.003	B2
Dibutyl phthalate (PAE)	-	-	-	-	-	-	0.1	4	-	-	D
Dicamba	-	-	-	F '88	0.3	0.3	0.03	1	0.2	-	D
Dichloroacetic acid	F	zero	0.06[3]	D '93	5	5	0.004	0.1	-	-[4]	B2
Dichlorobenzene o-	F	0.6	0.6	F '87	9	9	0.09	3	0.6	-	D
Dichlorobenzene m-[5]	-	-	-	F '87	9	9	0.09	3	0.6	-	D
Dichlorobenzene p-	F	0.075	0.075	F '87	11	11	0.1	4	0.075	-	C
Dichlorodifluoromethane	-	-	-	F '89	40	40	0.2	5	1	-	D
Dichloroethylene (1,1-)	F	0.007	0.007	F '87	2	1	0.01	0.4	0.007	-	C
Dichloroethane (1,2-)	F	zero	0.005	F '87	0.7	0.7	-	-	-	0.04	B2
Dichloroethylene (cis-1,2-)	F	0.07	0.07	F '90	4	1	0.01	0.4	0.07	-	D
Dichloroethylene (trans-1,2-)	F	0.1	0.1	F '87	20	1	0.02	0.7	0.1	-	D
Dichloromethane	F	zero	0.005	D '93	10	2	0.06	2	-	0.5	B2
Dichlorophenol (2,4-)	-	-	-	D '94	0.03	0.03	0.003	0.1	0.02	-	E
Dichloropropane (1,2-)	F	zero	0.005	F '87	-	0.09	-	-	-	0.06	B2
Dichloropropene (1,3-)	-	-	-	F '88	0.03	0.03	0.03	1	-	0.04	B2
Dieldrin	-	-	-	F '88	0.0005	0.0005	0.00005	0.002	-	0.0002	B2
Diethyl phthalate (PAE)	-	-	-	-	-	-	0.8	30	-	-	D

[1] Under review

[2] 1998 Final Rule for Disinfectants and Disinfection By-products: The total for trihalomethanes is 0.08 mg/L.

[3] 1998 Final Rule for Disinfectants and Disinfection By-products: The total for five haloacetic acids is 0.06 mg/L.

[4] A quantitative risk estimate has not been determined.

[5] The values for m-dichlorobenzene are based on data for o-dichlorobenzene.

Table B.1 Drinking Water Standards and Health Advisories (Cont.)

Chemicals	Standards			Status HA Document	Health Advisories						Cancer Group
					10-kg child		RfD			mg/L at	
	Status Reg.	MCLG (mg/L)	MCL (mg/L)		One-day (mg/L)	Ten-day (mg/L)	(mg/kg/ day)	DWEL (mg/L)	Lifetime (mg/L)	10^{-4} Cancer Risk	
Diisopropyl methylphosphonate	-	-	-	F '89	8	8	0.08	3	0.6	-	D
Dimethrin	-	-	-	F '88	10	10	0.3	10	2	-	D
Dimethyl methylphosphonate	-	-	-	F '92	2	2	0.2	7	0.1	0.7	C
Dimethyl phthalate (PAE)	-	-	-	-	-	-	-	-	-	-	D
Dinitrobenzene (1,3-)	-	-	-	F '91	0.04	0.04	0.0001	0.005	0.001	-	D
Dinitrotoluene (2,4-)	-	-	-	F '92	0.5	0.5	0.002	0.1	-	0.005	B2
Dinitrotoluene (2,6-)	-	-	-	F '92	0.4	0.4	0.001	0.04	-	0.005	B2
Dinitrotoluene (2,6 & 2,4)[1]	-	-	-	F '92	-	-	-	-	-	0.005	B2
Dinoseb	F	0.007	0.007	F '88	0.3	0.3	0.001	0.04	0.007	-	D
Dioxane p-	-	-	-	F '87	4	0.4	-	-	-	0.3	B2
Diphenamid	-	-	-	F '88	0.3	0.3	0.03	1	0.2	-	D
Diquat	F	0.02	0.02	-	-	-	0.002	0.07	-	-	D
Disulfoton	-	-	-	F '88	0.01	0.01	0.00004	0.001	0.0003	-	E
Dithiane (1,4-)	-	-	-	F '92	0.4	0.4	0.01	0.4	0.08	-	D
Diuron	-	-	-	F '88	1	1	0.002[2]	0.07	0.01	-	D
Endothall	F	0.1	0.1	F '88	0.8	0.8	0.02	0.7	0.1	-	D
Endrin	F	0.002	0.002	F '87	0.02	0.005	0.0003	0.01	0.002	-	D
Epichlorohydrin	F	zero	TT[3]	F '87	0.1	0.1	0.002	0.07	-	0.4	B2
Ethylbenzene	F	0.7	0.7	F '87	30	3	0.1	3	0.7	-	D
Ethylene dibromide (EDB)[4]	F	zero	0.00005	F '87	0.008	0.008	-	-	-	0.00005	B2
Ethylene glycol	-	-	-	F '87	20	6	2	70	14	-	D
Ethylene Thiourea (ETU)	-	-	-	F '88	0.3	0.3	0.00008	0.003	-	0.02	B2
Fenamiphos	-	-	-	F '88	0.009	0.009	0.00025	0.009	0.002	-	D

[1] technical grade.

[2] New OPP RfD = 0.003 mg/kg/day.

[3] When epichlorohydrin is used in drinking water systems, the combination (or product) of dose and monomer level shall not exceed that equivalent to an epichlorohydrin- based polymer containing 0.01% monomer dosed at 20 mg/L.

[4] 1,2-dibromomethane

Table B.1 Drinking Water Standards and Health Advisories (Cont.)

Chemicals	Standards			Status HA Document	Health Advisories						Cancer Group
					10-kg child		RfD			mg/L at	
	Status Reg.	MCLG (mg/L)	MCL (mg/L)		One-day (mg/L)	Ten-day (mg/L)	(mg/kg/ day)	DWEL (mg/L)	Lifetime (mg/L)	10^{-4} Cancer Risk	
Fluometuron	-	-	-	F '88	2	2	0.01	0.5	0.09		D
Fluorene (PAH)	-	-	-	-	-	-	0.04	1	-	-	D
Fonofos	-	-	-	F '88	0.02	0.02	0.002	0.07	0.01	-	D
Formaldehyde	-	-	-	D '93	10	5	0.15	5	1	-	B1[1]
Glyphosate	F	0.7	0.7	F '88	20	20	0.12	4	0.7	-	D
Heptachlor	F	zero	0.0004	F '87	0.01	0.01	0.0005	0.02	-	0.0008	B2
Heptachlor epoxide	F	zero	0.0002	F '87	0.01	-	0.00001	0.0004	-	0.0004	B2
Hexachlorobenzene	F	zero	0.001	F '87	0.05	0.05	0.0008	0.03	-	0.002	B2
Hexachlorobutadiene	-	-	-	F '89	0.3	0.3	0.002	0.07	0.001	0.05	C
Hexachlorocyclopentadiene	F	0.05	0.05	-	-	-	0.007	0.2	-	-	D
Hexachloroethane	-	-	-	F '91	5	5	0.001	0.04	0.001	-	C
Hexane (n-)	-	-	-	F '87	10	4	-	-	-	-	D
Hexazinone	-	-	-	F '96	3	2	0.05[3]	2	0.4	-	D
HMX[4]	-	-	-	F '88	5	5	0.05	2	0.4	-	D
Indeno[1,2,3,-c,d]pyrene (PAH)	-	-	-	-	-	-	-	-	-	-	B2
Isophorone	-	-	-	F '92	15	15	0.2	7	0.1	4	C
Isopropyl methylphosphonate	-	-	-	F '92	30	30	0.1	4	0.7	-	D
Isopropylbenzene (cumene)	-	-	-	D '87	11	11	0.1	4	-	-	D
Lindane[5]	F	0.0002	0.0002	F '87	1	1	0.0003	0.01	0.0002	-	C
Malathion	-	-	-	F '92	0.2	0.2	0.02	0.8	0.1	-	D
Maleic hydrazide	-	-	-	F '88	10	10	0.5	20	4	-	D
MCPA[6]	-	-	-	F '88	0.1	0.1	0.00057	0.02	0.004	-	D
Methomyl	-	-	-	F '88	0.3	0.3	0.025	0.9	0.2	-	E
Methoxychlor	F	0.04	0.04	F '87	0.05	0.05	0.005	0.2	0.04	-	D
Methyl ethyl ketone	-	-	-	F '87	75	7.5	0.6	20	-	-	D
Methyl parathion	-	-	-	F '88	0.3	0.3	0.00025	0.009	0.002	-	D

[1] Carcinogenicity based on inhalation exposure.

[2] New OPP RfD = 2 mg/kg/day.

[3] The Health Advisory is based on a new OPP RfD rather than the IRIS RfD.

[4] HMX = octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine

[5] Lindane = γ-hexachlorocyclohexane

[6] MCPA = 4(chloro-2-methoxyphenoxy)acetic acid

[7] New OPP RfD = 0.0015 mg/kg/day

This TSTP has not been validated in the field.

Table B.1 Drinking Water Standards and Health Advisories (Cont.)

Chemicals	Standards			Status HA Document	Health Advisories						Cancer Group
					10-kg child		RfD			mg/L at 10^{-4} Cancer Risk	
	Status Reg.	MCLG (mg/L)	MCL (mg/L)		One-day (mg/L)	Ten-day (mg/L)	(mg/kg/day)	DWEL (mg/L)	Lifetime (mg/L)		
Metolachlor	-	-	-	F '88	2	2	0.15[1]	0.5	0.1	-	C
Metribuzin	-	-	-	F '88	5	5	0.025[2]	0.9	0.2	-	D
Monochloroacetic acid	F	-	0.06[3]	-	-	-	-	-	-	-	-
Monochlorobenzene	F	0.1	0.1	F '87	4	4	0.02	0.7	0.1	-	D
Naphthalene	-	-	-	F '90	0.5	0.5	0.02	0.7	0.1	-	C
Nitrocellulose (non-toxic)	-	-	-	F '88	-	-	-	-	-	-	-
Nitroguanidine	-	-	-	F '90	10	10	0.1	4	0.7	-	D
Nitrophenol p-	-	-	-	F '92	0.8	0.8	0.008	0.3	0.06	-	D
Oxamyl (Vydate)	F	0.2	0.2	F '87	0.2	0.2	0.025	0.9	0.2	-	E
Paraquat	-	-	-	F '88	0.1	0.1	0.0045	0.2	0.03	-	C
Pentachlorophenol	F	zero	0.001	F '87	1	0.3	0.03	1	-	0.03	B2
Phenanthrene (PAH)	-	-	-	-	-	-	-	-	-	-	D
Phenol	-	-	-	D '92	6	6	0.6	20	4	-	D
Picloram	F	0.5	0.5	F '88	20	20	0.07[4]	2	0.5	-	D
Polychlorinated biphenyls (PCBs)	F	zero	0.0005	D '93	-	-	-	-	-	0.01	B2
Prometon[5]	-	-	-	F '88	0.2	0.2	0.015	0.5	0.1	-	D
Pronamide	-	-	-	F '88	0.8	0.8	0.075	3	0.05	-	C
Propachlor	-	-	-	F '88	0.5	0.5	0.01	0.5	0.09	-	D
Propazine	-	-	-	F '88	1	1	0.02	0.7	0.01	-	C
Propham	-	-	-	F '88	5	5	0.02	0.6	0.1	-	D
Pyrene (PAH)	-	-	-	-	-	-	0.03	-	-	-	D
RDX 6	-	-	-	F '88	0.1	0.1	0.003	0.1	0.002	0.03	C
Simazine	F	0.004	0.004	F '88	0.5	0.5	0.005	0.2	0.004	-	C
Styrene	F	0.1	0.1	F '87	20	2	0.2	7	0.1	-	C
2,4,5-T (Trichlorophenoxyacetic acid)	-	-	-	F'88	0.8	0.8	0.01	0.4	0.07	-	D

[1] New OPP RfD = 0.1 mg/kg/day

[2] New OPP RfD = 0.013 mg/kg/day

[3] 1998 Final Rule for Disinfectants and Disinfection By-products: the total for five haloacetic acids is 0.06 mg/L.

[4] New OPP RfD = 0.2 mg/kg/day

[5] Under review.

[6] RDX = hexahydro-1,3,5- trinitro-1, 3,5- triazine

Table B.1 Drinking Water Standards and Health Advisories (Cont.)

| Chemicals | Standards | | | Status HA Document | Health Advisories | | | | | | Cancer Group |
| | Status Reg. | MCLG (mg/L) | MCL (mg/L) | | 10-kg child | | RfD (mg/kg/ day) | DWEL (mg/L) | Lifetime (mg/L) | mg/L at 10^{-4} Cancer Risk | |
					One-day (mg/L)	Ten-day (mg/L)					
2,3,7,8-TCDD (Dioxin)	F	zero	3E-08	F '87	0.000001	1E-07	1E-09	4E-08	-	2E-08	B2
Tebuthiuron	-	-	-	F '88	3	3	0.07	2	0.5	-	D
Terbacil	-	-	-	F '88	0.3	0.3	0.01	0.4	0.09	-	E
Terbufos	-	-	-	F '88	0.005	0.005	0.0001	0.005	0.0009	-	D
Tetrachloroethane (1,1,1,2-)	-	-	-	F '89	2	2	0.03	1	0.07	0.1	C
Tetrachloroethane (1,1,2,2-)	-	-	-	F '89	0.04	0.04	0.00005	0.002	0.0003	0.02	C
Tetrachloroethylene	F	zero	0.005	F '87	2	2	0.01	0.5	0.01	-	-
Trichlorofluoromethane	-	-	-	F '89	7	7	0.3	10	2	-	D
Toluene	F	1	1	D '93	20	2	0.2	7	1	-	D
Toxaphene	F	zero	0.003	F '96	0.004	0.004	0.0004	0.01	-	0.003	B2
2,4,5-TP (Silvex)	F	0.05	0.05	F '88	0.2	0.2	0.008	0.3	0.05	-	D
Trichloroacetic acid	F	0.3	0.06[1]	D '96	4	4	0.1	4	0.3	-	C
Trichlorobenzene (1,2,4-)	F	0.07	0.07	F '89	0.1	0.1	0.001	0.05	0.01	-	D
Trichlorobenzene (1,3,5-)	-	-	-	F '89	0.6	0.6	0.006	0.2	0.04	-	D
Trichloroethane (1,1,1-)	F	0.2	0.2	F '87	100	40	0.035	1	0.2	-	D
Trichloroethane (1,1,2-)	F	0.003	0.005	F '89	0.6	0.4	0.004	0.1	0.003	0.06	C
Trichloroethylene 2	F	zero	0.005	F '87	-	-	0.007	0.2	-	0.2	B2
Trichlorophenol (2,4,6-)	-	-	-	D '94	0.03	0.03	0.0003	0.01	-	0.3	B2
Trichloropropane (1,2,3-)	-	-	-	F '89	0.6	0.6	0.006	0.2	0.04	-	-
Trifluralin	-	-	-	F '90	0.08	0.08	0.0075	0.3	0.005	0.5	C
Trimethylbenzene (1,2,4-)	-	-	-	D '87	-	-	-	-	-	-	D
Trimethylbenzene (1,3,5-)	-	-	-	D '87	10	-	-	-	-	-	D
Trinitroglycerol	-	-	-	F '87	0.005	0.005	-	-	0.005	0.2	-
Trinitrotoluene (2,4,6-)	-	-	-	F '89	0.02	0.02	0.0005	0.02	0.002	0.1	C
Vinyl chloride[2]	F	zero	0.002	F '87	3	3	-	-	-	0.002	A
Xylenes	F	10	10	D '93	40	40	2	70	10	-	D

[1] 1998 Final Rule for Disinfectants and Disinfection By-products: The total for five haloacetic acids is 0.06 mg/L.

[2] Under review

Table B.1 Drinking Water Standards and Health Advisories (Cont.)

DEFINITIONS

The following definitions for terms used in the Tables are not all-encompassing, and should not be construed to be "official" definitions. They are intended to assist the user in understanding terms found on the following pages.

Action Level: The concentration of a contaminant which, if exceeded, triggers treatment or other requirements which a water system must follow. For lead or copper it is the level which, if exceeded in over 10% of the homes tested, triggers treatment.

Cancer Group: A qualitative weight-of-evidence judgement as to the likelihood that a chemical may be a carcinogen for humans. Each chemical is placed into one of the following five categories:

Group Category
A: Human carcinogen
B: Probable human carcinogen:
B1: indicates limited human evidence;
B2: indicates sufficient evidence in animals and inadequate or no evidence in humans
C: Possible human carcinogen
D: Not classifiable as to human carcinogenicity
E: Evidence of noncarcinogenicity for humans

This categorization is based on EPA's 1986 Guidelines for Carcinogen Risk Assessment. The Proposed Guidelines for Carcinogen Risk Assessment which were published in 1996, when final, will replace the 1986 cancer guidelines.

10^{-4} Cancer Risk: The concentration of a chemical in drinking water corresponding to an estimated lifetime cancer risk of 1 in 10,000.

DWEL: Drinking Water Equivalent Level. A lifetime exposure concentration protective of adverse, non-cancer health effects, that assumes all of the exposure to a contaminant is from drinking water.

HA: Health Advisory. An estimate of acceptable drinking water levels for a chemical substance based on health effects information; a Health Advisory is not a legally enforceable Federal standard, but serves as technical guidance to assist Federal, state, and local officials.

> **One-day HA:** The concentration of a chemical in drinking water that is not expected to cause any adverse noncarcinogenic effects for up to one day of exposure.

> **Ten-day HA:** The concentration of a chemical in drinking water that is not expected to cause any adverse noncarcinogenic effects for up to ten days of exposure.

> **Lifetime HA:** The concentration of a chemical in drinking water that is not expected to cause any adverse noncarcinogenic effects for a lifetime of exposure.

Table B.1 Drinking Water Standards and Health Advisories (Cont.)

LED$_{10}$: Lower Limit on Effective Dose$_{10}$. The 95% lower confidence limit of the dose of a chemical needed to produce an adverse effect in 10% of those exposed to the chemical, relative to the control.

MCLG: Maximum Contaminant Level Goal. A non-enforceable health goal which is set at a level at which no known or anticipated adverse effect on the health of persons occur and which allows an adequate margin of safety.

MCL: Maximum Contaminant Level. The highest level of a contaminant that is allowed in drinking water. MCLs are set as close to the MCLG as feasible using the best available treatment technology and taking cost into consideration. MCLs are enforceable standards.

RfD: Reference Dose. An estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime.

SDWR: Secondary Drinking Water Regulations. Non-enforceable Federal guidelines regarding cosmetic effects (such as tooth or skin discoloration) or aesthetic effects (such as taste, odor, or color) of drinking water.

TT: Treatment Technique. A required process intended to reduce the level of a contaminant in drinking water.

ABBREVIATIONS
D: Draft
F: Final
NA: Not Applicable
NOAEL: No-Observed-Adverse-Effect-Level
OPP: Office of Pesticide Programs
P: Proposed
Reg: Regulation
TT: Treatment Technique

Source: U.S. EPA 2000.

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