US ERA ARCHIVE DOCUMENT



# Generic Sampling and Analysis Plan for Large Cruise Ships in Alaska Waters

## U.S. Environmental Protection Agency

Oceans and Coastal Protection Division Office of Wetlands, Oceans, and Watersheds

Engineering and Analysis Division Office of Science and Technology

Office of Water 1200 Pennsylvania Avenue, NW Washington, D.C. 20460

June 2, 2004

#### **DISCLAIMER**

Neither the United States Government nor any of its employees, contractors, subcontractors, or their employees make any warrant, expressed or implied, or assume any legal liability or responsibility for any third party's use of, or the results of, such use of any information, apparatus, product, or process discussed in this report, or represents that its use by such party would not infringe on privately owned rights.

The primary contact regarding questions or comments on this document is:

Dr. Elizabeth Kim
U.S. Environmental Protection Agency
Oceans and Coastal Protection Division, OWOW (4504T)
1200 Pennsylvania Avenue, NW
Washington, DC 20460
(202) 566-1270 (telephone)
(202) 566-1546 (fax)
kim.elizabeth@epa.gov

For detailed technical inquiries on this document:

Donald Anderson
U.S. Environmental Protection Agency
Engineering and Analysis Division, OST (4303T)
1200 Pennsylvania Avenue NW
Washington, DC 20460
(202) 566-1021 (telephone)
(202) 566-1053 (fax)
anderson.donaldf@epa.gov

## TABLE OF CONTENTS

		Page
1.0	Intro	DDUCTION
	1.1	Background 1-
	1.2	Objectives and Scope
2.0	Crius	SE SHIP OVERVIEW
2.0	2.1	Graywater and Blackwater Generation and Treatment
	2.2	Cruise Ship MSDs
		2.2.1 Activated Oxidation
		2.2.2 Reverse Osmosis
		2.2.3 Aerobic Biological Oxidation Combined with Ultrafiltration 2-4
3.0	SAMP	LING APPROACH
5.0	3.1	Cruise Ship Selection
	3.2	Sampling Point Selection
	3.3	Analyte Selection
	3.4	Sample Collection
	5.1	3.4.1 Flow Measurement Approach
		3.4.2 Graywater Characterization Samples
		3.4.3 Graywater and Blackwater Treatment and Final Effluent
		Samples
		3.4.4 Treatment Residue Samples
		3.4.5 Source Water Sample
		3.4.6 Quality Assessment Samples 3-10
	3.5	Preservation, Shipping, and Analysis
	3.6	Field Measurements
	3.7	Sample Labeling
	3.8	Chain-of-Custody Record
	3.9	Quality Assurance/Quality Control
	3.10	Sample Splitting
4.0	SAMP	LING ACTIVITIES4-
	4.1	Sampling Team Organization
	4.2	Pre-Visit Preparation
	4.3	Field Sampling Activities 4-2
	4.4	Logistics
		4.4.1 Cruise Ship Contacts
		4.4.2 EPA Contacts
		4.4.3 Analytical Laboratories
		4.4.4 ERG Contacts
		4.4.5 Freight Forwarders
5.0	SAMP	LE SHIPMENT 5-1
	5.1	Sample Set Preparation

## TABLE OF CONTENTS

		F	Page
	5.2	Sample Packing	5-3
6.0	Refer	ENCES	6-1
Appendix A:	LIST	OF CONSTITUENTS FOR ANALYSIS	

## LIST OF TABLES

		Page
3-1	Samples for Collection On Board Large Cruise Ships in Alaska Waters .	3-15
3-2	Standard Analytical Methods and Procedures for Samples Collected On Board Large Cruise Ships in Alaska Waters	3-16
3-3	Summary of Sample Container and Preservation Requirements	3-18
3-4	Sampling Point Field Measurements	3-19

## LIST OF FIGURES

		Page
3-1	Flow Meter Measurement Data Sheet	3-20
3-2	Graywater Generation Data Sheet	3-21
3-3	Pesticide, Fungicide, and Rodenticide Use Data Sheet	3-22
3-4	Collection, Holding, and Transfer (CHT) Tank Data Sheet	3-23
3-5	Wastewater Treatment Unit Data Sheet	3-24
3-6	Source Water Data Sheet	3-25
3-7	Sample Preservation Log Sheet	3-26
3-8	Field Sampling Log Sheet	3-27
3-9	Example SCC Traffic Report	3-28

### 1.0 Introduction

The Engineering and Analysis Division (EAD) and the Office of Wetlands, Oceans, and Watersheds (OWOW) of the U.S. Environmental Protection Agency (EPA) is currently conducting a ship visit and sampling program to further evaluate sewage and graywater pollutant discharges and treatment technologies for large cruise ships navigating in Alaska waters. This "generic" sampling plan provides general sampling procedures and methods to be followed when conducting sampling activities while on board selected cruise ships. Sampling will be performed by EPA's technical contractor, Eastern Research Group, Inc. (ERG). This document, in combination with the generic health and safety plan and the vessel-specific sampling and analysis plans (SAPs), is intended to serve as a guide to the ERG field sampling crew, a review mechanism for EPA personnel, and a source of procedural information for vessel personnel.

## 1.1 <u>Background</u>

The EPA is currently conducting a data collection effort aimed at ultimately developing new wastewater discharge regulations for large cruise vessels (greater than 500 passengers) that discharge treated sewage (blackwater) or graywater in the waters of the Alexander Archipelago or the navigable waters of the United States within the State of Alaska or within the Kachemak Bay National Estuarine Research Reserve (hereafter referred to as Alaska waters). Such regulations are authorized by "Title XIV - Certain Alaskan Cruise Ship Operations" of the Miscellaneous Appropriations Bill (H.R. 5666) passed by Congress on December 21, 2000 in the Consolidated Appropriations Act of 2001 (Pub. L. 106-554)(Sections 1401 - 1414), also known as the Murkowski Bill. The law defines sewage to mean human body wastes and wastes from toilets and other receptacles intended to receive or retain body waste. Graywater means only galley, dishwasher, bath, and laundry wastewater; the term does not include other wastes or waste streams. Graywater and blackwater discharges to Alaska waters are also regulated by State law (AS 46-03.460 - 46.03.490).

Due to the overlap of the state and federal law, large cruise ships have one of three options for graywater and blackwater discharge and compliance monitoring:

- 1. Hold their graywater and/or blackwater for discharge only outside of Alaska waters. There are no monitoring requirements for these discharges.
- 2. Discharge graywater and/or blackwater only when the vessel is at least one nautical mile from shore and traveling at least six knots. The discharge must meet the following effluent standards: 150 mg/L for total suspended solids and 200 fecal coliform colonies per 100 mL. Third party sampling of final vessel effluent (discharge) is conducted twice per season for an extensive list of parameters.
- 3. Obtain certification from the U.S. Coast Guard for continuous discharge of graywater and/or blackwater, regardless of vessel location or speed. The discharge must meet the following effluent standards: geometric mean of 20 fecal coliform colonies per 100 mL (not more than 10% of samples greater than 40 fecal coliform colonies per 100 mL), total residual chlorine less than or equal to 10 μg/L, and meet 40 CFR 133.102 secondary treatment standards (BOD, TSS, and pH). Certification sampling includes collection of 5 effluent samples (either effluent from treatment or final vessel discharge) prior to arrival in Alaska waters, followed by sampling twice per month for a limited list of parameters. In addition, sampling per Option 2) is also required.

## 1.2 <u>Objectives and Scope</u>

For Work Assignment 1-09, EAD is preparing to collect and analyze samples to further evaluate pollutants present in graywater and blackwater generated on large cruise vessels that operate in Alaska waters, and to determine the capability of various types of wastewater treatment systems to remove these pollutants prior to discharge. This sampling and analysis data, along with information collected from literature searches and engineering analyses of the design, performance, and cost of wastewater treatment systems will be used to develop effluent reduction benefits and discharge standards for all large cruise vessels that operate in Alaska waters.

The fiscal year 2004 sampling and analysis program will focus on collecting data from three to five cruise vessels discharging treated blackwater and graywater into Alaska waters. Each sampling event will include between three and five, 24-hour sampling periods, depending on the vessel's schedule, including periods when the ship is underway and in port. In addition to the untreated and treated graywater and blackwater samples, quality control (QC) samples consisting of trip blanks, equipment blanks, and duplicate samples will also be collected.

This sampling program complements and augments current compliance monitoring programs in several ways. First, EPA's sampling program will provide data to perform an engineering assessment of the design, operation, maintenance, and performance of graywater and blackwater treatment systems. Specifically, EPA will collect information regarding system design and day-to-day operation and maintenance, and will expand the sampling to focus not only on the treated effluent, but also include samples of the influent to wastewater treatment, effluent from individual treatment units, and any treatment residues. Second, EPA's sampling program will provide information regarding pollutant concentrations and loadings for individual graywater sources (e.g., galley, laundry). Available graywater characterization data are very limited; therefore, graywater sampling is one of the focuses of this program.

Third, EPA's sampling program will provide information to develop time-phased "flow profiles" for the sampled waste streams to analyze patterns and variability in graywater and blackwater flows both throughout the day (e.g., day versus night, mealtimes) and between days (e.g., while underway, in port). Again, available flow profile data are very limited; therefore, collecting this information is one of the focuses of this program. Fourth, where ever possible, EPA plans to collect flow-weighted composite samples, which will be more representative than grab samples that are collected for compliance monitoring.

Fifth, EPA's sampling program includes additional sampling parameters, including E. coli and Enterococci. E. coli is a subgroup of fecal coliform that indicates possible presence of enteric pathogens. Enterococci is a subgroup of fecal streptococcus and is the most

efficient bacterial indicator of water quality. (Fecal streptococcus is a subgroup of fecal coliform used to differentiate human versus animal sources of these microbiologicals.) Epidemiological studies suggest a positive relationship between high concentrations of E. coli and enterococci in ambient waters and incidents of gastrointestinal illnesses associated with swimming. The studies support the use of E. coli and enterococci (instead of fecal coliform) as indicators of microbiological pollution (1)(2).

#### 2.0 CRUISE SHIP OVERVIEW

Due to concerns regarding the quality and quantity of commercial passenger vessel wastewater discharged into Alaska waters and the potential effects of those discharges, environmentalists, government agencies, the cruise ship industry, and other stakeholders formed the Alaska Cruise Ship Initiative in 1999 (3). In 2000, this work group began a voluntary sampling program to test the graywater and blackwater discharges from large cruise vessels that operate in Alaska waters. This sampling program determined that traditional Marine Sanitation Devices (MSDs) on passenger vessels, both large and small, were unable to effectively treat blackwater. In addition, untreated shower and galley water contained bacteria and suspended solids concentrations equal to or exceeding treated blackwater. Since then, some cruise vessels have attempted to improve their existing wastewater treatment systems, while others have replaced their traditional MSDs with new treatment technologies to meet new Federal (33 CFR 159, Subpart E) and State (AS 46.03.460 - 46.03.490) standards for graywater and blackwater discharges in Alaska waters (4). In 2003, thirty large cruise vessels (greater than 500 passengers) operated in Alaska waters with passenger and crew totals ranging between 815 and 3,750 persons (5). Eighteen of these ships have installed advanced wastewater treatment for continuous discharge in Alaska waters under 33 CFR 159.309; the remaining ships hold their treated or untreated blackwater and graywater on board for discharge outside of Alaska waters (6).

### 2.1 Graywater and Blackwater Generation and Treatment

Commercial passenger vessels generate a variety of waste streams, including blackwater and graywater, which are the subject of this report. Information provided to EPA by the Alaska Department of Environmental Conservation (ADEC) shows many of the cruise vessels combine blackwater and graywater for treatment in the same system. Only one vessel, Carnival Spirit operated by Carnival Cruise Lines, is known to treat blackwater and graywater separately. Another vessel, Mercury operated by Celebrity Cruises, treats blackwater in a traditional MSD and then combines the treated blackwater with raw graywater before further treatment in a reverse osmosis system. Some cruise vessels may have multiple treatment

systems to handle graywater and blackwater generated from different areas of the vessel. In all vessels, graywater and blackwater enters a holding tank(s) prior to treatment. Additional holding tanks may collect treated graywater and blackwater for storage for subsequent controlled discharge based on location and/or vessel speed.

## 2.2 Cruise Ship MSDs

Historically, two types of MSDs were used on cruise vessels to treat blackwater: maceration-chlorination and biological-chemical disinfection. (Graywater was historically discharged without treatment.) The maceration-chlorination system reduces biosolids through oxidation and disinfects. In general, the process mixes blackwater with sea water and then passes this solution between electrolytic cells that breakdown some organics while simultaneously generating hypochlorite. Disadvantages of this system are the generation of excess chlorine, which is toxic to marine life, and poor performance described previously.

Biological-chemical disinfection systems operate similar to land-based biological treatment systems for municipal and industrial wastewater. The treatment system includes screening to remove grit and debris, aerobic biological treatment to remove BOD and some nutrients, clarification and filtration to remove solids, and final disinfection to destroy pathogens. Two major disadvantages of this system on board cruise vessels include use of sea water in blackwater and/or graywater systems that can destroy the aerobic microorganisms, and intermittent periods of low flow or no flow, which also affects the viability of the microorganisms.

The problems associated with these MSDs led to the 2000 sampling effort by the Alaska Cruise Ship Initiative. The results of this voluntary sampling effort determined that total suspended solids (TSS) and fecal coliform concentrations in treated blackwater were high, and in most cases far exceeded the MSD manufacturer's performance certifications. In addition, graywater analysis indicated that bacteria concentrations, TSS, and biochemical oxygen demand (BOD, 5-day) in this effluent equaled or often exceeded treated blackwater. The Alaska Cruise Ship Initiative did not investigate the cause of poor treatment performance; however, possible

explanations include inadequate adaptation of shore-based processes for use on board ships, inadequate operation and/or maintenance, highly concentrated wastes from low flush toilets, adverse effects from shipboard cleansers and other sources, and inconsistent influent flow rates.

The poor performance of the MSDs historically used on cruise vessels has caused cruise vessel operators to evaluate new advanced wastewater treatment design. These include activated oxidation, reverse osmosis and aerobic biological oxidation combined with ultrafiltration. A description of each technology is provided in the following subsections.

#### 2.2.1 Activated Oxidation

Activated oxidation with a biological component is intended to oxidize dissolved organic pollutants, remove solids, and kill microorganisms. The Bio-Oxidation CleanSea® System (the only activated oxidation system used in Alaska waters) is comprised of six main components:

- C Primary Hydroxyl-PFM solids separation/oxidation tank;
- C Bioreactors (Hydroxyl-F<sup>3</sup>R);
- C Secondary PFM solids separation;
- C Oxidation/disinfection tank;
- C Controls and oxidant generation equipment; and
- C Sludge dewatering and drying equipment.

A proprietary oxidant is used in the activated oxidation treatment system. The bioreactor includes a suspended plastic media to provide a surface for microbial growth. Polymer is added to the primary solids separation tank to aid in clarification. Solids collected from the system can be dewatered on board and incinerated. Finally, the treated blackwater is disinfected using ozone. Unlike chlorine, ozone residuals dissipate quickly and therefore effluents are much less toxic to marine life.

This system is installed on one cruise vessel operating in Alaska waters (4).

ADEC has not collected any samples from this vessel to date. The vessel does not discharge in Alaska waters at this time, but instead holds water and discharges outside the 3 mile limit.

#### 2.2.2 Reverse Osmosis

Reverse osmosis (RO) is a membrane treatment technology that relies on a pressure differential across a membrane to separate wastewater into a purified permeate and concentrated waste. RO has been installed on two ships operating in Alaska waters (4). At least one of these vessels uses ultraviolet light (UV) disinfection after the RO system.

## 2.2.3 Aerobic Biological Oxidation Combined with Ultrafiltration

These systems employ an integrated system of enhanced aerobic biological treatment and low-pressure membrane filtration. Manufacturers for systems found on board cruise ships include Hamworthy KSE Limited, Zenon Environmental and Scanship Maritime. In the process, ultrafiltration membranes separate the treated water from the mixed liquor . In effect, the membranes perform the functions of the secondary settler and tertiary filter of the activated sludge process in a conventional wastewater treatment plant. Sludge is wasted directly from the aeration tank to maintain an operating mixed liquor suspended solids (MLSS) concentration between 10,000 and 15,000 mg/L (7). An estimated 18 cruise vessels that operated in Alaska waters have installed this technology to treat both blackwater and graywater (4). Some vessels also treat with UV for final disinfection.

### 3.0 SAMPLING APPROACH

This section provides a general discussion of planned sampling procedures, methods, and logistics for conducting sampling activities while on board selected cruise ships. Vessel-specific SAPs will contain detailed information regarding specific sampling points and locations, sampling methodologies, analytes, sampling frequency and duration, schedule, and logistics for sampling on board individual ships.

### 3.1 Cruise Ship Selection

EPA will base cruise vessel selection on information submitted in the ADEC Vessel Specific Sampling Plans (VSSPs), industry sampling data, ADEC sampling data, and input from individual cruise lines and trade associations. EPA will use the following criteria to select cruise vessels that encompass the range of cruise vessels, wastewater treatment technologies, and graywater and blackwater characteristics found within the cruise industry.

- C Treatment system type: only Type II systems ("advanced" or "traditional") will be sampled;
- C Treatment technology (i.e., reverse osmosis, bio-reactor/ultrafiltration);
- C Number of treatment systems;
- C Number of passengers on board (actual);
- C Discharge practices;
- C Wastewater treated: blackwater, graywater, or both;
- C Treatment technology performance; and
- C Ship schedule and/or logistics.

Vessels will be selected for sampling primarily based on use of selected graywater and blackwater treatment technologies and to characterize typical graywater and blackwater and the variety and performance of treatment technologies. Cruise vessel-specific selection criteria will

be contained in either the sampling episode reports (SERs) and/or SAPs prepared for each cruise vessel sampled by EPA. EPA anticipates three to five, 24-hour sampling periods will be conducted on each vessel while underway and in port.

## 3.2 <u>Sampling Point Selection</u>

Table 3-1 lists the proposed sampling points on board cruise vessels. The proposed sampling points were selected by EPA to:

- C Determine the flow profile and characteristics of graywater generated from the galley, accommodations, dishwashing, and laundry;
- C Determine the effectiveness of the graywater and/or blackwater treatment system(s) at removing the targeted pollutants;
- C Determine the characteristics of graywater and blackwater discharges, including treated wastewater and untreated wastewaters held for discharge outside state waters;
- C Determine the characteristics of treatment system residues (e.g., biological treatment sludge, reverse osmosis concentrate, etc.) to evaluate disposal options;
- C Determine any background levels of analytes in cruise ship source water; and
- C Verify the quality of the data by collecting duplicate samples, trip blank(s), and equipment blank(s).

Untreated graywater samples will be collected from piping from graywater collection or holding tanks to characterize graywater sources on board the cruise vessel, including the galley, dishwashing, accommodations (e.g, bath, shower), and laundry. Due to the potentially large number of graywater generating locations on board the cruise ship, the actual location where each gray water samples will be collected will be determined during the ship visit and described in the vessel-specific SAPs. Note that untreated graywater characterization samples will likely be collected at a reduced frequency and/or reduced number of vessels as compared to wastewater treatment samples.

Influent and effluent samples will be collected from each of the vessel's graywater and/or blackwater treatment systems to evaluate treatment performance, along with final vessel effluent (discharge) samples and treatment residue samples. Intermediate wastewater treatment samples may also be collected within the treatment train. For example, samples may be collected following aerobic biological treatment and prior to membrane filtration, and following membrane filtration and prior to disinfection. Intermediate wastewater treatment samples will allow EPA to specifically characterize the performance of individual treatment units in addition to the effectiveness of the overall treatment train.

The specific sampling points and locations, samples, and list of parameters selected for each ship will be described in the vessel-specific SAPs prepared for each cruise vessel sampled.

#### 3.3 **Analyte Selection**

Analytes that may be included in an EPA/EAD sampling program include those in the classes of pollutants listed below. Note that some parameters (e.g., pesticides, dioxins and furans, and chlorinated biphenyls congeners will be analyzed at a reduced frequency as compared to other parameters, and will be analyzed for at certain sampling points but not at others. The vessel-specific SAPs will specify the list of parameters and collection frequency for each sampling point.

- C Fecal coliforms;
- C Escherichia coli (E. coli);
- C Enterococci;
- C Biochemical oxygen demand, 5-day (BOD<sub>5</sub>);
- C Chemical oxygen demand (COD);
- C Total organic carbon (TOC);
- C Total suspended solids (TSS);
- C Settleable solids (SS);
- C Total dissolved solids (TDS);
- C Total Kieldahl nitrogen (TKN);
- C Ammonia as nitrogen;
- C Nitrate/nitrite as nitrogen:
- C Total phosphorus;
- C Sulfate;

- C Chloride;
- C Alkalinity;
- C Hexane extractable material (HEM);
- C Silica-Gel Treated Hexane Extractable Material (SGT-HEM);
- C Volatile organics;
- C Semivolatile organics;
- C Metals (total and dissolved);
- C Cyanide (total and available);
- C Organo-phosphorous pesticides;
- C Organo-halide pesticides;
- C Chlorinated biphenyls congeners (PCBs); and
- C Dioxins and furans.

Table 3-1 lists pollutants that will be analyzed at each sampling point, and Table 3-2 lists the analytical methods that will be used. Appendix A of this document lists the individual parameters included in each analytical method. In addition to these analytes, the sampling crew will conduct field measurements at all sampling points (see Section 3.6).

Certain conventional and non-conventional pollutants (Group I and Group II) will be collected in the same sample bottle at some sampling points. "Group I" parameters include TDS, TSS, chloride, sulfate, and alkalinity. "Group II" parameters include TOC, COD, ammonia as nitrogen, nitrate/nitrite as nitrogen, TKN, and total phosphorus. HEM and SGT-HEM will also be collected in the same sample bottle at each sampling point. All other parameters will be collected in individual bottles.

Currently, some cruise ships operate incinerators for reducing the volume of wastewater treatment system residues prior to disposal. Incineration of waste and residuals from various industrial sectors have produced ash that contains metals, semivolatile organics, dioxin and furans. One ash grab sample will be collected from each vessel selected for the sampling program that uses on-board incineration of wastewater treatment sludge. The ash sample will be analyzed for metals, semivolatile organics, and dioxins/furans.

Dissolved metals samples will be analyzed for filterable waste streams only. At a minimum, dissolved metals samples will be collected from each treatment system effluent and from the ship's final effluent. Some graywater samples and intermediate treatment system

samples may also be filterable to yield a dissolved metals sample. Dissolved metals samples will not be collected for untreated blackwater.

Due to the very short sample holding times for microbiologicals (fecal coliforms, E. coli, and enterococci - 6 hours),  $BOD_5$  (48 hours), and SS (48 hours), an on-board laboratory will be used for analysis of these samples.

## 3.4 <u>Sample Collection</u>

Much of the information about the collection of samples for this sampling program is summarized in a series of tables as follows:

- C Table 3-1, summarizes the sampling points and analytes to be studied;
- C Table 3-2, summarizes the parameters, analytical method numbers, and laboratory measurement techniques; and
- C Table 3-3, summarizes the parameters, bottle types, sample volume, and preservation requirements.

The sampling program on each vessel will consist of three to five 24-hour sample collection periods and will be specified in the vessel-specific SAPs.

To characterize the wastestreams on board vessels, the samplers will employ varying methods of sample collection depending on the sampling point, pollutant parameters, and the nature of the sample flow and composition at each sampling point. The following subsections provide general descriptions of the anticipated sample collection techniques.

Vessel-specific SAPs will contain detailed information regarding specific sampling points and locations, sampling methodologies, analytes, and sampling frequency and duration for each ship.

In general, samplers will work in teams of two to ensure that proper sampling techniques are followed and adequate notes are taken at each sampling location. Samplers will

wear disposable gloves, tyvek suit, and safety eyewear, and will observe precautions while collecting samples, remaining aware of the potential biohazards present.

Sample containers and bottles will be purchased pre-cleaned and certified and will not require rinsing with sample. Samplers will take care not to touch the insides of bottles or lids/caps during sampling. All samples collected during the sampling episode will be cooled immediately in an ice-water bath to 4°C and then placed into coolers containing bagged ice to maintain a sample temperature of 4°C throughout sample storage, shipment, and receipt at the analytical laboratories.

### 3.4.1 Flow Measurement Approach

Flow measurement data will be collected to support both the treatment system/final cruise vessel effluent discharge and the graywater characterization sampling efforts. The availability of existing equipment on board the cruise vessel, the accessibility of piping and tankage, and the capability of removing liquids from transfer lines will determine how flows are measured. Prior to each sampling event, vessel-specific information will be evaluated and the methodology for measuring flows will be determined.

In general, if existing flow totalizers are available at any sampling location, these data will be recorded on the data sheet provided in Figure 3-1. If totalizer data is not available, then a series of instantaneous flow rates will be measured and recorded using an ultrasonic flow meter installed by the samplers, and the duration of each discharge event will be recorded. The flow measurements will provide the amount of wastewater processed in the periods corresponding to the analytical data collected. In the event that neither totalizer data nor reliable flow measurements can be made for a specific sampling point, flow rate estimates can be calculated using tank level indicator readings or pump capacities and operating times.

Flow-weighted composite samples of graywater, treatment system influent/intermediate/effluent, and final cruise vessel effluent will be collected using an automatic sampling machine. Automatic composite samples will be collected isokinetically.

That is, the velocity in the sampling device should equal the velocity in the "main" pipe system to allow for collection of flow-proportional samples.

### 3.4.2 Graywater Characterization Samples

Graywater characterization samples that will be collected include galley, accommodations, dishwashing, and laundry. Note that graywater characterization samples will likely be collected at a reduced frequency and/or reduced number of vessels as compared to wastewater treatment samples. Samples can be collected only when graywater is flowing through the collection tank discharge pipes; therefore, an automatic compositor will be electronically linked to an ultrasonic flow meter installed on the discharge line. The flow meter will signal the compositor to collect a sample each time a fixed quantity of graywater has passed through the discharge line.

During each 24-hour sampling period, a composite sample of up to 20-liters will be collected in 10-L glass composite sample containers to provide the required sample volume listed in Table 3-3, plus additional volume for laboratory quality control (see Section 3.4.6) and sample spillage. Composite sample containers will be maintained on ice throughout the collection period. The same composite sample containers will be used at each sampling point each day; they will be rinsed with fresh sample prior to beginning a new 24-hour composite. Equally-sized composite sample aliquots will be collected in proportion to the amount flowing through each tank discharge line during each sampling period (See Section 3.4.1, Flow Measurement Approach, for more information). Sample aliquots will be collected through Teflon tubing. At the conclusion of each 24-hour sampling period, sample fractions will be poured from the composite sample containers into individual sample bottles using the procedure described in Section 5.1. Bottles will normally be filled to the shoulder of the bottle, leaving a small space for expansion and mixing. Filtering of samples for analysis of dissolved metals will be performed immediately upon receipt at the on-board field laboratory.

Up to four grab samples for HEM/SGT-HEM, VOCs, and microbiologicals will be collected at each sampling point during each 24-hour sampling period. Grab sample

collection frequency for these parameters will be determined based on each cruise vessel's schedule and will be specified in the vessel-specific SAPs. An equal number of graywater grab samples will be collected during peak and off-peak generation periods. Each grab sample for microbiologicals and HEM/SGT-HEM will be analyzed separately at the analytical laboratory. The VOC grab fractions will be composited at the laboratory for one analysis per sampling point per day.

Grab samples will be collected directly into sample fraction bottles when possible. When not possible (e.g., the pump cycle on a graywater collection tank is too quick to allow for collection of all grab samples), VOC samples will be collected into a specially-cleaned 1-L widemouth jar; the 40-ml VOC vials will be subsequently filled with sample from the widemouth jar. All VOC vials will be filled leaving a convex meniscus at the top of the bottle, with no air bubbles present; when the VOC lid is screwed on a small volume of water will be displaced and no air should be present in the bottle. All VOC vials will be pre-preserved with two drops of HCl per vial for biological activity. If field measurements (see Section 3.6) indicate free chlorine is present in the graywater samples at concentrations greater than 0.03 mg/L, then 3 granules of sodium thiosulfate will be added to the sample vials prior to sample collection.

Graywater generation information will be recorded each day on the graywater generation data sheet provided in Figure 3-2. In addition, information regarding the use of pesticides, fungicides, and rodenticides and their potential to enter graywater and blackwater systems will be recorded on the data sheet provided in Figure 3-3. Finally, information regarding the graywater collection, holding, and transfer system will be recorded on the data sheet provided in Figure 3-4.

### 3.4.3 Graywater and Blackwater Treatment and Final Effluent Samples

Influent and effluent wastewater samples will be collected from each graywater and/or blackwater treatment system on board the cruise vessels. Intermediate wastewater treatment samples may also be collected within the treatment train. For example, samples may

be collected following aerobic biological treatment and prior to membrane filtration, and following membrane filtration and prior to disinfection. Intermediate wastewater treatment samples will allow EPA to specifically characterize the performance of individual treatment units. In addition, each graywater and/or blackwater discharge point (outfall) from the cruise vessel will be sampled. Wastewater treatment influent, intermediate, and effluent samples, as well as and final discharge samples, will typically be analyzed for all pollutant groups, with the exception of influent to disinfection, which will be analyzed for microbiologicals only.

During each 24-hour sampling period, a composite sample and grab samples will be collected at each wastewater treatment and final effluent sampling point using the same procedure as described for graywater samples in Section 3.4.2.

Information regarding the design, operation, and maintenance of the wastewater treatment units will be recorded on the data sheet provided in Figure 3-5. In addition, information regarding the blackwater collection, holding, and transfer system will be recorded on the data sheet provided in Figure 3-4.

## 3.4.4 Treatment Residue Samples

Grab samples of treatment system residue will be collected during the sampling episode. The residue sample will be collected to represent the actual material that is being either discharged, incinerated, or removed from the vessel. Residue type and physical characteristics will be determined by the on board wastewater treatment system. For example, biological treatment systems generate a concentrated sludge that may be further dewatered and incinerated on board or discharged while at sea. Reverse osmosis systems generate a concentrated liquid stream that may be recycled to the treatment system influent, discharged at sea, or held in tanks until the vessel reaches port and the tank can be pumped. In any case, the residue sample will be the final waste stream that is prepared for disposal. Residue samples will be analyzed for the same pollutants as blackwater and graywater samples, with the exception of ash samples following incineration. Ash samples will be analyzed for semivolatile organics, metals, and dioxins and furans only.

#### 3.4.5 Source Water Sample

A source water grab sample will be collected from the ship's potable water system to determine if any of the targeted pollutants are present as background contamination. The location where the source water sample will be collected will be specified in the vessel-specific SAPs. The source water sample will be analyzed for all of the target parameters.

Information regarding the potable water source and treatment will be recorded on the data sheet provided in Figure 3-6.

### 3.4.6 Quality Assessment Samples

Duplicate samples will be collected as part of the quality assurance program for sampling. Duplicate samples are collected as separate aliquots in the field. Results of the duplicate analyses will be used to evaluate precision, including variability in sample collection, handling, preparation, and analysis. Duplicate samples will be collected on a minimum of 10% of all chemical analyses for this program, and will be collected at the effluent from wastewater treatment sampling point. Exceptions include HEM/SGT-HEM and PCBs for which duplicate samples will not be collected. Microbiological duplicate samples will be collected as a lesser frequency of one duplicate per 20 samples.

Trip blanks will be collected and analyzed for volatile organics (VOCs). Trip blanks will consist of HPLC water poured into sampling bottles in the ERG sampling room and shipped to the sampling location. The trip blank will be shipped back (unopened) to the laboratory along with collected samples. This blank will be used to evaluate possible VOC contamination arising during shipment and handling of samples.

Equipment blanks will be collected and analyzed for semivolatile organics and total metals for any sampling equipment, other than sample bottles, that come into direct contact with samples. For example, if an automatic sampling machine is used, an equipment blank will be collected and analyzed. The equipment blank will consist of HPLC water poured over or

pumped through sampling equipment. Equipment blanks are used to evaluate possible contamination caused by sampling equipment or by sampling equipment decontamination procedures.

As part of standard laboratory quality control (QC), matrix effects on analytical performance are assessed through the analysis of matrix spikes and laboratory duplicates. For non-isotope dilution procedures (i.e., all but Methods 1613 and 1668) these analyses are conducted on 10 percent of the samples from a given matrix (e.g., aqueous, sludge) within a sampling event. Consequently, additional sample volume must be collected for these QC analyses. (Matrix effects assessment QC samples are not required for isotope dilution procedures.) The ERG sampling team will be responsible for collecting, labeling, and shipping the laboratory CQ volumes. Laboratory QC volumes will be collected as part of the composite volume and poured into separate sample bottles at the same time as other sample aliquots are prepared.

Laboratory duplicates will be collected as QC samples specifically for microbiologicals and will be collected as a single samples that is split and analyzed as two separate samples. Laboratory duplicates will be collected at a frequency of one per 20 samples at the effluent from wastewater treatment. Sampling crew quality control samples will be collected from the source water as a part of the quality assurance program to ensure that sampling members are not contaminating the samples with microbiologicals during sample collection. In addition, several other microbiological QC procedures will be required prior to sampling, such as positive and negative controls, dilution water blanks, and media and sample bottle sterility checks.

#### 3.5 Preservation, Shipping, and Analysis

All samples will be maintained on ice immediately upon collection. Chemical preservatives will be added on board according to method-specified protocols either upon sample collection (i.e., grab samples) or following preparation of sample fractions from the composite sample (see Section 5.1). Table 3-3 lists the analytical fraction type, sample container, sample

volume, and preservation method for each type of analysis. Preservation may need to be repeated as chemical reactions progress in samples. The type and amount of preservation used will be recorded on sample preservation log sheets (Figure 3-7). The samples will be packed in ice chests with a sufficient quantity of wet ice to maintain a temperature of 4°C (+/- 2°C) until the cruise vessel arrives in port.

If the cruise ship docks in Juneau, Alaska, the samples can be prepared for overnight shipment via Federal Express to laboratories specified by EPA's Sample Control Center (SCC). If the cruise ship docks in either Ketchikan or Sitka, Alaska, the samples will be shipped via Alaska Airlines Goldstreak Air Cargo to Juneau where the samples will be transferred to Federal Express for continued shipment to the laboratory. All samples being shipped via Federal Express from Juneau will be packed in ice chests containing double-bagged wet ice. All samples shipped from Ketchikan or Sitka to Juneau via Alaska Airlines Gold Streak will be packed in ice chests containing blue ice.

#### **3.6** Field Measurements

Temperature, pH, salinity, conductivity, turbidity, sulfide, hardness, and free and total chlorine will be measured and recorded by the sampling crew at each sampling point when each grab sample is collected. A 1-liter glass jar will be filled during collection of each grab sample set for field measurements. Temperature and pH will be measured immediately after the collection of the field measurement aliquot; the other field measurements will be conducted shortly thereafter, either in the field (preferably) or in the sample staging area. Samplers will follow applicable test kit calibration procedures specified by the manufacturer. Table 3-4 summarizes the field measurements, how they are to be taken, and the measurement frequency.

Field sampling log sheets (Figure 3-8) will be completed at each sampling point for each 24-hour sampling period. This sheet will record the sampling methodology, names of the samplers, sample collection times, field measurements, and any notes and observations.

## 3.7 <u>Sample Labeling</u>

Each sample will be coded with a unique sample number and labeled at the time of collection. The self-adhesive label will be completed in indelible ink and will contain the following information:

- C Sample number;
- C Sampling episode number;
- C Sampling point description;
- C Analysis to be performed;
- C Sample bottle type;
- C Date of sample collection; and
- C Preservation used.

Once applied to the sample container, labels will be covered with clear tape to prevent tampering, abrasion, smearing, or loss during transit.

#### 3.8 <u>Chain-of-Custody Record</u>

To maintain a record of sample collection, shipment, and receipt by the laboratory, a SCC Traffic Report will be filled out for each sample fraction at each sampling location. These forms will be used to document sample custody transfer from the field to the laboratory. SCC Traffic Reports will be completed for all samples sent off the cruise vessel for analysis. At the time of sample shipment, a copy of the traffic report will be sent to SCC, another copy will be kept by sampling personnel, and the remainder of the copies will be transmitted with the samples to the analytical laboratory. Figure 3-9 includes an example SCC Traffic Report. When the samples are received by the designated analytical laboratory, a copy of the traffic report will be sent to SCC to acknowledge receipt and the condition of the samples.

#### 3.9 Quality Assurance/Quality Control

Quality assurance/quality control (QA/QC) procedures applicable to the large cruise vessel project are outlined in the *Quality Assurance Project Plan for Rulemaking Support* 

*for Large Cruise Ships in Alaska Waters* (8). The QA/QC program for sample collection on board large cruise vessels will include the following:

- C Sampling according to the <u>EAD Sampling Guide</u>, Viar and Company, June 1991;
- C Documentation for samples through laboratory Chain-of-Custody Records;
- C Collection of duplicate samples;
- C Collection of trip blank(s) for VOC analyses; and
- C Collection of equipment blank(s) for semivolatile organics and metals.

## 3.10 <u>Sample Splitting</u>

The cruise vessel being sampled has the option to collect duplicate samples (split samples) at each of the sampling points. If this option is exercised, the cruise vessel owner or their representative will supply all of the personnel, equipment, glassware, and reagents required to collect the split samples and to coordinate the analysis of samples.

Table 3-1 Samples for Collection On Board Large Cruise Ships in Alaska Waters

Analytical Parameter	Galley	Dish- washing	Laundry	Accommo- dations	Influent to Wastewater Treatment (g)	Wastewater Treatment Intermediate (h)	Effluent From Wastewater Treatment	Effluent From Wastewater Treatment (Duplicate)	Cruise Vessel Discharge	Wastewater Treatment Residue (i)	Source Water	Trip Blank	Equip- ment Blank
Microbiologicals (a)	X	X	X	X	X	X	X	X	X		X		
Volatile Organics	X	X	X	X	X		X	X	X	X	X	X	
Semivolatile Organics	X	X	X	X	X		X	X	X	X	X		X
Total Metals	X	X	X	X	X		X	X	X	X	X		X
Dissolved Metals (b)	X	X	X	X			X	X	X		X		X
Cyanide (c)	X	X	X	X	X		X	X	X	X	X		
HEM/SGT-HEM (d)	X	X	X	X	X		X		X				
Biochemical Oxygen Demand (5-day)	X	X	X	X	X		X	X	X	X	X		
Settleable Solids	X	X	X	X	X		X	X	X	X	X		
Group I (e)	X	X	X	X	X		X	X	X	X	X		
Group II (f)	X	X	X	X	X		X	X	X	X	X		
Organo-Phosphorus Pesticides	X	X			X								
Organo-Halide Pesticides	X	X			X								
Chlorinated Biphenyls Congeners					X								
Dioxins/Furans			X							X			

- (a) Microbiologicals include fecal coliforms, E. coli, and enterococci.
- (b) Dissolved metals samples will be analyzed for filterable waste streams only.
- (c) Includes both total and available cyanide.
- (d) HEM is hexane extractable material. SGT-HEM is silica gel treated hexane extractable material.
- (e) Group I includes total suspended solids (TSS), total dissolved solids (TDS), sulfate, chloride, and alkalinity.
- (f) Group II includes total organic carbon (TOC), chemical oxygen demand (COD), ammonia as nitrogen, nitrate/nitrite as nitrogen, total Kjeldahl nitrogen (TKN), and total phosphorus.
- (g) Influent may include graywater, blackwater, or a combined graywater/blackwater mixture.
- (h) If wastewater treatment intermediate is influent to disinfection, then only microbiologicals will be analyzed.
- (i) If residue is ash from incineration of wastewater treatment sludge, then only dioxins/furans, semivolatile organics, and total metals will be analyzed.

Table 3-2

## **Standard Analytical Methods and Procedures** for Samples Collected On Board Large Cruise Ships in Alaska Waters

Method No.	Title	Method Type
SM 9222D	Fecal Coliforms	Membrane filtration
SM 9223B	Escherichia Coli (E. coli)	Multiple tube/multiple well
ASTM D6503-99	Enterococci	Multiple tube/multiple well
EPA 160.2	Residue, Non-filterable (TSS)	Gravimetric
EPA 160.5	Settleable Matter (SS)	Volumetric
EPA 160.1	Total Dissolved Solids (TDS)	Gravimetric
SM 2320 B	Alkalinity	Titrimetric
EPA 375.1, 375.3, or 375.4	Sulfate	Colorimetric, Gravimetric, or Turbidimetric
EPA 325.2 or 325.3	Chloride	Colorimetric or Titrimetric
EPA 351.2, 351.3, or 351.4	Total Kjeldahl Nitrogen (TKN)	Colorimetric, Titrimetric, or Potentiometric
EPA 350.1, 350.2, or 350.3	Ammonia as Nitrogen	Colorimetric, Titrimetric, or Potentiometric
EPA 353.1, 353.2, or 353.3	Nitrate/Nitrite as Nitrogen	Colorimetric or Spectrophotometric
EPA 365.2 or 365.4	Total Phosphorus	Colorimetric
EPA 405.1	Biochemical Oxygen Demand (BOD <sub>5</sub> )	Titrimetric
EPA 410.1, 410.2, 410.3, or 410.4	Chemical Oxygen Demand (COD)	Titrimetric or Colorimetric
EPA 415.1	Total Organic Carbon (TOC)	Combustion or Oxidation
335.2	Total Cyanide	Titrimetric or Spectrophotometric
1677	Available Cyanide	Titrimetric or Spectrophotometric
EPA 1664A	Hexane Extractable Material and Silica Gel Treated Hexane Extractable Material (HEM/SGT-HEM)	Gravimetric
EPA 200.7, 200.8, 200.9, and 245.7 (Mercury only)	Metals by Inductively Coupled Plasma Atomic Emission Spectrometry, Mass Spectrometry, and Atomic Absorption Spectroscopy	GFAA, ICP, ICP/MS and CVAA
EPA 624	Volatile Organic Compounds by GC/MS	GC/MS
EPA 625	Semivolatile Organic Compounds by GC/MS	GC/MS
EPA 1613B	Dioxins and Furans by Isotope Dilution HRGC/MS	HRGC/MS
EPA 1657	Organo-Phosphorous Pesticides	GC-FPD
EPA 1656	Organo-Halide Pesticides	GC-HSD

## **Table 3-2 (Continued)**

Method No.	Title	Method Type
EPA 1668A	Chlorinated Biphenyls Congeners by Isotone Dilution HRGC/MS	HRGC/MS

Table 3-3 **Summary of Sample Container and Preservation Requirements** 

Parameter	Sample Container	On-Board Preservation (d)
Fecal Coliforms	120 ml sterile bottle (c)	100 mg/L Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , 4°C
E. coli	120 ml sterile bottle (c)	100 mg/L Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , 4°C
Enterococci	120 ml sterile bottle (c)	100 mg/L Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , 4°C
Volatile Organics	Two 40-mL glass vials (c)	3 granules (10 mg) Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> per vial, 2 drops HCl per vial, 4°C
Semivolatile Organics	Two 1-L amber glass bottles	80 mg/L Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , 4°C
Total Metals	500-mL plastic bottle	None required
Dissolved Metals	500-mL plastic bottle	0.45 um filtration
HEM/SGT-HEM	1-L wide mouth glass jars (c)	HCl or H <sub>2</sub> SO <sub>4</sub> to pH <2, 4°C
Cyanide, Total	500-mL plastic bottle	Ascorbic acid (0.6 g/L) to remove Cl <sub>2</sub> , NaOH to pH >12, 4°C. If sulfide is present, add 2 g lead carbonate to precipitate sulfide prior to raising pH. If aldehydes are present, add 20 mL of a 3.5% ethylenediamine solution per 1 L of sample after raising the pH.
Cyanide, Available	500-mL amber glass bottle	Ascorbic acid (0.6 g/L) to remove Cl <sub>2</sub> , NaOH to pH >12, 4°C. If sulfide is present, add 2 g lead carbonate to precipitate sulfide prior to raising pH. If aldehydes are present, add 20 mL of a 3.5% ethylenediamine solution per 1 L of sample after raising the pH.
Biochemical Oxygen Demand (5-day)	1-L plastic bottle	4°C
Settleable Solids	1-L plastic bottle	4°C
Group I (a)	1-L plastic bottle	4°C
Group II (b)	1-L and 500 mL glass bottles	H <sub>2</sub> SO <sub>4</sub> to pH <2, 4°C
Dioxins and Furans	Two 1-L amber glass bottles	If pH>9, H <sub>2</sub> SO <sub>4</sub> to pH 7-9 80 mg/L Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , 4°C
Organo-Phosphorus Pesticides	Two 1-L amber glass bottles	NaOH or H <sub>2</sub> SO <sub>4</sub> to pH 5-9 80 mg/L Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , 4°C
Organo-Halide Pesticides	Two 1-L amber glass bottles	NaOH or H <sub>2</sub> SO <sub>4</sub> to pH 5-9 80 mg/L Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , 4°C
Chlorinated Biphenyls Congeners	Two 1-L amber glass bottles	H <sub>2</sub> SO <sub>4</sub> to pH 2-3 80 mg/L Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , 4°C

<sup>(</sup>a) Group I includes total dissolved solids (TDS), total suspended solids (TSS), sulfate, chloride, and alkalinity.

<sup>(</sup>b) Group II includes total organic carbon (TOC), chemical oxygen demand (COD), ammonia as nitrogen, nitrate/nitrite as nitrogen, total Kjeldahl nitrogen (TKN), and total phosphorus.

<sup>(</sup>c) Grab samples for microbiologicals, volatile organics, HEM/SGT-HEM analysis will be collected separately for each composite aliquot.

<sup>(</sup>d) Addition of sodium thiosulfate is required only if residual chlorine is present in the sample at a concentration greater than 0.03 mg/L.

Table 3-4
Sampling Point Field Measurements

Field Measurements	Method	Frequency
Temperature	Thermometer	Each time grab samples (e.g., VOCs) are collected
Turbidity	Turbidity meter	Each time grab samples (e.g., VOCs) are collected
Salinity	Salinity meter	Each time grab samples (e.g., VOCs) are collected
Conductivity	Conductivity meter	Each time grab samples (e.g., VOCs) are collected
Sulfide	Colorimetric test kit	Each time grab samples (e.g., VOCs) are collected.
рН	Four color indicator strip	Each time grab samples (e.g., VOCs) are collected
Hardness	Titrimetric test kit	Each time grab samples (e.g., VOCs) are collected
Free and Total Chlorine	Colorimetric test kit	Each time grab samples (e.g., VOCs) are collected

# 3-20

## Flow Meter Measurement Data Sheet

Vessel:						Disch	narge:					
Meter Information												
Meter Type: Serial #:								Calibration:				
Install Location:								Date:	Time: Gallons:			
De-Install	Information							Date:	Time:	Gallons:		
Day/		Gall	ons						Gall	ons		
Day/ Date	Time	Totalizer Daily V <sub>s</sub> Al	Alarn	18	Day/Date	Time	Totalizer	Daily	$V_s$	Alarms		

Figure 3-1. Flow Meter Measurement Data Sheet

# **GRAYWATER GENERATION DATA SHEET** Vessel: Date: Recorded By: Vessel Point(s) of Contact: Number of Passengers and Number of Crew Actually on Board: Unusual Maintenance or Operational Activities Described By Vessel Point(s) of Contact: Number and Time of Meals Served by Day (include passengers and crew): Breakfast: Lunch: Dinner: Other Meals: Were Dishwashers Operated? (Circle one) Yes / No If yes, what weight, number of pieces, or number of loads were washed? What times were dishes washed by day? Estimated volume of water per load: Detergent name (obtain MSDS if available): Was Laundry Washed? (Circle one) Yes / No If yes, number of hours per day laundry was operated: Weight, number of pieces, or number of loads washed per day: What times were dishes washed by day? Estimated volume of water per load: Detergent and other chemicals names (obtain MSDS if available): Other Sources (e.g., small pantries, steward stations, cleaning stations): Times these sources are generated: Estimated volume per source:

Figure 3-2. Graywater Generation Data Sheet

PESTICIDE, FUNGICIDE, AND RODENTICIDE USE DATA SHEET						
Vessel: Date: Recorded by:						
Pesticides Used On-Bo	oard: yes or no (cir	cle one)				
Pesticide Name	Target Pest(s)	•	MSDS Obtained (yes/no)			
List Locations Where I	Pesticides are Norma	lly Applied and Stored	On-Board and Dates Applied:			
Potential to Enter Gray	water/Blackwater Sy	ystems (e.g., application	n, spills, floor drains)?			
Person(s) Responsible	for Pesticide Applica	ation:				
Fungicides Used On-H	Board: yes or no (ci	ircle one)				
Fungicide Name	Target Fungi	Amount Used/yr	MSDS Obtained (yes/no)			
			d On-Board and Dates Applied:			
Potential to Enter Gray	water/Blackwater Sy	ystems (e.g., application	n, spills, floor drains)?			
Person(s) Responsible	for Fungicide Applic	cation:				
Rodenticides Used Or	1-Board: yes or no	(circle one)				
Rodenticide Name	Target Rodent	Amount Used/yr	MSDS Obtained (yes/no)			
List Locations Where Rodenticides are Normally Applied and Stored On-Board and Dates Applied:						
Potential to Enter Graywater/Blackwater Systems (e.g., application, spills, floor drains)?						
Person(s) Responsible	for Rodenticide App	lication:				

Figure 3-3. Pesticide, Fungicide, and Rodenticide Use Data Sheet

COLLECTION, HOLDING, AND TRANSFER (CHT) TANK DATA SHEET						
Vessel: Date: Recorded by:						
Tank Number or Identification:						
Wastewater Source(s):						
Tank Volume: m³ or gallons						
Does the Tank Have Vacuum: yes or no (circle one):						
Vacuum: mm Hg						
Tank Material of Construction:						
Is this a double bottom tank: yes or no (circle one)?						
Normal Operating Volume: m <sup>3</sup>						
Automated Tank Gauging and Discharge System: yes or no (circle one)						
Discharge Type: batch or continuous (circle one)						
Totalizer or Flow Meter on Discharge Line: yes or no (circle one)						
Discharge Flow Rate: m³/min or m³/day						
Wastewater Destination After Leaving the Tank:						
Approximate Diameter of Discharge Line: inches						
Screens or Filters Present on Either Influent or Discharge Lines (describe):						
Chemical Additions to Tank:  Chemical Name Purpose Amount MSDS (yes/no)  kg/day kg/day kg/day						
Is sludge removed from this tank (describe frequency, amount, destination)?:						

Figure 3-4. Collection, Holding, and Transfer (CHT) Tank Data Sheet

WASTEWATER TREATMENT UNIT DATA SHEET								
Vessel: Date: Recorded by:								
Description of Treatment Un	it:							
Manufacturer:								
Model:								
Design Drawings Obtained:	Design Drawings Obtained: yes or no (circle one)							
Design Capacity:	gpd or gpm (circl	e one)						
Typical Operating Flow Rate	e: gpd o	or gpm (circle o	one)					
Operational period: ho	ours							
Chemical Additions: Chemical	Amount	Units	MSDS Obtained					
Electrical Requirements:								
Volts: Amps:	Horsepower	::						
Sludge Generation: yes or no (circle one) If yes, describe frequency, amount, and destination:								
Was maintenance performed on treatment unit: yes or no (circle one) If maintenance was performed, estimate labor: hours								
List operating parameters recorded (e.g., flow, temperature, pressure, pH), typical values, and range for this unit. Record or obtain copy or printout of logs for the duration of the sampling episode.								

Figure 3-5. Wastewater Treatment Unit Data Sheet

SOURCE WATER DATA SHEET
Vessel: Date: Recorded by:
Is Potable Water Generated On-Board the Vessel: yes or no (circle one)
Describe the On-Board Potable Water Treatment and Disinfection Method:
Port (City) Where Source Water is Obtained if Not Generated On-Board:
Treatment Method for Source Water Obtained in Port:
Disinfection Method for Source Water Obtained in Port:
Fluoride Added to Water Obtained in Port: yes or no (circle one)
Additional Disinfection Performed On Water Obtained in Port: yes or no (circle one)
Describe Additional On-Board Disinfection Method:
Description of Source Water Sample Collection Point On-Board Cruse Ship:

Figure 3-6. Source Water Data Sheet

Preservation Chemicals - List Strength of Solution from Bottle							
HCl		Ascor	bic Acid				
H <sub>2</sub> SO <sub>4</sub>		NaOH	Ι				
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>			Carbonate				
Sample Number	Analysis	Date	Name	Chemical	Initial pH	Final pH	Number of Drops

Figure 3-7. Sample Preservation Log Sheet

Date:										
Sampling Ep	oisode: _									
Sampling Po	int:									
Sample Num	ibers:									
Manual Com			Grab 🗌							
Time of Com	positing	period, if	applicable:							
					м □ РМ м □ РМ					
Equipment U	sed:									
Samplers' Na	imes:									
Aliquot	Time	Temp °C	Turbidity (NTU)	рН	Sulfide (mg/L)	Salinity (ppt)	Conductivity (μS/cm)	Hardness (mg/L)	Free Chlorine (mg/L)	Total Chlorine (mg/L)
2										
3										
4										
5										
6										
Composite										
Notes: (inclu	de observ	ations of	odor and co	lor of ea	nch aliquot	, take pictu	res if necessary	y)		

Figure 3-8. Field Sampling Log Sheet

						United Sta	ites										
		<b>5</b> A		ı	Envir	ronmental Protection Agency					EPISODE N	O:					
	EF	A	1			Washington, D	C 204	460			RANGE OF	RANGE OF SAMPLE NOS:					
	l	JSEPA	A ENGI	NEER	ING AN	REPORT ID ANALYSIS DIVISIC ROL CENTER	Ν			Return com	pleted form to: P.O. BOX 1407  ALEXANDRIA, VA 223  (703) 519-1140				/A 2231	3	
INDU	JSTRI <i>A</i>	AL FIR	M SAM	PLED		SHIPPIN	G & INF	FORM	ATION	<u> </u>							
NAME:						SHIP TO:											
CITY:						ATTN:											
STATE:						CARRIER:											
INDUSTRIAL	CATEG	ORY:				AIRBILL:											
						DATE SHIPPED:											
CONFIDEN <sup>*</sup>	TIAL (Y	′/N):				SAMPLING OFFICE/	SAMPL	ER:									
			S	SAMP	LE PO	INT DESCRIPTION	1					SA	AMPLE	E ANA	LYSE	S	
SAMPLE NUMBER	SOURCE WATER (city, river, well)	IN LINE PROCESS	UNREATED EFFLUENT (raw wastewater)	TREATED EFFLUENT	OTHER (specify)	ADDITIONAL SAMPLE DESCRIPTION	DH LEVEL	PRESERVED (YN)	G=GRAB / C=COMPOSITE	SAMPLE COLLECTION TIME / DATE							
Comment	s:		•		•		7		•		•		•	•			

EPA Form 7500-50 (Rev 6-94) Previous editions are obselete.

Page 1: SCC Copy Copy of Page 1: Sampler Copy

Page 2: Lab Copy Copy of Page 2: Lab Copy for return to SCC

Figure 3-9. Example SCC Traffic Report

#### 4.0 SAMPLING ACTIVITIES

This section discusses the sampling team organization, ship visit preparation, and sampling activities.

#### 4.1 <u>Sampling Team Organization</u>

The sampling crew will consist of a crew chief from ERG, five to six crew members from ERG, and one EPA representative. The actual number of ERG crew members will be determined based on the number of sampling points on the cruise vessel. The crew chief will be responsible for all sample collection, preservation, and shipping activities on board. After completion of the visit, the analytical results from each laboratory will be collated. This information will be summarized and transmitted, along with a trip report, to EPA. After EPA review, the report will be forwarded to the cruise line for their review.

#### 4.2 **Pre-Visit Preparation**

Prior to the sampling episode, the ERG crew chief will prepare a vessel-specific SAP outlining planned sampling activities, anticipated health and safety requirements and procedures (for both ship visit and sampling activities), the sample team organization, cruise vessel names and contacts, and the names and addresses of analytical laboratories. The ERG Health and Safety Coordinator, Kevin Sikora, will identify the vessel-specific health and safety requirements.

The ERG crew chief will distribute the vessel-specific SAP to each team member and make sure they are completely familiar with the vessel-specific health and safety requirements. Cruise vessel personnel shall be given copies of the generic plan and vessel-specific SAP prior to the start of sampling.

The ERG crew chief will also coordinate the procurement and shipment of all necessary sampling and health and safety equipment.

#### 4.3 Field Sampling Activities

On board each cruise vessel, the ERG crew chief, in conjunction with the EPA Work Assignment Manager (WAM), will meet with cruise vessel personnel to determine whether samples can be collected at each of the planned sampling points. Upon making the decision to collect samples, the ERG crew chief will update the descriptions of the proposed sampling points, if necessary, in consultation with EPA and cruise vessel personnel. If necessary, additional equipment and glassware will be obtained. The revised description shall include:

- C A sample point description and collection procedure for each sample point;
- C A list of the sample fractions to be collected at each point:
- C A list of potential physical hazards (such as pH, temperature, and potentially hazardous equipment);
- C A list of potential chemical hazards associated with each sample point;
- C A list of proposed health and safety procedures.

Prior to sampling, the ERG crew chief will also notify the Health and Safety Coordinator of any revised sampling activity descriptions along with recommended revisions to the proposed health and safety procedures. Together, they will review the proposed health and safety procedures, incorporate any vessel-specific changes indicated by the Health and Safety Coordinator, and gain approval for sampling from the Health and Safety Coordinator before proceeding with sampling activities.

Sample fractions collected will be labeled, sealed, and placed in coolers for shipment to the laboratory once the cruise vessel docks. The Traffic Report forms will be completed and placed in plastic sleeves inside the coolers. The coolers will then be taken to the nearest Federal Express office and shipped to the SCC laboratories. Because of the very short sample holding times for microbiologicals, BOD<sub>5</sub>, and SS an on-board laboratory will be used

for analysis of these samples. At the conclusion of the sampling episode, the sampling equipment will be prepared for return shipping.

The ERG crew chief will contact SCC prior to sampling in order to confirm the laboratories and to communicate the number of samples being collected. The SCC crew chief will also contact SCC after shipping samples to communicate shipping information.

#### 4.4 <u>Logistics</u>

This section of the sampling plan summarizes cruise vessel contacts, analytical laboratory contacts and addresses, and sampling team personnel and support functions.

#### 4.4.1 Cruise Ship Contacts

To be determined prior to sampling.

#### 4.4.2 EPA Contacts

Don Anderson
Engineering and Analysis Division
U.S. Environmental Protection Agency
Ariel Rios Building
1200 Pennsylvania Avenue, NW
Mail Code 4303T
Washington, D.C. 20460
(202) 566-1021

Elizabeth Kim
Office of Wetlands, Oceans, and Watersheds
U.S. Environmental Protection Agency
Ariel Rios Building
1200 Pennsylvania Avenue, NW
Mail Code 4504T
Washington, D.C. 20460
(202) 566-1270

#### 4.4.3 Analytical Laboratories

To be determined for each sampling trip.

#### 4.4.4 ERG Contacts

Debbie Falatko (Project Manager) - Chemical Engineer Jennifer Biancuzzo - Environmental Engineer Amanda Thepvongs - Chemical Engineer Eastern Research Group, Inc. 14555 Avion Parkway, Suite 200 Chantilly, VA 20151 (703) 633-1600

#### 4.4.5 Freight Forwarders

Federal Express
9203 Bonnett Way
Juneau, Alaska 99801
General Information (800) 238-5355
Weekday Hours: 7:30 am to 5 pm
Last Express Drop-off: 8:30 am, no Sat pickup

Federal Express Airport Area 6050 Rockwell Anchorage, Alaska 99502 General Information (800) 238-5355 Last Express Drop-off: 2 pm M-F, 3pm Sat

Federal Express
705 Pike Street
Seattle, Washington 98101
General Information (800) 238-5355
Weekday Hours: 12 pm to 5:15 pm
Last Express Drop-off: 5:15 pm M-F, no Sat pickup

Alaska Airlines Goldstreak Air Cargo

#### 5.0 SAMPLE SHIPMENT

All sample containers will be labeled with ERG's standard address labels. All samples will be tracked using SCC Traffic Report forms. Custody will be maintained by the ERG crew chief from sample collection through shipment.

All samples will be packaged and shipped in accordance with DOT or IATA regulations. The general IATA packaging requirements for air shipment are as follows:

- "Inner packaging must be so packed, secured or cushioned as to prevent their breakage or leakage and so as to control their movement within the outer packaging during normal conditions of transport. Cushioning material must not react dangerously with the contents of the inner packaging. Any leakage of the contents must not substantially impair the protective properties of the cushioning material. Unless otherwise provided in this paragraph or in the Packing Instructions, liquids in Classes, 3, 4, 5, 6, or 8 of Packing Groups I or II in glass or earthenware inner packaging, must be packaged using material capable of absorbing the liquid. Absorbent material must not react dangerously with the liquid. Absorbent material is not required...." (IATA Dangerous Goods Regulations, 5.0.16).
- C "When filling receptacles for liquids, sufficient ullage (outage) must be left to ensure that neither leakage nor permanent distortion of the receptacle will occur as a result of an expansion of the liquid caused by temperatures likely to prevail during transport. Liquids must not completely fill a receptacle at a temperature of 55°C (130°F)." (IATA Dangerous Goods Regulations, 5.0.12).

The packing and labeling procedures in the following subsections may be used for non-hazardous samples. Hazardous samples will be identified based on consultation with the hazardous shipments contact, and appropriate hazardous shipping procedures will be followed. Based on process considerations, samples collected on board large cruise vessels will not be classified as IATA dangerous goods.

#### 5.1 <u>Sample Set Preparation</u>

Samples are collected as a series of "fractions," or bottles designated for particular analyses requiring the same preservation. A typical, comprehensive water sample set consists of sample fractions for all pollutants listed in Section 3.3 collected over a 24-hour period.

At the end of the compositing period, sampling points will include approximately 20 liters of sample collected in two 10-L composite sample containers. The content of the composite sample containers will be thoroughly mixed using a third, clean composite sample container. To perform this mixing, half of each composite sample container will be poured into the third jar then the two half-full composite sample containers will be combined into one. Repeat this process two more times to ensure proper mixing. Field measurements (described in Section 3.6) of the mixed sample contained in each composite sample container will be used to verify mixing. Sample fractions will be poured from the composite sample containers into individual sample bottles using the following procedure.

- C Swirl and shake the composite sample container to re-suspend settled solids;
- C Fill each sample bottle to about ½ of its empty volume;
- C Mix the remaining volume in the composite sample container; and
- C In reverse order, fill the sample bottles.

Cyanide samples will be composited separately from the other pollutant parameters. Up to four grab samples during each 24-hour sampling period will be collected for cyanide analyses in separate 1-L amber glass jars and preserved according to Table 3-3. After the sampling period ends, the four one liter grab samples will be composited by mixing in a sampling point-specific composite jar and then poured into separate bottles for analysis of total and available cyanide.

#### 5.2 <u>Sample Packing</u>

All samples from the cruise vessel may be packed according to the following guidelines:

- 1. Tighten the lid on each filled sample bottle, being careful not to overtighten the lid. Clean the sample bottle with a cloth rag or paper towel.
- 2. Label each sample bottle. (Sample labeling is discussed in Section 3.6 of this document.) Cover the label with clear tape to protect this information.
- 3. Wrap each glass sample bottle with "bubble wrap". The bubble wrap must fit snugly and completely cover the sample bottle. Each "bubble-wrapped" container and plastic container must then be enclosed in an individual sealable plastic freezer bag.
- 4. Place two garbage bags inside each other in a cooler.
- 5. Place sample bottles in garbage bags in the cooler with proper end up and close bag with twist-tie.
- 6. Arrange sealed plastic freezer bags filled with ice on top of the sample bottles (if ice is to be used as a preservative). Put at least  $4 \times \frac{1}{2}$  gallons of ice (4 × 2.5 lbs of ice) in each large cooler and  $2 \times \frac{1}{2}$  gallons of ice (2 × 2.5 lbs of ice) in each small cooler. More ice should be used when ambient temperatures are very high. The ice should be placed inside the second garbage bag. Close the second garbage bag with a twist-tie. Any additional free space should be filled with packing material so that the sample containers will not shift during shipment.
- 7. Seal the SCC Traffic Report or Chain-of-Custody form (as applicable) in a plastic sleeve and tape securely to the inside of the cooler lid.
- 8. Place a "Return to ..." label on the inside of the cooler lid.
- 9. Close cooler.
- 10. Make several wraps with tape around the cooler perpendicular to the seal to ensure that the lid will remain closed if the latch is accidentally released or damaged.
- 11. Tape the cooler drain plug so it will not open.

12. Place a completed address label on the lid of the cooler including name, address, and telephone number of the receiving laboratory and the return address and telephone number of the shipper.

#### 6.0 REFERENCES

- 1. U.S. Environmental Protection Agency. <u>Health Effects Criteria for Fresh</u>
  <u>Recreational Waters, EPA-600/1-84-004</u>, Research Triangle Park, NC, August 1984.
- 2. U.S. Environmental Protection Agency. <u>Health Effects Criteria for Marine Recreational Waters, EPA-600/1-80-031</u>, Research Triangle Park, NC, August 1983.
- 3. Alaska Cruise Ship Initiative: Historical Information; http://www.state.ak.us/dec/water/cruise\_ships/cruiseinitiative.htm.
- 4. Eley, W. D., Cape International, Inc., and Morehouse, C.H., State of Alaska, Department of Environmental Conservation, "Evaluation of New Technology for Shipboard Wastewater Treatment," 2003.
- 5. State of Alaska, Department of Environmental Conservation, "2003 Large Commercial Passenger Vessels Discharge Status and Wastewater Treatment," <a href="http://www.state.ak.us/dec/water/cruise-ships/2003largeshipwwtable.htm">http://www.state.ak.us/dec/water/cruise-ships/2003largeshipwwtable.htm</a>.
- 6. State of Alaska, Department of Environmental Conservation, "Cruise Ship Fact Sheet Frequently Asked Questions," http://www.state.ak.us/dec/water/cruise\_ships/pdfs/cruisefaqs.pdf.
- 7. Dixon, D., and Daly, J., "Enhanced MARPOL IV Sewage and Graywater Pollution Prevention Holland America Line Westours Case Study," 2002.
- 8. Eastern Research Group, Inc., Quality Assurance Project Plan for Rulemaking Support for Large Cruise Ships in Alaska Water. March 2004.

# Appendix A LIST OF CONSTITUENTS FOR ANALYSIS

Table A-1

List of Constituents for Analysis Volatile Organic Analytes

CAS Number	Common Name	Technique	Method
107131	ACRYLONITRILE	GCMS	1624
71432	BENZENE	GCMS	1624
75274	BROMODICHLOROMETHANE	GCMS	1624
74839	BROMOMETHANE	GCMS	1624
75150	CARBON DISULFIDE	GCMS	1624
107142	CHLOROACETONITRILE	GCMS	1624
108907	CHLOROBENZENE	GCMS	1624
75003	CHLOROETHANE	GCMS	1624
67663	CHLOROFORM	GCMS	1624
74873	CHLOROMETHANE	GCMS	1624
10061015	CIS-1,3-DICHLOROPROPENE	GCMS	1624
4170303	CROTONALDEHYDE	GCMS	1624
124481	DIBROMOCHLOROMETHANE	GCMS	1624
74953	DIBROMOMETHANE	GCMS	1624
60297	DIETHYL ETHER	GCMS	1624
107120	ETHYL CYANIDE	GCMS	1624
97632	ETHYL METHACRYLATE	GCMS	1624
100414	ETHYLBENZENE	GCMS	1624
74884	IODOMETHANE	GCMS	1624
78831	ISOBUTYL ALCOHOL	GCMS	1624
108383	M-XYLENE	GCMS	1624
80626	METHYL METHACRYLATE	GCMS	1624
75092	METHYLENE CHLORIDE	GCMS	1624
1-952	O+P XYLENE	GCMS	1624
127184	TETRACHLOROETHENE	GCMS	1624
56235	TETRACHLOROMETHANE	GCMS	1624
108883	TOLUENE	GCMS	1624
156605	TRANS-1,2-DICHLOROETHENE	GCMS	1624
10061026	TRANS-1,3-DICHLOROPROPENE	GCMS	1624
110576	TRANS-1,4-DICHLORO-2-BUTENE	GCMS	1624
75252	TRIBROMOMETHANE	GCMS	1624
79016	TRICHLOROETHENE	GCMS	1624
75694	TRICHLOROFLUOROMETHANE	GCMS	1624
108054	VINYL ACETATE	GCMS	1624
75014	VINYL CHLORIDE	GCMS	1624
75343	1,1-DICHLOROETHANE	GCMS	1624
75354	1,1-DICHLOROETHENE	GCMS	1624

**Table A-1 (Continued)** 

CAS Number	Common Name	<u>Technique</u>	Method
		_	
71556	1,1,1-TRICHLOROETHANE	GCMS	1624
630206	1,1,1,2-TETRACHLOROETHANE	GCMS	1624
79005	1,1,2-TRICHLOROETHANE	GCMS	1624
79345	1,1,2,2-TETRACHLOROETHANE	GCMS	1624
106934	1,2-DIBROMOETHANE	GCMS	1624
107062	1,2-DICHLOROETHANE	GCMS	1624
78875	1,2-DICHLOROPROPANE	GCMS	1624
96184	1,2,3-TRICHLOROPROPANE	GCMS	1624
126998	1,3-BUTADIENE, 2-CHLORO	GCMS	1624
142289	1,3-DICHLOROPROPANE	GCMS	1624
123911	1,4-DIOXANE	GCMS	1624
78933	2-BUTANONE	GCMS	1624
110758	2-CHLOROETHYLVINYL ETHER	GCMS	1624
591786	2-HEXANONE	GCMS	1624
67641	2-PROPANONE	GCMS	1624
107186	2-PROPEN-1-OL	GCMS	1624
107028	2-PROPENAL	GCMS	1624
126987	2-PROPENENITRILE, 2-METHYL-	GCMS	1624
107051	3-CHLOROPROPENE	GCMS	1624
108101	4-METHYL-2-PENTANONE	GCMS	1624

57 VOLATILE ANALYTES

Table A-2

List of Constituents for Analysis Semivolatile Organic Analytes

CAS			
Number	Common Name	Technique	Method
83329	ACENAPHTHENE	GCMS	1625
208968	ACENAPHTHYLENE	GCMS	1625
98862	ACETOPHENONE	GCMS	1625
98555	ALPHA-TERPINEOL	GCMS	1625
62533	ANILINE	GCMS	1625
137177	ANILINE, 2,4,5-TRIMETHYL-	GCMS	1625
120127	ANTHRACENE	GCMS	1625
140578	ARAMITE	GCMS	1625
82053	BENZANTHRONE	GCMS	1625
108985	BENZENETHIOL	GCMS	1625
92875	BENZIDINE	GCMS	1625
56553	BENZO(A)ANTHRACENE	GCMS	1625
50328	BENZO(A)PYRENE	GCMS	1625
205992	BENZO(B)FLUORANTHENE	GCMS	1625
191242	BENZO(GHI)PERYLENE	GCMS	1625
207089	BENZO(K)FLUORANTHENE	GCMS	1625
65850	BENZOIC ACID	GCMS	1625
1689845	BENZONITRILE, 3,5-DIBROMO-4-HYDROXY-	GCMS	1625
100516	BENZYL ALCOHOL	GCMS	1625
91598	BETA-NAPHTHYLAMINE	GCMS	1625
92524	BIPHENYL	GCMS	1625
92933	BIPHENYL, 4-NITRO	GCMS	1625
111911	BIS(2-CHLOROETHOXY)METHANE	GCMS	1625
111444	BIS(2-CHLOROETHYL) ETHER	GCMS	1625
108601	BIS(2-CHLOROISOPROPYL) ETHER	GCMS	1625
117817	BIS(2-ETHYLHEXYL) PHTHALATE	GCMS	1625
85687	BUTYL BENZYL PHTHALATE	GCMS	1625
86748	CARBAZOLE	GCMS	1625
218019	CHRYSENE	GCMS	1625
7700176	CROTOXYPHOS	GCMS	1625
84742	DI-N-BUTYL PHTHALATE	GCMS	1625
117840	DI-N-OCTYL PHTHALATE	GCMS	1625
621647	DI-N-PROPYLNITROSAMINE	GCMS	1625
53703	DIBENZO(A,H)ANTHRACENE	GCMS	1625
132649	DIBENZOFURAN	GCMS	1625
132650	DIBENZOTHIOPHENE	GCMS	1625

CAS			
Number	Common Name	Technique	Method
84662	DIETHYL PHTHALATE	GCMS	1625
131113	DIMETHYL PHTHALATE	GCMS	1625
67710	DIMETHYL SULFONE	GCMS	1625
101848	DIPHENYL ETHER	GCMS	1625
122394	DIPHENYLAMINE	GCMS	1625
882337	DIPHENYLDISULFIDE	GCMS	1625
76017	ETHANE, PENTACHLORO-	GCMS	1625
62500	ETHYL METHANESULFONATE	GCMS	1625
96457	ETHYLENETHIOUREA	GCMS	1625
206440	FLUORANTHENE	GCMS	1625
86737	FLUORENE	GCMS	1625
118741	HEXACHLOROBENZENE	GCMS	1625
87683	HEXACHLOROBUTADIENE	GCMS	1625
77474	HEXACHLOROCYCLOPENTADIENE	GCMS	1625
67721	HEXACHLOROETHANE	GCMS	1625
1888717	HEXACHLOROPROPENE	GCMS	1625
142621	HEXANOIC ACID	GCMS	1625
193395	INDENO(1,2,3-CD)PYRENE	GCMS	1625
78591	ISOPHORONE	GCMS	1625
120581	ISOSAFROLE	GCMS	1625
475207	LONGIFOLENE	GCMS	1625
569642	MALACHITE GREEN	GCMS	1625
72333	MESTRANOL	GCMS	1625
91805	METHAPYRILENE	GCMS	1625
66273	METHYL METHANESULFONATE	GCMS	1625
124185	N-DECANE	GCMS	1625
629970	N-DOCOSANE	GCMS	1625
112043	N-DODECANE	GCMS	1625
112958	N-EICOSANE	GCMS	1625
630013	N-HEXACOSANE	GCMS	1625
544763	N-HEXADECANE	GCMS	1625
924163	N-NITROSODI-N-BUTYLAMINE	GCMS	1625
55185	N-NITROSODIETHYLAMINE	GCMS	1625
62759	N-NITROSODIMETHYLAMINE	GCMS	1625
86306	N-NITROSODIPHENYLAMINE	GCMS	1625
10595956	N-NITROSOMETHYLETHYLAMINE	GCMS	1625
614006	N-NITROSOMETHYLPHENYLAMINE	GCMS	1625
59892	N-NITROSOMORPHOLINE	GCMS	1625
100754	N-NITROSOPIPERIDINE	GCMS	1625

CAS			
Number	Common Name	Technique	Method
		<del></del>	
630024	N-OCTACOSANE	GCMS	1625
593453	N-OCTADECANE	GCMS	1625
646311	N-TETRACOSANE	GCMS	1625
629594	N-TETRADECANE	GCMS	1625
638686	N-TRIACONTANE	GCMS	1625
68122	N,N-DIMETHYLFORMAMIDE	GCMS	1625
91203	NAPHTHALENE	GCMS	1625
98953	NITROBENZENE	GCMS	1625
90040	O-ANISIDINE	GCMS	1625
95487	O-CRESOL	GCMS	1625
95534	O-TOLUIDINE	GCMS	1625
95794	O-TOLUIDINE, 5-CHLORO-	GCMS	1625
106478	P-CHLOROANILINE	GCMS	1625
106445	P-CRESOL	GCMS	1625
99876	P-CYMENE	GCMS	1625
60117	P-DIMETHYLAMINOAZOBENZENE	GCMS	1625
100016	P-NITROANILINE	GCMS	1625
608935	PENTACHLOROBENZENE	GCMS	1625
87865	PENTACHLOROPHENOL	GCMS	1625
700129	PENTAMETHYLBENZENE	GCMS	1625
198550	PERYLENE	GCMS	1625
62442	PHENACETIN	GCMS	1625
85018	PHENANTHRENE	GCMS	1625
108952	PHENOL	GCMS	1625
534521	PHENOL, 2-METHYL-4,6-DINITRO-	GCMS	1625
92842	PHENOTHIAZINE	GCMS	1625
23950585	PRONAMIDE	GCMS	1625
129000	PYRENE	GCMS	1625
110861	PYRIDINE	GCMS	1625
108462	RESORCINOL	GCMS	1625
94597	SAFROLE	GCMS	1625
7683649	SQUALENE	GCMS	1625
100425	STYRENE	GCMS	1625
95158	THIANAPHTHENE	GCMS	1625
62555	THIOACETAMIDE	GCMS	1625
492228	THIOXANTHE-9-ONE	GCMS	1625
95807	TOLUENE, 2,4-DIAMINO-	GCMS	1625
217594	TRIPHENYLENE	GCMS	1625
20324338	TRIPROPYLENEGLYCOL METHYL ETHER	GCMS	1625

CAS			
Number	Common Name	<u>Technique</u>	Method
		-	
694804	1-BROMO-2-CHLOROBENZENE	GCMS	1625
108372	1-BROMO-3-CHLOROBENZENE	GCMS	1625
121733	1-CHLORO-3-NITROBENZENE	GCMS	1625
1730376	1-METHYLFLUORENE	GCMS	1625
832699	1-METHYLPHENANTHRENE	GCMS	1625
134327	1-NAPHTHYLAMINE	GCMS	1625
605027	1-PHENYLNAPHTHALENE	GCMS	1625
96128	1,2-DIBROMO-3-CHLOROPROPANE	GCMS	1625
95501	1,2-DICHLOROBENZENE	GCMS	1625
122667	1,2-DIPHENYLHYDRAZINE	GCMS	1625
87616	1,2,3-TRICHLOROBENZENE	GCMS	1625
634366	1,2,3-TRIMETHOXYBENZENE	GCMS	1625
120821	1,2,4-TRICHLOROBENZENE	GCMS	1625
95943	1,2,4,5-TETRACHLOROBENZENE	GCMS	1625
1464535	1,2,3,4-DIEPOXYBUTANE	GCMS	1625
96231	1,3-DICHLORO-2-PROPANOL	GCMS	1625
541731	1,3-DICHLOROBENZENE	GCMS	1625
291214	1,3,5-TRITHIANE	GCMS	1625
106467	1,4-DICHLOROBENZENE	GCMS	1625
100254	1,4-DINITROBENZENE	GCMS	1625
130154	1,4-NAPHTHOQUINONE	GCMS	1625
2243621	1,5-NAPHTHALENEDIAMINE	GCMS	1625
615225	2-(METHYLTHIO)BENZOTHIAZOLE	GCMS	1625
91587	2-CHLORONAPHTHALENE	GCMS	1625
95578	2-CHLOROPHENOL	GCMS	1625
2027170	2-ISOPROPYLNAPHTALENE	GCMS	1625
120752	2-METHYLBENZOTHIOAZOLE	GCMS	1625
91576	2-METHYLNAPHTHALENE	GCMS	1625
88744	2-NITROANILINE	GCMS	1625
88755	2-NITROPHENOL	GCMS	1625
612942	2-PHENYLNAPHTALENE	GCMS	1625
109068	2-PICOLINE	GCMS	1625
243174	2,3-BENZOFLUORENE	GCMS	1625
608275	2,3-DICHLOROANILINE	GCMS	1625
3209221	2,3-DICHLORONITROBENZENE	GCMS	1625
58902	2,3,4,6-TETRACHLOROPHENOL	GCMS	1625
933755	2,3,6-TRICHLOROPHENOL	GCMS	1625
120832	2,4-DICHLOROPHENOL	GCMS	1625
105679	2,4-DIMETHYLPHENOL	GCMS	1625

CAS			
Number	Common Name	Technique	Method
51285	2,4-DINITROPHENOL	GCMS	1625
121142	2,4-DINITROTOLUENE	GCMS	1625
95954	2,4,5-TRICHLOROPHENOL	GCMS	1625
88062	2,4,6-TRICHLOROPHENOL	GCMS	1625
719222	2,6-DI-TER-BUTYL-P-BENZOQUINONE	GCMS	1625
99309	2,6-DICHLORO-4-NITROANILINE	GCMS	1625
87650	2,6-DICHLOROPHENOL	GCMS	1625
606202	2,6-DINITROTOLUENE	GCMS	1625
56495	3-METHYLCHOLANTHRENE	GCMS	1625
99092	3-NITROANILINE	GCMS	1625
91941	3,3'-DICHLOROBENZIDINE	GCMS	1625
119904	3,3'-DIMETHOXYBENZIDINE	GCMS	1625
1576676	3,6-DIMETHYLPHENANTHRENE	GCMS	1625
92671	4-AMINOBIPHENYL	GCMS	1625
101553	4-BROMOPHENYL PHENYL ETHER	GCMS	1625
89634	4-CHLORO-2-NITROANILINE	GCMS	1625
59507	4-CHLORO-3-METHYLPHENOL	GCMS	1625
7005723	4-CHLOROPHENYLPHENYL ETHER	GCMS	1625
100027	4-NITROPHENOL	GCMS	1625
101144	4,4'-METHYLENEBIS(2-CHLOROANILINE)	GCMS	1625
203546	4,5-METHYLENE PHENANTHRENE	GCMS	1625
99558	5-NITRO-O-TOLUIDINE	GCMS	1625
57976	7,12-DIMETHYLBENZ(A)ANTHRACENE	GCMS	1625

176 STANDARD SEMIVOLATILE ANALYTES

## List of Constituents for Analysis -Metal Analytes

Table A-3

CAS			
<u>Number</u>	Common Name	<u>Technique</u>	Method
7429905	ALUMINUM	ICP	1620
7440360	ANTIMONY	FURNAA	1620
7440382	ARSENIC	FURNAA	1620
7440393	BARIUM	ICP	1620
7440417	BERYLLIUM	ICP	1620
7440428	BORON	ICP	1620
7440439	CADMIUM	ICP	1620
7440702	CALCIUM	ICP	1620
7440473	CHROMIUM	ICP	1620
7440484	COBALT	ICP	1620
7440508	COPPER	ICP	1620
7439896	IRON	ICP	1620
7439921	LEAD	ICP	1620
7439954	MAGNESIUM	ICP	1620
7439965	MANGANESE	ICP	1620
7439976	MERCURY	CVAA	1620
7439987	MOLYBDENUM	ICP	1620
7440020	NICKEL	ICP	1620
7782492	SELENIUM	FURNAA	1620
7440224	SILVER	ICP	1620
7440235	SODIUM	ICP	1620
7440280	THALLIUM	FURNAA	1620
7440315	TIN	ICP	1620
7440326	TITANIUM	ICP	1620
7440622	VANADIUM	ICP	1620
7440655	YTTRIUM	ICP	1620
7440666	ZINC	ICP	1620

27 METALS ANALYTES

Table A-4

List of Constituents for Analysis Organo-Phosphorous Pesticide Analytes

CAS			
<u>Number</u>	Common Name	<u>Technique</u>	Method
2642719	AZINPHOS ETHYL	GC-FPD	1657
86500	AZINPHOS ETHYL AZINPHOS METHYL	GC-FPD GC-FPD	1657
470906	CHLORFEVINPHOS	GC-FPD	1657
2921882	CHLOROPYRIFOS	GC-FPD	1657
56724	COUMAPHOS	GC-FPD	1657
7700176	CROTOXYPHOS	GC-FPD	1657
78488	DEF	GC-FPD	1657
8065483	DEMETON	GC-FPD	1657
8065483A	DEMETON A	GC-FPD	1657
8065483B	DEMETON A DEMETON B	GC-FPD	1657
333415	DIAZINON	GC-FPD	1657
97176	DICHLOFENTHION	GC-FPD	1657
62737	DICHLORVOS	GC-FPD	1657
141662	DICROTOPHOS	GC-FPD	1657
60515	DIMETHOATE	GC-FPD GC-FPD	1657
78342	DIOXATHION	GC-FPD	1657
78342 298044	DISULFOTON	GC-FPD GC-FPD	1657
2104645	EPN	GC-FPD GC-FPD	1657
563122	ETHON	GC-FPD GC-FPD	1657
13194484	ETHOPROP		1657
52857	FAMPHUR	GC-FPD	1657
115902	FENSULFOTHION	GC-FPD	1657
55389	FENTHION	GC-FPD	1657
680319	HEXAMETHYLPHOSPHORAMIDE	GC-FPD	1657
21609905	LEPTOPHOS	GC-FPD	1657
121755	MALATHION	GC-FPD	1657
150505	MERPHOS	GC-FPD	1657
10265926	METHAMIDOPHOS	GC-FPD	1657
5598130	METHYL CHLORPYRIFOS	GC-FPD	1657
298000	METHYL PARATHION	GC-FPD	1657
953173	METHYL TRITHION	GC-FPD	1657
7786347	MEVINPHOS	GC-FPD	1657
6923224	MONOCROTOPHOS	GC-FPD	1657
300765	NALED	GC-FPD	1657
56382	PARATHION (ETHYL)	GC-FPD	1657
298022	PHORATE	GC-FPD	1657
732116	PHOSMET	GC-FPD	1657
13171216	PHOSPHAMIDON	GC-FPD	1657
297994	PHOSPHAMIDON E	GC-FPD	1657
23783984	PHOSPHAMIDON Z	GC-FPD	1657

CAS			
<u>Number</u>	Common Name	<u>Technique</u>	Method
200042	DONNEL	CC EDD	1.657
299843	RONNEL	GC-FPD	1657
3689245	SULFOTEPP	GC-FPD	1657
35400432	SULPROFOS (BOLSTAR)	GC-FPD	1657
107493	TEPP	GC-FPD	1657
13071799	TERBUFOS	GC-FPD	1657
22248799	TETRACHLORVINPHOS	GC-FPD	1657
34643464	TOKUTHION	GC-FPD	1657
52686	TRICHLORFON	GC-FPD	1657
327980	TRICHLORONATE	GC-FPD	1657
78308	TRICRESYLPHOSPHATE	GC-FPD	1657
512561	TRIMETHYLPHOSPHATE	GC-FPD	1657

51 ORGANO-PHOSPHORUS PESTICIDE ANALYTES

Table A-5
List of Constituents for Analysis Organo-Halide Pesticide Analytes

CAS			
<u>Number</u>	Common Name	<u>Technique</u>	Method
30560191	АСЕРНАТЕ	GC-HSD	1656
50594666	ACIFIUORFEN	GC-HSD	1656
15972608	ALACHLOR	GC-HSD	1656
309002	ALDRIN	GC-HSD	1656
1912249	ATRAZINE	GC-HSD	1656
1861401	BENFLURALIN (BENEFIN)	GC-HSD	1656
319846	"-BHC	GC-HSD	1656
319857	\$-BHC	GC-HSD	1656
58899	(-BHC (LINDANE)	GC-HSD	1656
319868	*-BHC	GC-HSD	1656
314409	BROMACIL	GC-HSD	1656
1689992	BROMOXYNIL OCTANOATE	GC-HSD	1656
23184669	BUTACHLOR	GC-HSD	1656
2425061	CAPTAFOL	GC-HSD	1656
133062	CAPTAN	GC-HSD	1656
786196	CARBOPHENOTHION (TRITHION)	GC-HSD	1656
57749	CHLORDANE	GC-HSD	1656
5103719	" -CHLORDANE (CIS-CHLORDANE)	GC-HSD	1656
5103742	( -CHLORDANE (TRANS-CHLORDANE)	GC-HSD	1656
510156	CHLORBENZILATE	GC-HSD	1656
2675776	CHLORONEB (TERRANEB)	GC-HSD	1656
5836102	CHLOROPROPYLATE (ACARALATE)	GC-HSD	1656
1897456	CHLOROTHALONIL	GC-HSD	1656
96128	DBCP (DIBROMOCHLOROPROPANE)	GC-HSD	1656
1861321	DCPA (DACTHAL)	GC-HSD	1656
72548	4,4'-DDD (TDE)	GC-HSD	1656
72559	4,4'-DDE	GC-HSD	1656
50293	4,4'-DDT	GC-HSD	1656
2303164	DIALLATE (AVADEX)	GC-HSD	1656
2303164A	DIALLATE À	GC-HSD	1656
2303164B	DIALLATE B	GC-HSD	1656
117806	DICHLONE	GC-HSD	1656
115322	DICOFOL	GC-HSD	1656
60571	DIELDRIN	GC-HSD	1656
959988	ENDOSULFAN I	GC-HSD	1656
33213659	ENDOSULFAN II	GC-HSD	1656
1031078	ENDOSULFAN SULFATE	GC-HSD	1656
72208	ENDRIN	GC-HSD	1656
7421934	ENDRIN ALDEHYDE	GC-HSD	1656
53494705	ENDRIN KETONE	GC-HSD	1656
55283686	ETHALFLURALIN (SONALAN)	GC-HSD	1656
2593159	ETRIDIAZOLE	GC-HSD	1656

CAS			
<u>Number</u>	Common Name	<u>Technique</u>	Method
60168889	FENARIMOL (RUBIGAN)	GC-HSD	1656
76448	HEPTACHLOR	GC-HSD	1656
1024573	HEPTACHLOR EPOXIDE	GC-HSD	1656
465736	ISODRIN	GC-HSD	1656
33820530	ISOPROPALIN (PAARLAN)	GC-HSD	1656
143500	KEPONE	GC-HSD	1656
72435	METHOXYCHLOR	GC-HSD	1656
21087649	METRIBUZIN	GC-HSD	1656
2385855	MIREX	GC-HSD	1656
1836755	NITROFEN (TOK)	GC-HSD	1656
27314132	NORFLUORAZON	GC-HSD	1656
12674112	PCB-1016	GC-HSD	1656
11104282	PCB-1221	GC-HSD	1656
11141165	PCB-1232	GC-HSD	1656
53469219	PCB-1242	GC-HSD	1656
12672296	PCB-1248	GC-HSD	1656
11097691	PCB-1254	GC-HSD	1656
11096825	PCB-1260	GC-HSD	1656
82688	PCNB (PENTACHLORONITROBENZENE)	GC-HSD	1656
40487421	PENDAMETHALIN (PROWL)	GC-HSD	1656
61949766	CIS-PERMETHRIN	GC-HSD	1656
61949777	TRANS-PERMETHRIN	GC-HSD	1656
72560	PERTHANE (ETHYLAN)	GC-HSD	1656
1918167	PROPACHLOR	GC-HSD	1656
709988	PROPANIL	GC-HSD	1656
139402	PROPAZINE	GC-HSD	1656
122349	SIMAZINE	GC-HSD	1656
8001501	STROBANE	GC-HSD	1656
5902512	TERBACIL	GC-HSD	1656
5915413	TERBUTHYLAZINE	GC-HSD	1656
8001352	TOXAPHENE	GC-HSD	1656
43121433	TRIADIMEFON (BAYLETON)	GC HSD	1656
1582098	TRIFLURALIN	GC-HSD	1656

75 ORGANO-HALIDE PESTICIDE ANALYTES

#### Table A-6

## **List of Constituents for Analysis - Chlorinated Biphenyls Congeners**

There are 209 possible congeners, 12 of which have toxicological significance (i.e., the "toxic" PCBs identified by the World Health Organization). Method 1668A can unambiguously determine 126 of the 209 congeners as separate chromatographic peaks. The remaining 83 congeners do not appear as separate peaks, but elute from the gas chromatograph in groups of 2 to 6 congeners that cannot be completely resolved by the instrumentation. Ten of the 12 "toxic" congeners are resolved, and the remaining two congeners (PCB 156 and PCB 157) elute as a congener pair. (Because PCB 156 and 157 have identical toxicity equivalency factors (TEFs), it is possible to accurately calculate PCB toxic equivalence (TEQ) based on the 12 toxic congeners.)

For reporting purposes, each sample will be associated with 126 results that represent the 126 single PCB congeners, and another 33 results that represent co-eluting congener groups for the remaining 83 congeners, for a total of 159 PCB congener "results." In addition, each sample will be associated with 10 values corresponding to the 10 possible levels of chlorination for the parent biphenyl. Each of these 10 values represents the sum of the concentrations of all of the congeners in a given level of chlorination (i.e., a total of the monchlorinated PCBs, a total of the di-chloro PCBs, etc.). Finally, each sample is associated with a grand total PCB value, which represents the sum of the 126 congener results plus the 33 values for the co-eluting congeners. In summary, each analysis will include 170 unique PCB results (126+33+10+1), and 11 of these results represent totals drawn from the first 159 records (126+33).

159 congeners, including the following 12 "toxic" congeners:

Common Name	<u>Technique</u>	Method
3,3'4,4'-TeCB	HRGCMS	1668
3,4,4',5-TeCB	HRGCMS	1668
2,3,3'4,4'-PeCB	HRGCMS	1668
2,3,4,4',5-PeCB	HRGCMS	1668
2,3'4,4',5-PeCB	HRGCMS	1668
2',3,4,4',5-PeCB	HRGCMS	1668
3,3'4,4',5-PeCB	HRGCMS	1668
2,3,3',4,4',5-HxCB	HRGCMS	1668
2,3,3'4,4',5'-HxCB	HRGCMS	1668
2,3',4,4',5,5'-HxCB	HRGCMS	1668
3,3'4,4',5,5'-HxCB	HRGCMS	1668
2,3,3',4,4',5,5'-HpCB	HRGCMS	1668

209 PCB CONGENERS

Table A-7

List of Constituents for Analysis Dioxin and Furan Analytes

CAS <u>Number</u>	Common Name	<u> Cechnique</u>	Method
3268879	OCTACHLORODIBENZO-P-DIOXIN	HRGCMS	1613
39001020	OCTACHLORODIBENZOFURAN 1,2,3,4,6,7,8-HEPTACHLORODIBENZO-P-DIOXIN	HRGCMS	1613
35822469		S HRGCMS	1613
67562394	1,2,3,4,6,7,8-HEPTACHLORODIBENZOFURAN 1,2,3,4,7,8-HEXACHLORODIBENZO-P-DIOXIN	HRGCMS	1613
39227286		HRGCMS	1613
70648269	1,2,3,4,7,8-HEXACHLORODIBENZOFURAN	HRGCMS	1613
55673897	1,2,3,4,7,8,9-HEPTACHLORODIBENZOFURAN	HRGCMS	1613
57653857	1,2,3,6,7,8-HEXACHLORODIBENZO-P-DIOXIN	HRGCMS	1613
57117449	1,2,3,6,7,8-HEXACHLORODIBENZOFURAN	HRGCMS	1613
40321764	1,2,3,7,8-PENTACHLORODIBENZO-P-DIOXIN	HRGCMS	1613
57117416	1,2,3,7,8-PENTACHLORODIBENZOFURAN	HRGCMS	1613
19408743	1,2,3,7,8,9-HEXACHLORODIBENZO-P-DIOXIN	HRGCMS	1613
72918219	1,2,3,7,8,9-HEXACHLORODIBENZOFURAN	HRGCMS	1613
60851345	2,3,4,6,7,8-HEXACHLORODIBENZOFURAN	HRGCMS	1613
57117314	2,3,4,7,8-PENTACHLORODIBENZOFURAN	HRGCMS	1613
1746016	2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN	HRGCMS	1613
51207319	2,3,7,8-TETRACHLORODIBENZOFURAN	HRGCMS	1613

17 DIOXIN ANALYTES