

***North West CruiseShip Association  
Discharge of Effluents in Certain Alaska Waters by Cruise Vessel  
Operations***

**Quality Assurance Project Plan  
For  
Sampling and Analysis of Treated Sewage and  
Graywater  
From  
Commercial Passenger Vessels**

***Submitted to fulfill certain requirements of  
33 CFR 159 United States Title 33 Code of Federal Regulations Part  
159 and Alaska Statute 46.03.460 – 46.03.490 and 18 AAC 69***

**Effective February 1, 2010 – January 31, 2013**

## TABLE OF CONTENTS

<b>APPROVAL PAGE</b>	<b>5</b>
<b>TERM OF QAPP</b>	<b>6</b>
<b>ACRONYMS/ABBREVIATIONS USED</b>	<b>7</b>
<b>MANAGEMENT AND CONTRACTORS</b>	<b>8</b>
North West CruiseShip Association	8
Individual Vessel Representatives	8
Small Cruise Ships and Alaska Marine Highway System	8
Lab Project Manager	8
Sampling Team Leader	8
Wastewater Analysis Laboratory	9
Project Quality Assurance Officer	10
US Coast Guard COTP	10
ADEC Project Manager	10
ADEC Water Quality Assurance Officer	10
<b>PROGRAM ORGANIZATIONAL AND DATA FLOW CHART</b>	<b>11</b>
<b>PURPOSE</b>	<b>12</b>
<b>APPLICABILITY</b>	<b>14</b>
Blind Duplicate Samples	15
Quality Objectives and Criteria for Measurement Data	15
Measurement Quality Objectives	16
Detectability	16
Precision	16
Bias (Accuracy)	17
Completeness	18
Representativeness	18
Comparability	19
Special Training Requirements/Certification	19
Documentation and Records	20

Sample schedule and Vessel/Sample Identification	20
Field Records (Required for both unannounced and continued compliance samples)	20
Laboratory Records	21
Chain of Custody	22

**SAMPLING PROCESS DESIGN 22**

Sampling Method Requirements	23
Sample Collection Procedures	23

Sample Handling and Custody Requirements	27
Sample Custody	27
Sample Temperature and Condition	27
Sample Holding Times	28
Sample Disposal	28

Analytical Methods and Quality Control Requirements	28
---	----

Instrument/Equipment Testing, Inspection, and Maintenance Requirements; Calibration and Frequency	36
---	----

Inspection/Acceptance Requirements for Supplies and Consumables	37
---	----

Inspection/Acceptance Requirements (Non-Direct Measurements)	37
--	----

Data Management	37
-----------------	----

**ASSESSMENT/OVERSIGHT 37**

Assessments and Response Actions	37
Field Assessments	37
Laboratory Assessments	38
Precision	38
Corrective Action	39

Reports to Management	39
-----------------------	----

**DATA VALIDATION AND USABILITY 40**

Data Review, Verification, and Validation	40
---	----

Reconciliation with Data Quality Objectives	40
---	----

**BIBLIOGRAPHY 41**

APPENDIX A - ALASKA CRUISE SHIP SAMPLING CHECKLIST FOR ALL SAMPLING EVENTS (USCG/ADEC)	42
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APPENDIX B - ALASKA CRUISE SHIP DATA REVIEW CHECKLIST	43
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<b>APPENDIX C - 40 CFR 136 APPLICABLE LIST OF APPROVED BIOLOGICAL METHODS FOR WASTEWATER</b>	<b>44</b>
<b>APPENDIX D— 40 CFR 136 APPLICABLE LIST OF APPROVED INORGANIC TEST PROCEDURES</b>	<b>45</b>
<b>APPENDIX E— 40 CFR 136 APPLICABLE LIST OF APPROVED TEST PROCEDURES FOR NON-PESTICIDE ORGANIC COMPOUNDS</b>	<b>57</b>
<b>APPENDIX F— DISTRIBUTION LIST</b>	<b>65</b>

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This document control information will appear in the upper right corner of each page of the Quality Assurance Project Plan (QAPP). Each revision of the QAPP will be assigned a revision number obtained by adding 1 (one) to the previous revision number.

On the bottom of each page will be found:

Cruise Ship Wastewater Monitoring # Quality Assurance Project Plan

### **Term of QAPP**

This Quality Assurance Project Plan will remain in effect until January 31, 2013 unless the U.S. Coast Guard or Alaska Department of Environmental Conservation notifies the other parties that a new plan is required. If necessary, a new approval page with updated contact information and signatures may be submitted as an appendix to this plan.

## Acronyms/Abbreviations Used

ADEC	Alaska Department of Environmental Conservation
BNA	Base/Neutrals, Acids
BOD	Biochemical Oxygen Demand – 5-day test
CFR	Code of Federal Regulations
COC	Chain of Custody
COD	Chemical Oxygen Demand
COTP	US Coast Guard Captain of the Port
DMR-QA	Discharge Monitoring Report Quality Assurance
EPA	Environmental Protection Agency
HDPE	High Density Polyethylene
HCl	Hydrochloric Acid
H <sub>2</sub> SO <sub>4</sub>	Sulfuric Acid
HNO <sub>3</sub>	Nitric Acid
MDL	Method Detection Limit
MQO	Measurement Quality Objective
MSD	Marine Sanitation Device
NaOH	Sodium Hydroxide
NWCA	North West Cruiseship Association
%R	Percent Recovery
PQL	Practical Quantitation Limit (Minimum Reporting Level)
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QMP	Quality Management Plan
QC	Quality Control
RPD	Relative Percent Difference
RQ	Reportable Quantity per 40 CFR part 302
SM	Standard Methods
SW-846	Solid Waste Methods
SOP	Standard Operating Procedures
TSS	Total Suspended Solids
UAS	University of Alaska, Southeast
USCG	U.S. Coast Guard
VOCs	Volatile Organic Chemicals
VSSP	Vessel Specific Sampling Plan

## **Management and Contractors**

### **North West CruiseShip Association**

The North West CruiseShip Association (NWCA) represents the large cruise line companies undergoing wastewater testing in Alaska. Individual NWCA members are funding the sampling and analysis program for their own respective vessels. The costs incurred by the Project QA Officer will be distributed evenly among all participants in the program. All NWCA member line cruise ships that operate in Alaska waters will follow the provisions of this QAPP.

### **Individual Vessel Representatives**

The responsibility for adherence to the provisions of this QA/QC plan rests with the owner or operator as per federal regulation 33 CFR 159.317 (a) (1). Failure of vessel owners and operators to follow the provisions of this QA/QC plan will result in enforcement action by the State of Alaska under AS 46.03.

### **Small Cruise Ships and Alaska Marine Highway System**

Many other small cruise ship companies and the Alaska Marine Highway System (AMHS) may choose to follow this QAPP or they may submit their own QAPP to the ADEC in order to satisfy obligations under Alaska Statute 46.03 and 18 AAC 69.025.

### **Lab Project Manager**

The Lab Project Manager is responsible for ensuring that individual project components are executed in a timely and appropriate fashion. However it is the vessel owner or operator that is responsible for compliance. Responsibilities include:

- Submitting results within the time frame specified by law and this document.
- Communicating project information to the Coast Guard, ADEC, and cruise lines.
- Assuring that project participants have necessary training.
- Fielding questions and requests for information that arise during and after the project.
- Managing the financial aspect of the project, including the determination of billing and payment mechanisms.

### **Sampling Team Leader**

The contract sampling team leader will coordinate and conduct all unannounced and continued compliance sampling, except for random sampling by the USCG. The VSSP must be submitted by the vessel owner or operator to the ADEC and USCG Sector Juneau prior to sampling.<sup>1</sup> The ADEC will forward the approved VSSP to the sampling manager. The sampling team will design and keep confidential a sampling schedule only available to ADEC and USCG. Vessel operators will not be aware of the timing of sample collection for the two unannounced sampling events. Random sampling will be under the control of the USCG Sector Juneau. Sampling team leader will be available if random sampling takes place as the USCG directs.

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<sup>1</sup> ADEC: 21 days before sampling, [18 AAC 69.030](#)  
Coast Guard: w/in 30 days of initial entry, [33 CFR 159.317\(a\)\(3\)](#)

Samplers are responsible for sample collection, sample integrity and custody, field measurements, and accurate notes. THE SAMPLER MUST VERIFY THAT THE VESSEL IS DISCHARGING OVERBOARD DURING THE UNANNOUNCED SAMPLING EVENTS. If discrepancies exist on the VSSP, the sampler is to report them immediately to ADEC and the USCG. The sampler will provide a compilation of field notes, deviations from VSSP or QAPP plans (if applicable), and Chain of Custody to the laboratory personnel, Project Manager, and the Project Quality Assurance Officer upon completion of all sampling.

The sampler will notify the ADEC project manager 36 hours prior to the sampling event. This gives ADEC time to audit the sampling event.

### **Wastewater Analysis Laboratory**

Coast Guard accepted laboratories must be utilized for all sampling events per 33 CFR 159.317(6). Coast Guard Headquarters (CG- 5213) recently implemented standards for acceptance and promulgated a list of accepted laboratories which can be found via the Internet at <http://cgmix.uscg.mil/EQLabs/EqLabsSearch.aspx> . Guidance for the laboratory acceptance process is available from the USCG Sector Juneau. In order to obtain USCG acceptance, a laboratory must: affirm and attest to the fact that the company (including it's officials, employees, and associates) is not owned or controlled by a manufacturer, vendor, or supplier of a marine device that may be used in treatment of the ships' waste water system or any other ship board system including promotion of the same as described in 46 CFR 159.010-3, or any cruise line corporation or subsidiaries thereof; attest that it is not dependent on Coast Guard acceptance to remain in business; demonstrate that it performs all testing conducted under the supervision and assurance of its laboratory Quality Assurance/ Quality Control Manager who has sufficient experience in wastewater testing and attest that all analyses are performed per 46 CFR 159.010-3(a)(1) & (2); and provide current certifications for testing and attest to the fact that their facilities are adequate to perform the required tests. In circumstances when a Coast Guard accepted lab cannot be used, the affected Cruise Line must verbally notify the USCG Sector Juneau for confirmation of an exception if they want to use the lab results for continuous compliance. In order to receive this one-time exemption the Cruise Line must notify the USCG Sector Juneau within 72-hours after the sample is submitted to the non-Coast Guard accepted lab. Every effort should be made to notify the USCG before submission, or the sample results may not be accepted and become invalidated. In order for the test results to remain valid, the lab used for the one-time exemption must apply to the Coast Guard within 45 days following the sampling event and subsequently become a Coast Guard Accepted Laboratory. USCG Sector Juneau can be notified 24-hours a day via the Sector Command Center at 907-463-2980 or 907-463-2000. Written follow up or email, if needed, can be submitted via email to [D17-PF-SampleResults@uscg.mil](mailto:D17-PF-SampleResults@uscg.mil).

Laboratories performing bacterial analysis for samples collected within Alaska for the purposes of meeting requirements under the ADEC General Permit must have current State of Alaska Drinking Water Laboratory Certification for fecal coliform. Laboratories performing chemistries for samples collected within Alaska for the purposes of meeting requirements under the ADEC General Permit must either have current Drinking Water certification with the State of Alaska for applicable parameters or be a current NELAC certified laboratory for the parameters to be measured. Any lab performing bacterial or chemical analyses on samples collected within Alaska must demonstrate acceptable performance in an annual external blind Performance Test sample for each wastewater analyte and method of interest by self enrolling in a NELAC accredited PT

vendor program, with PT results mailed directly to both the ADEC DOW QA Officer and the Project QA Officer.

### **Project Quality Assurance Officer**

The Project Quality Assurance (QA) Officer is an independent individual that ensures that that ALL laboratories and sampling teams follow the laboratory's quality assurance program guidelines, this QAPP, and the VSSP. The Project QA Officer works independently to ensure quality of the data.

### **US Coast Guard COTP**

The USCG COTP will use data gathered in accordance with this plan to determine continuous compliance with federal law.

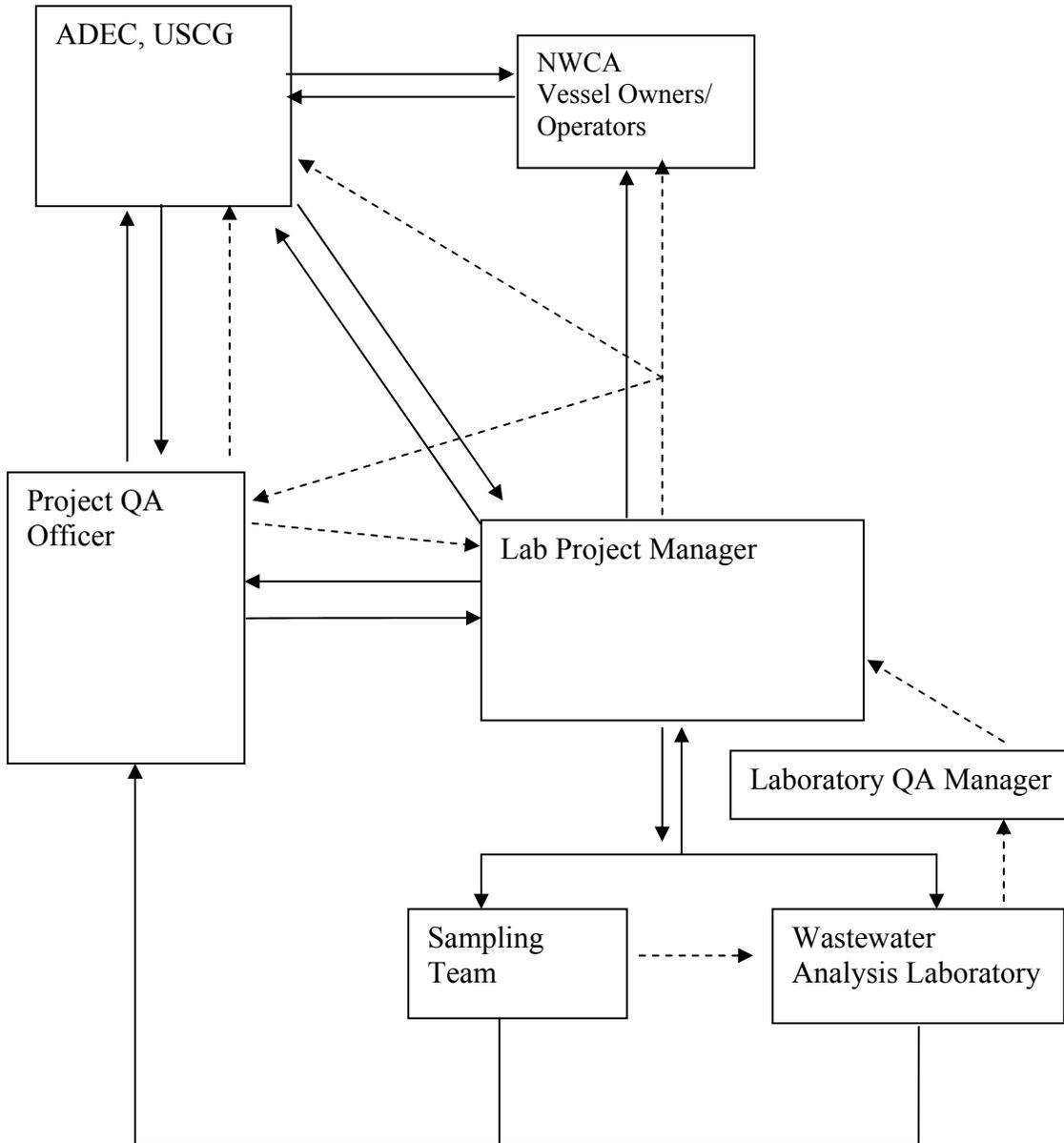
### **ADEC Project Manager**

The ADEC project manager manages the program to meet the requirements in the Alaska statute, regulation, and the approved QAPP.

### **ADEC Water Quality Assurance Officer**

The ADEC Water Quality Assurance Officer will review the QAPP to determine if it meets the State of Alaska's objectives for the data collection effort. The ADEC WQA Officer may review/audit data results and participate in sampling and laboratory audits.

### Program Organizational and Data Flow Chart



—————> Organization

- - - - -> Data Flow

## **Purpose**

This document is prepared and submitted to fulfill certain requirements of United States Title 33 Code of Federal Regulations 159.317, Alaska Statute 46.03.460- 46.03.490, and 18 AAC 69.025. Vessel owners may discharge treated sewage into Alaska waters less than one nautical mile from shore at a speed of less than six knots under 33 CFR 159.309(a)(1)-(4). Vessel owners will provide notification to the USCG for permission to discharge continuously into Alaska waters under the guidelines of 33 CFR 159.309(b)(1). Samples submitted to the USCG for initial discharge and ensuing continuous discharge under 33 CFR 159.309(b)(5) must also follow this QAPP.

Prior to any such discharge of treated sewage, the owner, operator or master, or other person in charge of a cruise vessel, will provide to the USCG SECTOR Juneau test results from at least five samples taken from the vessel, representative of the effluent to be discharged, on different days over a 30-day period or more which confirm that the water quality of the effluents proposed for discharge is in compliance with all limits included in 33 CFR 159. These samples should be evenly distributed within this 30-day period whenever logistically possible or on an extended period over 30 days. The samples will be taken in a manner that seeks to capture a typical wastewater discharge while still meeting the fecal coliform 6-hour holding time.

Samples must be collected and analyzed using land-based or mobile facilities that are accepted by the USCG. Results of this sampling must be submitted to the USCG SECTOR Juneau as a new application for continuous discharge for the next year season no earlier than 120 days and no later than 30 days prior to anticipated discharge into Alaska waters. Once satisfied, the USCG SECTOR Juneau at the request of vessel representative may send a letter of notification confirming intent of the vessel to discharge continuously into Alaska waters as defined in 33 CFR 159.307 for the calendar year of application. Upon receipt of the letter, the vessel owner shall demonstrate continued compliance while operating in Alaska waters through sampling and testing of the effluent for parameters listed in 33 CFR 159.309 (b) at a frequency of two samples per calendar month. The USCG SECTOR Juneau may witness any and all continued compliance sampling events. All sample results for the parameters indicated above must be within the stated limits of 33 CFR 159.309 (b) and must meet the data quality guidelines of this QAPP document to be considered valid.

Vessel owners can maintain continuous discharge certification while outside of Alaska waters by sampling and testing of the effluent for parameters listed in 33 CFR 159.309 (b) at a frequency of two samples per 60-day period, and there can not be greater than a 60-day period between any two samples. Samples must be collected and analyzed using either land-based or mobile facilities that are accepted by the USCG. In the event an accepted CG lab is unavailable, the vessel may request use of a particular lab for consideration via USCG SECTOR Juneau. The vessel owner will be requested to provide certain proof of accreditations or certification of the lab submittals and will allow a visit to the lab by Effluents Coordinator at the discretion of the USCG. USCG will make a determination to the acceptance of the laboratory and will notify the vessel owner.

Results for continued compliance testing that exceed the effluent limits in 33 CFR 159.309 (b) must be immediately reported to the USCG SECTOR Juneau. The vessel owner will initiate corrective action by: investigating and rectifying the cause of the exceedance; and resampling of the effluent to demonstrate that the effluent meets the limits in 33 CFR 159.309 (b).

Representative samples may be taken from the sampling point approved in the VSSP while the vessel is holding discharge and diverting effluent to a holding tank in order to demonstrate compliance with effluent limits while not discharging overboard. The USCG SECTOR Juneau may direct the vessel to retain onboard all effluents in certain situations due to continued exceedances of the effluent limits in 33 CFR 159.309 (b) either within or outside of Alaska waters or failure to present data for sampling and testing of the effluent for parameters listed in 33 CFR 159.309 (b) at the required frequency.

The local USCG SECTOR Juneau has also established a requirement of a minimum of two sampling events per vessel in a season while operating in the applicable waters of Alaska, and that these two sampling events are unannounced to the vessel beforehand. Additional sampling events are required for vessels operating under the General Permit issued by the State of Alaska. A “sampling event” is the collection of representative samples<sup>2</sup> of each wastewater type being discharged within Alaska waters. The number of samples in a sampling event is based upon the ship configuration, vessel wastewater management practices, and the wastewater quantities discharged while the sample team is on-board.

All compliance samples must be taken at a point in the system directly before being discharged overboard. Sample ports must be within 50 feet of the point of overboard discharge.<sup>3</sup> Both unannounced samples will be tested for conventional and priority pollutants in order to concurrently fulfill USCG and ADEC General Permit sampling requirements. Repeat sampling due to logistical or laboratory failures, duplicate samples, any other required samples will be scheduled as deemed necessary by the Sampling Team Leader.

In addition to the two scheduled unannounced sampling events, the USCG Sector Juneau may also direct the sampling team to conduct unscheduled random sampling for conventional and/or priority pollutants as directed in 33 CFR 159.317(5) at any time that they determine that additional samples are needed or necessary. This sampling will be scheduled at the request of the USCG Sector Juneau and will also be unannounced. The USCG will inform the sampling project manager 24 hours in advance to request any random sampling events. ADEC will be notified about these events by USCG Sector Juneau and will be invited for participation.

Lab reports should clearly state whether the sampling was conducted

- to obtain certification for continuous discharge
- to maintain continued compliance for continuous discharge

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<sup>2</sup> The VSSP for each vessel will list the proper location and timing of wastewater sampling. The samples will be taken in a manner that seeks to capture a typical wastewater discharge while still meeting the fecal coliform 6-hour holding time.

<sup>3</sup> Samples taken at the treatment system are sometimes of different quality than the samples taken at the discharge port. This will make it possible to fairly compare the data from all ships.

- to satisfy 33 CFR 159.317 and AS 46.03.465

The lab will submit the sample results directly to ADEC and USCG, but the owner/operator is responsible for meeting submittal deadlines.

## Applicability

This QAPP specifies the minimum requirements for sampling and analysis of treated sewage and/or graywater and other wastewaters as defined in AS 46.03.490, for vessels that are members of the North West CruiseShip Association. This QAPP is also applicable for any commercial passenger vessel that discharges treated sewage, graywater and/or other wastewater in the applicable waters of Alaska as defined in 33 CFR 159.305 and the waters of the Alexander Archipelago as defined in AS 46.03.490. All unannounced and/or random sampling events required by 33 CFR 159 and AS 46.03 shall be conducted in accordance with this QAPP and can be combined to complete requirements for both regulatory programs.

Owner or operators must comply with the guidelines in 33 CFR 159, 40 CFR 136.3, AS 46.03.460-46.03.490, and 18 AAC 69, 18 AAC 70 and this plan.

Each participating ship will be sampled within 30 days of initial entry into Alaska waters and subject to unannounced treated sewage and graywater sampling and analysis for conventional and priority pollutants as determined by the Coast Guard Sector Juneau. The second samples must be at least 21 days after the first sampling event. Continued compliance samples must be taken on separate calendar days and must be taken at least 24 hours apart. The USCG Sector Juneau Inspectors & ADEC may board vessels at any time to perform sampling inspections as necessary to implement 33 CFR 159 and AS 46.03.

This QAPP covers sampling and analysis for the parameters listed below. Analysis for conventional and priority pollutant parameters as required by the USCG under 33 CFR 159.317 are listed below. A sample that fails to provide valid results for all required pollutants will not be counted as an acceptable sample for purposes of meeting the minimum requirement of two samplings for conventional pollutants and one sample for priority pollutants.

Conventional pollutants (two sampling events):

- Total Suspended Solids (TSS)
- Settleable Solids (SS)
- Biochemical Oxygen Demand (BOD)
- Chemical Oxygen Demand (COD)
- Oil and Grease
- Total Organic Carbon
- Ammonia – Total
- Fecal Coliform
- pH
- Total and Free Residual Chlorine

- Specific Conductance (to measure seawater influx)
- Alkalinity
- Total Nitrogen (Ammonia, Nitrate plus Nitrite, and Total Kjeldahl Nitrogen (TKN))
- Total Phosphorus
- Nitrate (ADEC requirement only)

Priority Pollutants (two sampling events)

- Base/Neutrals, Acids
- Total Aromatic and Total Aqueous Hydrocarbons using BNA and VOC data
- Volatile Organic Chemicals (VOCs)
- Trace Metals (Total Recoverable and Dissolved)

### **Blind Duplicate Samples**

Blind sample duplicates will be collected on a minimum of 10% of the total number of samples collected for the project. All blind samples will be analyzed for both conventional pollutants and priority pollutants. Blind duplicate samples will be randomized to assess precision for all ships monitored within the program.

The purpose of the blind sample duplicates is to assess sampling and laboratory error and to assess overall method variability. Precision between the sample and its duplicate will be determined by calculating the relative percent difference between the two samples, in the same way that precision is measured between two laboratory-fortified blanks or a matrix spike/matrix spike duplicate. The use of duplicate samples extends the test of precision to the sampling method itself. The use of blind samples provides a test of the laboratory and is used to assess bias or analytical errors not detected by the laboratory (e.g., a false positive). Every effort will be made to ensure that the labeling of the samples does not disclose the duplicate nature of the samples to the laboratory staff. The samples will be analyzed by the same lab and for the same parameters.

The sampler will need to take a cubitainer (10 liters) of wastewater and thoroughly mix it. The sampler should then pour the contents of the cubitainer into individual sample bottles.

### **Quality Objectives and Criteria for Measurement Data**

DQOs are qualitative and quantitative statements derived from the DQO Process that:

- Clarify the monitoring objectives.
- Define the appropriate type of data.
- Specify the tolerable levels of decision errors for the monitoring program.

## Measurement Quality Objectives

Measurement Quality Objectives (MQOs) are a subset of DQOs. MQOs are derived from the monitoring project's DQOs. MQOs are designed to evaluate and control various phases (sampling, preparation, and analysis) of the measurement process to ensure that total measurement uncertainty is within the range prescribed by the project's DQOs. They define the acceptable quality of QAPP field and laboratory data for the project. MQO's are defined in terms of Precision, Bias, Representativeness, Detectability, Completeness, and Comparability.

### Detectability

Detectability is the ability of the method to reliably measure a pollutant concentration above background. Two components can be used to define detectability: method detection limit (MDL) and practical quantification limit (PQL) or reporting limit (RL).

- The MDL is the minimum value which the instrument can discern above background but no certainty to the accuracy of the measured value. For field measurements the manufacturer's listed instrument detection limit (IDL) can be used.
- The PQL or RL is the minimum value that can be reported with confidence (usually some multiple of the MDL).

Sample data measured below the MDL is reported as ND or non-detect. Sample data greater than the MDL but below the PQL or RL is reported as estimated data and must be flagged. Sample data measured above the PQL or RL is reported as reliable data unless otherwise qualified per the specific sample analysis. Individual analyte MDL and PQL limits are listed in Table 2.

### Precision

Precision is the ability to replicate the measurement. It is expressed as Relative Percent Difference (RPD). Overall project acceptance criteria for precision are analyte, matrix, and method specific and are listed in the Measurement Quality Objectives table. RPD is normally determined by the results of blind sample duplicates/replicates of collected samples, field replicate measurements (for direct measurements made in the field), and the analysis of laboratory control standard or matrix spike duplicates in the laboratory. The calculation for RPD is:

$$\frac{(X_1 - X_2)}{\frac{(X_1 + X_2)}{2}} \times 100$$

and is expressed as a percent.  $X_1$  = first sample measurement and  $X_2$  = second sample measurement. Precision limits for specific analytes are listed in Table 2.

If calculated from three or more replicates, relative standard deviation (RSD) is used rather than the relative percent difference (RPD):

$$RSD = \left( \frac{S}{Y} \right) \times 100$$

Where,

RSD = relative standard deviation

S = standard deviation

Y = mean of replicate analysis

Standard deviation, s, is defined as follows:

$$S = \sqrt{\frac{\sum_{i=1}^N (X_i - \bar{X})^2}{N - 1}}$$

Where,

S = standard deviation

$X_i$  = measured value of the  $i^{\text{th}}$  replicate

$\bar{X}$  = mean of replicate measurements

N = number of replicates

Laboratories also routinely assess precision of their measurements within a laboratory (matrix spike duplicates, lab split samples, laboratory-fortified blank duplicates, etc). The frequency of laboratory precision measurements and their acceptance criteria are analyte and method specific. Minimum acceptance criteria limits are specified in the respective EPA approved measurement methods and in each laboratory's approved Quality Assurance Manual. Calculations for laboratory precision are the same as above.

### **Bias (Accuracy)**

Overall bias for this QAPP is assessed through measurements of sample spike and matrix spike duplicate recoveries. Bias is the closeness of the measurement to the true level of the variable. Bias is expressed as percent recovery (%R). Bias criteria for %R vary depending on the analyte and the method. %R is normally determined by the use of known traceable laboratory standards. Acceptance limits for Bias for each analyte are listed in Table 2.

Laboratory bias is demonstrated through routine instrument calibrations, various types of QC checks (e.g., sample split measurements, sample spike recoveries, matrix spike duplicates, continuing calibration verification checks, internal standards, sample blank measurements (field and

lab blanks) and use of certified external Quality Control samples--external standards), etc. Bias is normally determined by the percent recovery of the target analyte in spiked samples/sample blanks and internal surrogate standards. Bias (percent recovery or % R) is calculated as follows:

$$\%R = \left( \frac{\text{Analyzed Value}}{\text{True Value}} \right) \times 100$$

Laboratory bias acceptance criteria limits must be within the respective EPA approved method criteria limits and as specified in the respective contract laboratory's Quality Assurance Manual. Analyte specific acceptance criteria limits vary dependent upon the measurement method. Each contracted laboratory will maintain on file with the Project QA Officer and the ADEC DOW QA Officer a current Quality Assurance Manual (including all appropriate method SOPs (standard operating procedures), electronic copies requested).

Field laboratory and data quality audits and 3<sup>rd</sup> party performance evaluation (PT) samples are independent (external) means to assess measurement bias for the monitoring project.

### **Completeness**

Completeness is a measure of how many planned measurements for each constituent actually resulted in valid reported data. It is expressed as a percentage of the total number of samples collected. The completeness criterion for this project is 80 percent of the compiled analytical data per each analytical parameter for each vessel participating in the program. Because of the variety of vessels and discharges sampled, and the possibility for weather or other shipping-related delays resulting in missed holding times, a completeness criterion of less than 100% is to be expected. The following equation is used to calculate completeness:

$$\text{Completeness} = \frac{T - (I + NC)}{T} \times 100$$

Where,

$T$  = Total number of expected measurements

$I$  = Number of invalid results

$NC$  = Number of results not produced (e.g., spilled sample, etc.)

### **Representativeness**

Representativeness is a measure of how well the sample reflects the typical wastewater effluent. Sample representativeness will be established by collecting cruise ship graywater, blackwater, and other wastewater discharge samples following vessel specific sampling plans (VSSP). The owner and operator is responsible for developing and submitting VSSPs to both agencies for each vessel participating in the program

The treatment system effluent will be considered representative for the two unannounced samples only if the vessel normally discharges continuously. If the vessel normally stores the wastewater in

holding tanks before discharging, the effluent from the holding tank will be sampled. The VSSP is designed to ensure that consistent sampling methods are followed and that samples are collected from appropriate and representative locations at appropriate times.

Vessel operation that differs from the VSSP may result in State of Alaska and/or the USCG rejection of samples.

### **Comparability**

Comparability is a measure of confidence with which one data set can be compared to another. It is addressed in the plan by 1) following EPA standardized sampling and analytical methods; 2) by using similar sampling and analytical methods as followed in last year's monitoring project; 3) ensuring that appropriate reporting limits are used; and 4) obtaining data of known and acceptable quality through the use of specified QC measures and QA assessment procedures.

Because of the different source types found on different vessels (e.g., a holding tank on some ships may contain both blackwater and graywater, while on others it may only contain graywater), careful definition of discharge types will be made in the VSSP. It is essential that these definitions be carried through to the end data user, as these differences could erroneously bias data interpretation.

The sampling team must make full use of ship records and logs, especially the Graywater and Sewage Discharge Record Book which includes the latitude and longitude at the beginning and end of discharge, identifying tanks, estimating volumes and calculating discharge rates (if any) at the time the sample is drawn. If the vessel is discharging continuously (not just certified but actually is in practice) then the sampler does not need to record latitude and longitude at the beginning and end of discharge, identifying tanks, estimating volumes of those tanks. The sampler needs to identify which treatment unit is discharging and the discharge rate. The vessel speed and longitude/latitude must be obtained by the sampler if the sample is taken while the vessel is discharging underway. Information added to the VSSP or changes to the VSSP during the sampling event must be recorded on the VSSP, COC, or in the field notes and must accompany the samples to the lab and be provided to the project data recipients as part of the complete unannounced sampling report.

### **Special Training Requirements/Certification**

Samplers will be trained in sampling methods, sample handling, chain of custody, and field measurements as outlined in 40 CFR 136. Additionally, samplers will receive appropriate training through their employer or their employer's designee, in any necessary shipboard safety procedures.

Laboratories used for USCG compliance purposes must be USCG accepted laboratories under the guidelines of 33 CFR 159.317(6). Laboratories used for ADEC compliance purposes will have a current Alaska Department of Environmental Conservation Drinking Water certification for microbiologicals or inorganics or home state or provincial equivalent. Laboratory analysts will be trained in accordance with each laboratory's QA Plan and Standard Operating Procedures (SOPs). Records of current certification, analyst training, and the laboratory QA documents listed above will be made available to the Project Manager and the Project QA Officer, and ADEC upon request. Laboratories will employ approved methods of testing as outlined in 40 CFR 136 and referenced in Appendices C-E, or as directed by the methods listed in table 2.

## Documentation and Records

### **Sample schedule and Vessel/Sample Identification**

The sampling team will work with the USCG and ADEC to develop a schedule of unannounced sampling events as required in 33 CFR 159.317 (a). The developed schedule of unannounced sampling events is confidential and is NOT shared with the vessels, nor are the vessels notified of such sampling events. The sampler must also notify the ADEC of its intent to sample at least 36 hours prior to sample collection. The two sampling events must be a minimum 21 days apart unless being conducted as a USCG random unannounced sampling event. For purposes of compliance with the State of Alaska, vessels discharging in Alaska waters must comply with the sampling and monitoring frequency outlined in the ADEC Large Commercial Passenger Vessel Wastewater Discharge General Permit.

Samples will be identified clearly on the chain of custody and sample bottles. For example, a sample from the overboard discharge from the *M/V HYPOTHETICA* will be identified as “OB Discharge,” as the description with associated dates and times. The Sample ID should clearly state where the sample was taken. All samplers should use the same sample ID system. From continuous discharges with one discharge point “OB Discharge” is appropriate. The sampler should fill out the checklist in Appendix A.

### **Field Records (Required for both unannounced and continued compliance samples)**

Field notes will be collected in bound field notebooks with numbered pages or recorded on pre-printed forms with specific information pertaining to the sampling event. On-board staff will witness the sampling and will initial the field notes. Included in the field notes for each sample are:

- Vessel name (e.g., *HYPOTHETICA*),
- Sampling personnel,
- Shipboard assistants,
- Signature or initials by the vessel crew in the field notes indicating that the sample port is correct,
- Sample date and times,
- Field measurements: pH, free chlorine, total chlorine, and temperature,
- Records on discharge flow rates (always) and holding tank volumes (only for underway sampling),
- Samples collected,
- Nature of sample: Composite or Grab,
- Waste type: blackwater, graywater, or mixed,
- Deviations from VSSP and/or QAPP,
- Unusual conditions and explanation of data anomalies,
- Latitude/longitude and speed at time of discharge being sampled (only for underway sampling),
- Copy of the Discharge record for the sampled discharge, which will include records on discharge flow rates (always) and holding tank volumes (only for underway sampling).

Cruise ship operators maintain a sewage and graywater discharge record book that records the date, times, volumes, and vessel location (latitude and longitude) for each wastewater discharge. These

records will be provided to the sampler. The sampler will collect and submit the discharge logs and field notes to the USCG, ADEC and company representative within three days of the sampling as an aid to subsequent determination of conventional and priority pollutant mass input. This information will also be included in final laboratory reports.

### **Laboratory Records**

Upon completion of laboratory analysis, laboratory data review, and data validation, the laboratory will issue a full report in an electronic format describing the results of analysis for each sample submitted. Prior to issuance of the analytical report to the vessel's representatives, ADEC, and the USCG Sector Juneau, the laboratory's QA manager will review and approve the report.

The final laboratory reports will identify whether a sample was taken to satisfy 33 CFR 159.317 and AS 46.03.465 or done in order to seek USCG approval for discharge without distance or speed limitations or is a continuous discharge compliance sample.

Components of the analytical report include:

- A short summary sheet discussing the sampling event and results.
- Sample information: ship name, sample names, waste type, date and time collected.
- Parameter name and method reference.
- Analytical result.
- Method Detection Limit.
- Practical Quantitation Limit (reporting limit).
- Date and time of sample preparation and date and time of analysis.
- Quality control information: blank results, spiked blank or laboratory control standard recovery, matrix spike/spike duplicate recoveries, relative percent differences between duplicate spike analyses.
- Chain of custody.
- Information documenting whether holding times were met.
- Case Narrative of deviations from methods, procedural problems with sample analysis, holding time exceedances, and any additional information that is necessary for describing the sample. This narrative should explain when results are outside the precision and accuracy required and the corrective actions taken to rectify these QC problems.
- Discharge logs and field notes, including records on discharge flow rates and holding tank volumes
- Cooler receipt forms, including information on each lab receiving samples.
- Photograph of sampling port taken during sampling event (unannounced samples only)
- Latitude and longitude information pertaining to each sample including which overboard port the waste was discharged through and the speed the vessel was traveling.
- Explanation of data abnormalities.
- A completed checklist containing all components of sampling (Appendix A).
- A completed checklist containing all components analysis and reporting (Appendix B).
- Electronic data file containing all laboratory results in Excel or .xml format.
- *(FOR ADEC ONLY) If applicable, a notification that this sample is a resample under 18 AAC 69.070*

## **Chain of Custody**

The original chain of custody form will accompany the sample to the laboratory. When portions of the sample are sent to another laboratory (e.g., for many of the priority pollutants), a copy of the chain of custody will be made and this will accompany the samples. At each transfer of the sample, the transfer will be indicated on the chain of custody form. The person listed on the Chain of Custody should have full sight or control of the sample at all times until it the COC is relinquished by that person and received by the next party signed on the COC.

A copy of the original chain of custody will be included with the final report including the COC transferring samples to other labs. Electronic scanned copies in PDF form are sufficient.

## **Sampling Process Design**

A vessel specific sampling plan (VSSP) will be developed for each ship by the ship engineers and submitted to the sampling team 30 days prior to entry into Alaska waters. The plan will include, as a minimum, the following:

- Vessel name.
- Passenger and crew capacity of ship.
- Daily water use per individual.
- Locations and capacities for treated sewage, graywater, and other wastewater tanks.
- Type of wastewater treatment systems.
- Each discharge pump type and rate
- Vessel schematic of discharge ports and corresponding sampling ports. The sample port must be no more than 50 feet from the OVERBOARD port.
- Description of discharges, including anticipated flow rates and tank volumes.
- Table containing type of discharge, type of sample (grab or composite), parameters (conventional or priority pollutants), location on the vessel where each sample is to be collected, and special circumstances.
- A narrative description of the time at which each sample is to be taken based upon circumstances that will yield a sample most likely to be representative of the average discharge that passes through the location where the sample is taken
- A description of the standards the owner or operator will use to determine a deviation from the plan
- Equipment required.

Each VSSP will be dated and a copy will be provided to the Project Manager, the cruise ship companies, Alaska Department of Conservation and the USCG. The VSSP will be submitted to the USCG Sector Juneau and the ADEC Project Manager within 30 days of each vessel's initial entry into the applicable waters of Alaska. The ADEC must approve the VSSP prior to sampling. After the first sampling event on a vessel, the VSSP may be updated. If it is updated, copies of the updated sampling plan will also be provided to the Project Manager, the vessel's owner or operator, ADEC and the USCG Sector Juneau before the second round of sampling occurs.

The purpose of providing the VSSP to the Project Manager and the cruise ship companies prior to sampling is to provide certainty that consistent sampling methods are followed and that samples are collected from appropriate and representative locations. Deviations from the sampling plan may

well occur; these will be noted in the field notes and notification will be given to ADEC and USCG Sector Juneau.

## **Sampling Method Requirements**

### **Sample Collection Procedures**

Specific sampling techniques for each vessel will be detailed in the VSSP. The following general guidelines are listed to provide consistency among the vessels utilizing this QAPP.

Samples will reflect a representative discharge of treated blackwater, graywater and other wastewaters into applicable waters of Alaska from an operable marine sanitation device, other treatment system, a holding tank or some combination as specified in the VSSP. In port sampling, in compliance with ADEC sampling events, will be conducted only if the vessel is certified to discharge in port. If samples must be taken while the ship is underway, care will be taken to assure sample representativeness and homogeneity. See VSSP for further details on sampling.

Samplers will ensure that proper sampling techniques are followed, adequate notes are taken during the sampling event, and proper sample custody is maintained. One sampler will be sufficient for all in-port sampling events. Samplers may work in teams of two if applicable for sampling events that must be performed while the vessel is underway. Samplers may be accompanied by sampling auditors and/or witnesses from regulatory agencies for both in-port and underway sampling events.

A volume of water equal to at least ten times the volume of the sample discharge line will first be discharged into a bucket or similar container to clear the line of standing water and possible contamination.

Samplers will wear disposable gloves, protective clothing and safety eyewear and will observe precautions while collecting samples, remaining aware of the potential biohazard present.

Samplers will contain all solid and liquid wastes generated during sampling (used gloves, paper towels, chlorine test waste, and overflow from filling of VOC sampling vials) and remove it from the ship at the conclusion of the sampling event.

Samplers will take care not to touch the insides of bottles or lids/caps during sampling.

Samples will be listed as “grab” on the Chain of Custody form.

Bottles will be pre-cleaned and will not require rinsing with sample. When sample bottles are pre-preserved, bottles must never be rinsed but will be filled only once with sample.

The required field tests will be performed prior to sampling in order to determine if residual chlorine is present. This will dictate the preservation procedures for the VOC and BNA analyses.

The practical quantitation limit for chlorine testing using field equipment is 0.1 mg/L. Some field instruments may display values below this level. Any values observed below this limit will be recorded as actual readings on the field notes but as <0.1 mg/L final data reports.

Sample fractions for microbiology will be cooled immediately in an ice-water bath and then placed into a cooler containing frozen blue ice or ice and water mixture to maintain a sample temperature of 0 - 6° C. Temperature will be measured and recorded at the time of sample collection and upon sample receipt at the laboratory to an accuracy of 0.1° C and a note shall be made on the chain of custody of the temperature of the cooler contents upon arrival at the laboratory. Samples received with any indication of ice formation are unacceptable.

Sample bottles will be filled sequentially. Bottles will normally be filled to the shoulder of the bottle, leaving a small space for expansion and mixing. VOC bottles will not be intentionally over-filled but carefully filled to achieve 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 will be present in the bottle.

EPA guidelines in 40 CFR 136 require that samples to be analyzed for dissolved metals must be filtered and preserved with nitric acid within 15 minutes after sample collection.

**TABLE 1 Sample Containers, Preservations, Holding Times, and Sample Types**

<b>LAB PARAMETER</b>	<b>CONTAINER</b>	<b>PRESERVATION</b>	<b>MAXIMUM HOLDING TIME</b>	<b>Grab or Composite</b>	<b>Minimum Representative Volume</b>
<b>Conventional Pollutants</b>					
Total Suspended Solids	P, FP, G	Cool, ≤6° C, do not freeze	7 days	Grab Only	100 ml
Settleable Solids	P, FP, G	Cool, ≤6° C, do not freeze	48 hours	Grab Only	1000 ml
Biochemical Oxygen Demand	P, FP, G	Cool, ≤6° C, do not freeze	48 hours	Grab Only	1000 ml
Ammonia – Total	P, FP, G	Cool, ≤6° C, H <sub>2</sub> SO <sub>4</sub> to pH <2, do not freeze	28 days	Grab Only	400 ml
Chemical Oxygen Demand	P, FP, G	Cool, ≤6° C, H <sub>2</sub> SO <sub>4</sub> to pH <2, do not freeze	28 days	Grab Only	50 ml
Specific Conductance	P, FP, G	Cool, ≤6° C, do not freeze	28 days	Grab Only	100 ml
Fecal Coliforms	Sterile PA, G	Cool, ≤6° C, 0.0008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , do not freeze	6 hours	Grab Only	100 ml
Alkalinity	P, FP, G	Cool, ≤6° C, do not freeze	14 days	Grab Only	100 ml
pH	P, FP, G	None	Analyze within 15 minutes in field	Grab Only	25 ml
Oil and Grease	G	Cool, ≤6° C, HCL or H <sub>2</sub> SO <sub>4</sub> to pH <2, do not freeze	28 days	Grab Only	1000 ml
Total Organic Carbon	P, FP, G	Cool, ≤6° C, HCL, H <sub>2</sub> SO <sub>4</sub> or H <sub>3</sub> PO <sub>4</sub> to pH <2, do not freeze	28 days	Grab Only	50 ml
Total Kjeldahl Nitrogen	P, FP, G	Cool, ≤6° C, H <sub>2</sub> SO <sub>4</sub> to pH <2, do not freeze	28 days	Grab Only	500 ml
Total Phosphorus	P, FP, G	Cool, ≤6° C, H <sub>2</sub> SO <sub>4</sub> to pH <2, do not freeze	28 days	Grab Only	50 ml
Temperature	P, FP, G	None	Analyze ASAP in field	Grab Only	1000 ml
Chlorine Residual	P, G	None	Analyze within 15 minutes in field	Grab Only	100 ml

LAB PARAMETER	CONTAINER	PRESERVATION	MAXIMUM HOLDING TIME	Grab or Composite	Minimum Representative Volume
Nitrate ****	P, FP, G	Cool, ≤6° C, do not freeze	48 hours	Grab Only	100 ml
<b>Priority Pollutants</b>					
BNA	G, FP-lined cap	Cool, ≤6° C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> if residual chlorine is detected above 0.1 mg/L, do not freeze	7 days until extraction, 40 days after extraction	Grab Only	1000 ml ***
VOCs	G, FP-lined septum	Cool, ≤6° C, 0.008% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> if residual chlorine is detected above 0.1 mg/L, HCL to pH <2, do not freeze	14 days	Grab Only	40 ml
Total Aromatic and Total Aqueous Hydrocarbons**	See BNAs and VOCs				
Total Mercury (CVAA)	P, FP, G	HNO <sub>3</sub> to pH <2, do not freeze	28 days	Grab Only	100 ml
Total Recoverable Metals	P, FP, G	HNO <sub>3</sub> to pH <2, or at least 24 hours prior to analysis, do not freeze	6 months	Grab Only	100 ml
Dissolved Metals	P, FP, G	Filtration w/0.45 micron filter within 15 min of collection, HNO <sub>3</sub> to pH <2, do not freeze	6 months	Grab Only	200 ml

Sample containers will normally be pre-preserved by the laboratory. Analyses can be consolidated into containers of matching sample preservation as long as adequate sample volume is collected for all tests. A 1 liter unpreserved bottle is sufficient to provide enough sample for the tests of BOD, TSS, pH, specific conductance, and alkalinity. A 1 liter bottle preserved with sulfuric acid is sufficient to provide enough sample for the tests of ammonia, COD, total phosphorus, and TKN. The tests of settleable solids, oil and grease, and BNA require a full liter of sample for extraction and cannot be consolidated with other tests. The sampler must measure the chlorine level before taking the VOC and BNA samples. If chlorine residual is detected above 0.1 mg/L during field measurement of chlorine, ascorbic acid provided by the lab will be added in the field to the BNA and PCB sample bottles until no chlorine is detected. The lab will provide decanting bottles with ascorbic acid. When chlorine is detected, the sample will be added first to the decanting bottle, and then will be decanted into the VOC vials. \*\*Total Aromatic and Total Aqueous Hydrocarbons will be calculated from the BNA and VOC results. \*\*\*Additional volume of

sample is required for matrix spike determination during the BNA analysis. The sampling team will take an additional 2L of sample from all priority pollutant duplicate sampling events for this purpose to provide matrix spike data at a frequency of 10% for project related samples. \*\*\*\* Required as twice seasonal test for ADEC permit only.

## **Sample Handling and Custody Requirements**

### **Sample Custody**

Samples and sample containers will be maintained in a secure environment, from the time the bottles leave the laboratory until the time the samples are received at the laboratory. The laboratories will maintain custody of bottles and samples using their normal custody procedures.

Blind field duplicates will be identified with discrete sampling labels and recorded as blind field duplicates in the sampler's field notebook.

To maintain the secure environment for samples on board ship and during transport, samples must be: 1) in the sampler's possession (line of sight); or 2) in a cooler sealed with signed and dated friable evidence tape or packing tape equivalent on opposing sides of the cooler; or 3) in a locked cooler for which only the sampler has the key. When the cooler is sealed, the method of securing the samples must be such that tampering with samples or bottles is not possible: The cooler must be secured so that the lid cannot be removed without breaking the evidence tape or cutting the lock, so that tampering would be evident.

Transfer of samples will be accomplished using the laboratory's chain of custody form. When samples are transferred between personnel, such transfer will be indicated on the chain of custody form with signature, date and time of transfer. The chain of custody will remain with the samples until received by the laboratory.

At any time during sample transfer, if custody is broken, a note must be made on the chain of custody form accompanying the sample. Upon receipt at the laboratory, the laboratory sample custodian will make note if a breach of custody has occurred (for example, if a custody seal has broken during transport).

### **Sample Temperature and Condition**

Samples will be held at 0 - 6° C. The sampler will fill a 1 liter HDPE bottle with the effluent sample to serve as a representative temperature blank. This bottle will be placed into the cooler at the same time as the first sample and will accompany all samples, and will be measured at the laboratory upon receipt of the samples to verify the temperature. The temperature of this blank will be recorded on the chain of custody at the time of sampling and upon receipt of the sample at the lab to demonstrate the initial and final temperature of the sample. Samples received with any indication of ice formation are unacceptable.

To maintain the temperature, extra blue ice will be kept frozen on board ship or ship ice will be used. Blue ice or ship ice will be exchanged just before shipment of samples to the lab, and may be exchanged more frequently during the sampling trip, as required.

Some samples may be at a temperature near body temperature (37° C) at time of sample collection. This temperature encourages growth of fecal coliform bacteria and thus these samples must be cooled as quickly as possible, without freezing them. The sample bottles for microbial testing shall be placed in a

water bath containing ice cubes provided on board ship. The bottles should be immersed in the water to the shoulder, rotated frequently, and ice should be added/water drained off as the ice melts for at least one hour or until the sample reaches a temperature of  $<6^{\circ}\text{C}$ . The sampler will fill a 120 ml HDPE bottle with the effluent sample to serve as a representative temperature blank. The temperature of this blank will also be recorded on the chain of custody at the time of sampling and upon receipt of the sample at the lab to demonstrate the initial and final temperature of the microbial sample. This temperature blank must also be measured /documented as being above freezing upon receipt with no indication of freezing of samples and temperature blank. To ensure custody of these samples that may not be able to be sealed in the cooler until the temperature is lowered, these bottles can be sealed with custody tape individually, as necessary.

In no event will samples be placed in refrigerators meant for human food or beverages.

### **Sample Holding Times**

Sample holding times are as described in Table 1 above. Planned sample shipping schedules will allow for the meeting of these holding times.

The most critical holding time will be that of fecal coliforms, which is defined by EPA as 6 hours to commencement of analysis. To meet this holding time, a stringent scheduling effort will be required by the laboratory and sampling team. If the normal discharge pattern is altered in order to adhere to this holding time, a note will be made of the change in the field notes and in the final quality control review.

### **Sample Disposal**

Samples collected for analysis shall be held by the laboratory for not less than three months from the sample collection date, or for an extended time period on an individual basis as directed by the Coast Guard and ADEC prior to the three month date.

## **Analytical Methods and Quality Control Requirements**

Water quality analytical methods that will be used throughout this project are outlined in Appendices C-E. All methods used for this project must be EPA approved Water and Wastewater analytical methods listed in 40 CFR 136. Only approved methods for water/wastewater (not drinking water) will be used for the analysis of microbiological samples. Any lab performing analytical work on samples collected within Alaska must provide and current electronic copy of their approved Quality Assurance Manual (and respective measurement method SOPs) to the ADEC Division of Water QA Officer as well as the Project QA Officer. These documents must specify calibration and quality control criteria, practices and procedures that are essential in the review, validation, verification and reporting of sample result data.

The USCG requires the analytical report within 15 calendar days after the sampling date for conventional pollutant analyses. The USCG requires the analytical report within 30 calendar days from the sampling date for priority pollutant analysis and associated conventional pollutant analyses from the same sampling event. The ADEC requires conventional and priority pollutants reports within 21 days of completion of laboratory analysis.

The MDL referred to in Table 2 is a statistically derived method detection limit, typically arrived at by repeat analyses performed by the laboratory, with a statistical EPA-defined calculation then performed (40 CFR 136 Appendix B). It is sometimes method-defined (as in BOD). The PQL (Practical Quantitation Limit) is the level at which the laboratory QA department feels comfortable reporting data. Because the

MDL is statistically derived, data can be detected at and near the MDL that are not accurate and that are frequently false positives. For this reason, many labs do not report at the MDL but report at some level, often approximately 3 times greater than the MDL (again, for statistical purposes). The MDL's and Reporting Limits are usually laboratory-specific standards and are not tied to compliance limits, and are not regulatory action levels. The MDL and PQL values in this document reflect typical laboratory performance at the present time and will serve as general targeted levels for this project. PQL values must be lower than compliance levels for any parameters with defined effluent limits in the ADEC General Permit. Actual data reporting levels may change due to ongoing detection limit studies and sample dilution due to matrix interferences. Percent recovery (accuracy) limits are directed by the official laboratory methods, or in the absence of such directives, are derived from laboratory performance. Current targeted guidelines for MDL's, RL's (minimum levels, PQL), and precision and accuracy requirements for the project are listed in the following table. Lab performance should not deviate more than 20% from these target values.

All methods used for analysis of conventional and priority pollutants under this QAPP must be referenced in 40 CFR Part 136. Applicable methods for the conventional and priority pollutants required by this plan are summarized in Appendices C, D, and E of this document.

**Table 2. Project Measurement Quality Objectives**

<b>PARAMETER</b>	<b>MDL (mg/l)</b>	<b>PQL (mg/l)</b>	<b>PRECISION (RPD, RSD)</b>	<b>BIAS (% Recovery)</b>
<b>Conventional Pollutants</b>				
Alkalinity	5	20	<20%	85 - 115 %
Ammonia – Total	0.15	0.5	<20%	80 - 120 %
Biochemical Oxygen Demand	2	2	<20%	70 - 130 %
Chemical Oxygen Demand	5	15	<20%	85 - 115 %
Chlorine Residual (total/free)	0.1	0.1	N/A	N/A
Fecal Coliforms	2 FC/100 ml	2 FC/100 ml	N/A	N/A
Oil and Grease	1.5	5	<20%	60-150%
pH	0.10 standard units	0.10 standard units	<20%	N/A
Settleable Solids	0.10 (ml/L)	0.10 (ml/L)	<20%	N/A
Specific Conductance	1 µmHos/cm	2 µmHos/cm	<20%	85 - 115 %
Total Nitrogen	1	5	N/A	N/A
Total Organic Carbon	0.3	1	<20%	85 - 115 %
Total Phosphorus	0.03	0.1	<20%	85 - 115 %
Total Suspended Solids	1.3	4	<20%	85 - 115 %
<b>Priority Pollutants</b>				
<ul style="list-style-type: none"> <li>Total Aromatic and Total Aqueous Hydrocarbons using BNA and VOC data</li> </ul>				

<b>PARAMETER</b>	<b>MDL (µg/l)</b>	<b>PQL (µg/l)</b>	<b>PRECISION (RPD)</b>	<b>BIAS (% Recovery)</b>
<b>Total Recoverable Metals</b>	<b>µg/l</b>	<b>µg/l</b>		
Antimony	0.8	2.5	<20%	85 - 115 %
Arsenic	0.8	2.5	<20%	85 - 115 %
Beryllium	0.5	1.5	<20%	85 - 115 %
Cadmium	0.65	2	<20%	85 - 115 %
Chromium	0.8	2.5	<20%	85 - 115 %
Copper	0.4	1	<20%	85 - 115 %
Lead	0.3	1	<20%	85 - 115 %
Mercury (Total)	0.65	2	<20%	85 - 115 %
Nickel	0.5	1.5	<20%	85 - 115 %
Selenium	1.5	5	<20%	85 - 115 %
Silver	0.3	1	<20%	85 - 115 %
Thallium	0.3	1	<20%	85 - 115 %
Zinc	0.9	2.5	<20%	85 - 115 %
<b>Dissolved Metals</b>	<b>µg/l</b>	<b>µg/l</b>		
Antimony	0.8	2.5	<20%	85 - 115 %
Arsenic	0.8	2.5	<20%	85 - 115 %
Beryllium	0.5	1.5	<20%	85 - 115 %
Cadmium	0.65	2	<20%	85 - 115 %
Chromium	0.8	2.5	<20%	85 - 115 %
Copper	0.4	1	<20%	85 - 115 %
Lead	0.3	1	<20%	85 - 115 %
Nickel	0.5	1.5	<20%	85 - 115 %
Selenium	1.5	5	<20%	85 - 115 %
Silver	0.3	1	<20%	85 - 115 %
Thallium	0.3	1	<20%	85 - 115 %
Zinc	0.9	2.5	<20%	85 - 115 %
<b>VOCs</b>				
1,1,1,2-Tetrachloroethane	0.5	2	<20%	75-125%

<b>PARAMETER</b>	<b>MDL (µg/l)</b>	<b>PQL (µg/l)</b>	<b>PRECISION (RPD)</b>	<b>BIAS (% Recovery)</b>
1,1,1-Trichloroethane	1.5	5	<20%	52-162%
1,1,2,2-Tetrachloroethane	1.5	5	<20%	46-157%
1,1,2-Trichloroethane	1.5	5	<20%	52-150%
1,1-Dichloroethane	1.5	5	<20%	59-155%
1,1-Dichloroethene	1.5	5	<20%	5-234%
1,1-Dichloropropene	1.5	5	<20%	75-125%
1,2,3-Trichlorobenzene	1.5	5	<20%	75-125%
1,2,3-Trichloropropane	1.5	5	<20%	80-120%
1,2,4-Trichlorobenzene	1.5	5	<20%	75-125%
1,2,4-Trimethylbenzene	1.5	5	<20%	75-125%
1,2-Dibromo-3- Chloropropane	3	10	<20%	70-130%
1,2-Dichlorobenzene	3	10	<20%	18-190%
1,2-Dichloroethane	1.5	5	<20%	49-155%
1,2-Dichloropropane	1.5	5	<20%	5-210%
1,3,5-Trimethylbenzene	0.5	2	<20%	70-130%
1,3-Dichlorobenzene	3	10	<20%	59-156%
1,3-Dichloropropane	0.5	2	<20%	75-130%
1,4-Dichlorobenzene	3	10	<20%	18-190%
2,2-Dichloropropane	1.5	5	<20%	60-130%
2-Butanone	15	50	<20%	60-140%
2-Chloroethyl Vinyl Ether	3	10	<20%	10-305%
2-Chlorotoluene	3	10	<20%	75-135%
2-Hexanone	6	20	<20%	60-140%
4-Chlorotoluene	3	10	<20%	75-130%
4-Isopropyltoluene	1	3	<20%	75-125%
4-Methyl-2-Pentanone	6	20	<20%	60-140%
Acetone	10	50	<20%	40-160%
Acrolein	30	100	<20%	40-160%
Acrylonitrile	30	100	<20%	65-130%
Benzene	1.5	5	<20%	37-151%
Bromobenzene	1.5	5	<20%	75-130%
Bromochloromethane	1	3	<20%	35-155%

<b>PARAMETER</b>	<b>MDL (µg/l)</b>	<b>PQL (µg/l)</b>	<b>PRECISION (RPD)</b>	<b>BIAS (% Recovery)</b>
Bromodichloromethane	1.5	5	<20%	80-130%
Bromoform	1.5	5	<20%	45-169%
Bromomethane	3	10	<20%	10-242%
Carbon Disulfide	3	10	<20%	60-130%
Carbon Tetrachloride	1.5	5	<20%	70-140%
Chlorobenzene	1.5	5	<20%	37-160%
Chloroethane	3	10	<20%	14-230%
Chloroform	1.5	5	<20%	51-138%
Chloromethane	3	10	<20%	10-273%
Cis-1,2-Dichloroethene	1.5	5	<20%	80-130%
Cis-1,3-Dichloropropene	1.5	5	<20%	5-227%
Dibromochloromethane	1.5	5	<20%	53-149%
Dibromomethane	1.5	5	<20%	80-130%
Dichlorodifluoromethane	3	10	<20%	60-140%
Ethylbenzene	1.5	5	<20%	37-162%
Hexachlorobutadiene	15	50	<20%	50-130%
Iodomethane	1.5	5	<20%	50-150%
Isopropylbenzene	1.5	5	<20%	70-130%
m&p Xylenes	1.5	5	<20%	75-120%
Methylene Chloride	3	10	<20%	10-221%
n-Butylbenzene	1.5	5	<20%	70-130%
n-Propylbenzene	3	10	<20%	70-130%
O-Xylene	1.5	5	<20%	80-125%
sec-Butylbenzene	1.5	5	<20%	70-130%
Styrene	1.5	5	<20%	85-125%
tert-Butyl Methyl Ether	1.5	5	<20%	70-130%
tert-Butylbenzene	1.5	5	<20%	70-125%
Tetrachloroethene	1.5	5	<20%	64-148%
Toluene	1.5	5	<20%	47-150%
Trans 1,2-Dichloroethene	1.5	5	<20%	54-156%
trans-1,3-Dichloropropene	1.5	5	<20%	17-183%
trans-1,4-Dichloro-2 Butene	3	10	<20%	70-130%
Trichloroethene	1.5	5	<20%	71-157%

<b>PARAMETER</b>	<b>MDL (µg/l)</b>	<b>PQL (µg/l)</b>	<b>PRECISION (RPD)</b>	<b>BIAS (% Recovery)</b>
Trichlorofluoromethane	3	10	<20%	17-181%
Trichlorotrifluoroethane	3	10	<20%	60-140%
Vinyl Acetate	1.5	5	<20%	60-140%
Vinyl Chloride	0.5	2	<20%	2-251%
<b>BNA</b>				
1,2-Diphenylhydrazine	1.5	5	<40%	60-140%
2,4,5-Trichlorophenol	1.5	5	<40%	60-140%
2,4,6-Trichlorophenol	1.5	5	<40%	37-144%
2,4-Dichlorophenol	1.5	5	<40%	55-130%
2,4-Dimethylphenol	5	15	<40%	15-130%
2,4-Dinitrophenol	8	25	<40%	25-191%
2,4-Dinitrotoluene	1.5	5	<40%	39-139%
2,6-Dinitrotoluene	1.5	5	<40%	50-158%
2-Chloronaphthalene	2	10	<40%	30-170%
2-Chlorophenol	1.5	5	<40%	23-134%
2-Methylnaphthalene	1.5	5	<40%	40-140%
2-Methylphenol	1.5	5	<40%	50-115%
2-Nitroaniline	1.5	5	<40%	50-115%
2-Nitrophenol	1.5	5	<40%	50-115%
3&4-Methylphenol	1.5	5	<40%	30-125%
3,3'-Dichlorobenzidine	5	25	<40%	30-170%
3-Nitroaniline	15	50	<40%	30-170%
4,6-Dinitro-2-methylphenol	8	25	<40%	25-181%
4-Bromophenyl Phenyl ether	1.5	5	<40%	50-140%
4-chloro-3-methylphenol	3	10	<40%	22-147%
4-Chloroaniline	1.5	5	<40%	30-170%
4-Chlorophenyl methylsulfone	6	20	<40%	30-170%
4-Chlorophenyl Phenyl ether	1.5	5	<40%	50-150%
4-Nitroaniline	15	50	<40%	40-110%
4-Nitrophenol	8	25	<40%	25-132%
Acenaphthene	1.5	5	<40%	40-145%

<b>PARAMETER</b>	<b>MDL (µg/l)</b>	<b>PQL (µg/l)</b>	<b>PRECISION (RPD)</b>	<b>BIAS (% Recovery)</b>
Acenaphthylene	1.5	5	<40%	33-145%
Anthracene	1.5	5	<40%	27-133%
Benzidine	50	200	<40%	30-170%
Benzo (A) Anthracene	1.5	5	<40%	33-143%
Benzo (A) Pyrene	1.5	5	<40%	17-163%
Benzo (B) Fluoranthene	1.5	5	<40%	24-159%
Benzo (g,h,i) Perylene	1.5	5	<40%	5-219%
Benzo (K) Fluoranthene	1.5	5	<40%	11-162%
Benzoic Acid	1.5	5	<40%	5-110%
Benzyl Alcohol	3	10	<40%	24-149%
Bis (2-Chloroethoxy) methane	1.5	5	<40%	33-184%
Bis (2-chloroethyl) ether	1.5	5	<40%	12-158%
Bis (2-Chloroisopropyl) ether	1.5	5	<40%	36-166%
Bis (2-Ethylhexyl) Phthalate	1.5	5	<40%	8-158%
Butyl Benzyl Phthalate	1.5	5	<40%	5-152%
Chrysene	1.5	5	<40%	17-168%
Dibenzo (a,h) Anthracene	1.5	5	<40%	5-227%
Dibenzofuran	1.5	5	<40%	50-130%
Diethyl Phthalate	1.5	5	<40%	5-114%
Dimethyl Phthalate	1.5	5	<40%	5-112%
Di-N-Butyl Phthalate	1.5	5	<40%	60-160%
Di-N-Octyl Phthalate	1.5	5	<40%	5-146%
Fluoranthene	1.5	5	<40%	26-137%
Fluorene	1.5	5	<40%	55-130%
Hexachlorobenzene	1.5	5	<40%	5-152%
Hexachlorocyclopentadiene	3	10	<40%	30-170%
Hexachloroethane	1.5	5	<40%	40-140%
Indeno (1,2,3-CD) Pyrene	1.5	5	<40%	5-171%
Isophorone	1.5	5	<40%	21-196%
Napthalene	3	10	<40%	21-133%
Nitrobenzene	1.5	5	<40%	35-180%
N-Nitrosodimethylamine	1.5	5	<40%	30-170%

PARAMETER	MDL (µg/l)	PQL (µg/l)	PRECISION (RPD)	BIAS (% Recovery)
N-Nitrosodi-N-Propylamine	1.5	5	<40%	5-230%
N-Nitrosodiphenylamine	3	10	<40%	60-140%
Pentachlorophenol	8	25	<40%	25-176%
Phenanthrene	1.5	5	<40%	50-140%
Phenol	1.5	5	<40%	5-112%
Pyrene	1.5	5	<40%	45-135%

### **Instrument/Equipment Testing, Inspection, and Maintenance Requirements; Calibration and Frequency**

Field instruments include a hand-held pH meter, chlorine residual colorimeter instrument, and a probe thermometer. These must be certified against a laboratory method for pH and chlorine and NIST certified thermometer. All field kits must have certified instruments. The temperature, pH, and chlorine certification and calibration must be submitted to ADEC Project Manager by May 31st and again by July 31<sup>st</sup> of each year that the QA/QC plan is valid.

Maintenance of the chlorine residual test kit includes keeping the sample vial rinsed after sample measurement, keeping the vial clean and free of fingerprints and oils, and keeping the colorimeter itself clean. An extra sample vial will be kept with the test kit in case of breakage or scratches to the sample vial. The field kit should be checked against the lab kit twice per season.

The analysis of pH in the field will be used for the official analytical result. A pH meter shall be used that ensures the most accurate reading possible in the expected range of pH values. This meter will be calibrated at a minimum frequency of once per week. The laboratory will supply reference buffers to the sampling team for field verification of the pH meter on each day of use. Buffers used for pH meter verification should span the expected range of sample pH measurements. If pH meter measurements are not within 0.1 pH units of the reference buffer's stated value, the sampler must recalibrate the meter using appropriate standards.

Temperature at or shortly after sample collection will be measured using either a temperature probe or with an independent thermometer readable to an accuracy of 0.1°C. The validity of the temperature probe will be checked early and late in the season against a NIST certified thermometer at a certified laboratory; differences between the temperature probe and the certified thermometer will be documented in the final quality assurance review of the data.

Laboratory instrument and calibration procedures are detailed in the QA Plans and SOPs from the certified laboratories. Copies of these plans will be provided electronically from the lab managers to the Project QA Officer and the ADEC DOW QA Officer.

## **Inspection/Acceptance Requirements for Supplies and Consumables**

Sample bottles will be visually inspected prior to sampling. If problems with bottles are noted, such as a cap that has fallen off an empty bottle, note of the problem will be made on the chain of custody form.

## **Inspection/Acceptance Requirements (Non-Direct Measurements)**

Historical data for this project includes only 10 years of monitoring, so data acceptance criteria will not be required for historical data acceptance.

On-board ship data to be recorded includes tank volume and pumping rate data from ship tracking systems and any documented occurrence of seawater influx. The data will be recorded as reported by shipboard staff in the Graywater and Blackwater Discharge Record Book and through direct observation by the sampling team.

## **Data Management**

Data Management includes accurate field notebook entries, completed Chain-of-Custody forms and laboratory data management documents. Laboratory data management procedures and processes are described in the Laboratory's Quality Management Plan. (This document is kept on file by the ADEC WQA Officer.)

The Lab Project Manager will report data directly to the Coast Guard, the ADEC Project Manager and the individual cruise lines after thorough review by the laboratory QA Manager within the regulatory time limits.

The Lab Project Manager will not be placed in the position of determining whether an analytical result represents a violation of federal or state laws or regulations.

## **ASSESSMENT/OVERSIGHT**

### **Assessments and Response Actions**

#### **Field Assessments**

The Project QA Officer will perform a field sampling audit on a minimum of two randomly selected sampling events during the project in order to evaluate the performance of the sampling team. The Project QA Officer must notify ADEC 36 hours prior to the audit in order to observe if desired. Follow-up field audits may be necessary pending audit findings. The initial field sampling audit will be conducted within 30 days of project initiation, with the second audit occurring midway through the project. Each audit will concentrate on sampling technique, sample handling, field records, field testing methods, and adherence to vessel specific sampling plans and the QAPP. These reports are due within 14 days of the audit. This report will be provided to the Lab Project Manager, ADEC Project Manager and the USCG for evaluation and corrective action, if necessary. The USCG and ADEC may also participate in random onboard field assessments of the sampling effort. The Project QA Officer and Lab Project Manager will be advised in a timely manner of the results of each USCG or ADEC onboard field assessment.

### **Laboratory Assessments**

Laboratories are subject to periodic and extensive audits by regulatory agency personnel as part of their certification. Reports of most recent 3<sup>rd</sup> party laboratory technical systems audits and EPA Drinking Water Blind Performance audits demonstrating competence in the respective methods will be made available to the ADEC Project Manager, ADEC Water Quality Assurance Officer, and the Project QA Officer prior to analysis of samples. The Project QA Officer will review any recent and pertinent technical systems audit reports of the analytical laboratories involved in this project.

The Project QA officer will use technical system audit report findings and recommendations to design an on-site technical systems audit of the project laboratories (in consultation with and support from technical experts at ADEC). The technical systems audit must be performed within the first 30 days of project initiation so any recommended enhancements to laboratory operations can be implemented early on in the project. The Project QA Officer must notify the ADEC Project manager within 36 hours of the audit date to give the ADEC the opportunity to observe if desired. The ADEC may perform additional lab audits of the commercial passenger vessel samples.

Based upon review of past lab audits, the Project QA Officer may recommend that a technical systems audit is not warranted. If the ADEC Project Manager disagrees, the technical audit must be performed.

The ADEC Project Manager and ADEC Water Quality Assurance Officer will be notified in advance and invited to participate in any audit, and a report of these findings will be presented to the ADEC Project Manager and the Lab Project Manager. Any deficiencies noted by the auditor will be corrected immediately, and the Lab Manager will note these changes in a corrective action report to the Project QA Officer and ADEC Project Manager. The Project QA Officer will also perform a technical systems audit on two sampling events in order to evaluate laboratory log-in, sample handling, preservation, and storage procedures.

Laboratories performing testing under this program must also participate in a DMR-QA (Discharge Monitoring Report Quality Assurance) performance sample study once annually with results sent directly to the Project QA Officer and the ADEC Water Quality Assurance Officer for all wastewater parameters (chemistry and microbiology) analyzed under this program.

### **Precision**

Blind sample duplicates will be collected on a minimum of 10% of the total number of samples collected for the project. All will be analyzed for conventional pollutants and priority pollutants. The purpose of the blind sample duplicates is to assess sampling and laboratory error and to assess overall method variability. Precision between the sample and its duplicate will be determined by calculating the relative percent difference between the two samples, in the same way that precision is measured between two laboratory-fortified blanks or a matrix spike/matrix spike duplicate. The use of duplicate samples extends the test of precision to the sampling method itself. The use of blind samples provides a test of the laboratory and is used to assess bias or analytical errors not detected by the laboratory (e.g., a false positive). Every effort will be made to ensure that the labeling of the samples does not disclose the duplicate nature of the samples to the laboratory. The samples will be analyzed by the same lab and for the same parameters. Duplicate samples will be evaluated as individual precision pairs, and overall measurement precision will be evaluated for each parameter for the monitoring season as an aggregate of

the pair analyses. Results of the duplicate analysis will be monitored by the Project QA Officer and submitted to the ADEC Project Manager.

In addition, the ADEC QA Officer may conduct a laboratory performance audit. The ADEC may submit a sample that contains a known concentration of analytes prepared and certified by a different laboratory. The ADEC will compare the results from the lab from the certified sample results to determine the laboratory performance. ADEC funds pay for this performance audit.

The ADEC may also submit two trip blank samples over the course of the sampling season. The trip blanks check to see if any outside contamination occurs during the sampling and analyzing process. ADEC funds pay for this trip blank analysis.

### **Corrective Action**

The laboratory or sampling manager will notify the Project QA Officer and ADEC project manager within 7 days, if errors are noted by the laboratory or sampling personnel. The Project QA Officer will then notify the Lab Project Manager and the party responsible for the error of the deficiency, and will recommend methods of correcting the deficiency. The responsible party will then immediately correct the problem and will send those corrections via email to the Project QA Officer, the Lab Project Manager, and ADEC Project Manager. The Project QA Officer will conduct a follow-up assessment to ensure recommended corrective actions are routinely being followed.

### **Reports to Management**

The Project QA Officer will issue audit reports in accordance with the following guidelines:

- Field sampling audits--Verbal on-site debriefing of audit findings to sampling personnel. Draft field audit report issued to sampling personnel and Lab Project Manager within one week of audit. Final audit report to Lab Project Manager and ADEC Project Manager within 2 weeks of end of audit. The Lab Project Manager will forward all corrective action reports to the ADEC Project Manager when completed.
- Technical laboratory audit—Verbal on-site debriefing of audit findings to laboratory personnel, and Lab Project Manager. Draft technical systems audit report to Lab Project Manager and ADEC Project Manager within 1-2 weeks of end audit (depending upon depth and extent of audit). Final technical systems audit report to Lab Project Manager and ADEC Project Manager within 2 – 4 weeks of end of audit (depending upon depth and extent of audit). Lab Project Manager will forward all corrective action reports to the ADEC Project Manager when completed.
- Blind duplicate samples—Draft report findings within one week of receiving/verifying results to Laboratory QA officer, Project Manager, and ADEC Project Manager.

At project conclusion, the Project QA Officer will issue an overall Quality Assurance Project Report to the USCG, ADEC Project Manager and ADEC Water Quality Assurance Officer, and vessel representatives detailing findings, problems and resolutions, data reliability and recommended enhancements for future monitoring projects, etc.

The ADEC Project Manager will submit the results of the any QA/QC audit reports to the Lab Project Manager and Laboratory Manager.

## **DATA VALIDATION AND USABILITY**

### **Data Review, Verification, and Validation**

During the project, the Project QA Officer will review at least 20% of field notes and laboratory data packages to detect correctable problems for the remainder of the study. The first data review must be submitted by June 15 of each year in order to correct any system problems early in the season. The other data reviews must be equally spaced throughout the season. Upon receipt of these completed data packages from the Project Manager, the Project Quality Assurance Officer will review data and field notes to verify that this QAPP was followed. Items reviewed will include:

- Comparison of dated vessel specific sampling plans with the QAPP to assure that the correct samples were taken.
- Comparison of dated sampling plans with field notes and custody forms to assure that planned samples were collected.
- Review of field notes and data to assure that information specified in the QAPP has been recorded.
- Review of laboratory data packets, particularly the QA/QC laboratory sheets.

Any problems noted will be immediately brought to the attention of the Lab Project Manager who will take appropriate corrective action as necessary. The ADEC Project Manager will also be notified. This data review must be completed and submitted to the ADEC within 40 days of the sampling event. Any review made outside the date will not be accepted.

### **Reconciliation with Data Quality Objectives**

The Project QA Officer will reconcile the data from this project with the Measurement Quality Objectives defined in this document following the validation and verification methods stated above. If an overall assessment of these elements cannot ensure that the data are of sufficient quality to meet objectives, then additional evaluation of raw data will be performed.

## BIBLIOGRAPHY

Documents referenced during the preparation of this document include:

1. April 13 *Alaska Cruise Ship Initiative Wastewater Work Group Protocol for Voluntary Wastewater Monitoring Program in 2001*.
2. *NWCA Cruise Ship Wastewater Monitoring 2009 Quality Assurance Project Plan*, January 23, 2009.
3. *EPA Requirements for QA Project Plans (QA/R-5)*, EPA/240/B-01/003 March 2001.
4. US Code of Federal Regulations; including 33 CFR 159 and 40 CFR 136.
5. *Water Quality Standards Handbook, Second Edition*, EPA-823-B-94-005a, August 1994.
6. *Compilation of the U.S. Environmental Protection Agency's Water Quality Criteria for the Priority Toxic Pollutants*, ADEC, September 1997.
7. *Methods for Chemical Analysis of Water and Wastes*, Environmental Protection Agency, Environmental Monitoring Systems Laboratory - Cincinnati (EMSL-CI), EPA-600/4-79-020, Revised March 1983 and 1979 where applicable. <http://www.epa.gov/cgi-bin/claritgw?op=Display&document=clserv:ORD:0167;&rank=4&template=epa>
8. *Standard Methods for the Analysis of Water and Wastewater*, 19<sup>th</sup> or 20<sup>th</sup> Edition, APHA/AWWA/WEF.
9. *EPA Test Methods for Evaluating Solid Wastes. Physical/Chemical Methods (SW-846)*. 3<sup>rd</sup> Edition Update 2B, January 1995.
10. *Manual for the Certification of Laboratories Analyzing Drinking Water*, 5<sup>th</sup> Edition EPA-815-R-05-004, January 2005.
11. *State of Alaska Department of Environmental Conservation Large Commercial Passenger Vessel Wastewater Discharge General Permit No. 2009DB0026*, State of Alaska Department of Environmental Conservation, 2010.

## Appendix A - Alaska Cruise Ship Sampling Checklist for All Sampling Events (USCG/ADEC)

Vessel Name \_\_\_\_\_

Sampler Name \_\_\_\_\_

Date \_\_\_\_\_

### I. Notification

- ADEC project manager notified 36 hours prior to the sampling event

### II. Type of Sampling

- Conventional pollutants only (unannounced)
- Conventional and priority pollutants. (unannounced)
  - If second unannounced sample, must be at least 21 days after the first sampling event.
- USCG Continuous Compliance Parameters
  - If second continuous compliance sample for month, must be at least 24 hours after first sample.
  - USCG Continuous Compliance Parameters
- ADEC General Permit Parameters
- Other (Example Re-sampling after exceedance of discharge limitations under 18 AAC 69.070 or 33 CFR 159)

### III. Sampling Notes (to include:)

- Vessel name
- Names of sampling personnel
- Names of shipboard assistants
- Signature or initials by the vessel crew in the field notes indicating that the sample port is correct
- Sample ID clearly stating where the sample was taken
- Sample date and times recorded on COC
- Field measurements: pH, chlorine residual, and temp recorded on COC
- Records collected on discharge flow rates (always) and holding tank volumes (only for underway sampling)
- Sample ports within 50 feet of the point of overboard discharge
- Nature of sample recorded (composite or grab)
- Waste type recorded (blackwater, graywater, or mixed)
- If deviations from VSSP and/or QAPP noted, reported to ADEC/USCG
- If unannounced sampling, sampler verified that vessel is discharging
- Latitude/longitude and speed at time of discharge being sampled is recorded (only for underway sampling),
- Copy of the Discharge record for the sampled discharge included (unannounced only)
- Chain of custody properly completed
- Samples delivered to laboratory within holding times for analyses

## Appendix B - Alaska Cruise Ship Data Review Checklist

Vessel Name \_\_\_\_\_

Date \_\_\_\_\_

Location \_\_\_\_\_

Sampling Team \_\_\_\_\_

Laboratory \_\_\_\_\_

### Sample Type:

- Continued Compliance
- ADEC General Permit
- Random Unannounced

### Final Report Package Includes:

- Sampling event summary sheet
- Analytical Report
  - Ship name
  - Sample ID's
  - Sample date and time collected
  - Parameter names and method references
  - Analytical results
  - Method Detection Limits (MDL's)
  - Practical Quantitation Limits (PQL's/reporting limits)
  - Date and time of sample preparation
  - Date and time of analysis
  - Verification that holding times were met
  - Quality control information: blank results, spiked blank of laboratory control standard recovery, matrix spike/spike duplicate recoveries, relative percent differences between duplicate spike analyses
  - Case narrative describing deviations from methods, procedural problems with sample analysis, explanation of data abnormalities, and any additional information that is necessary for describing the sample. This narrative should explain when results are outside the precision and accuracy limits and the corrective actions taken to rectify QC problems.
- Chain of custody form
- Cooler receipt forms with temperature indicated
- Discharge logs covering time of sampling. (For recirculated samples, provide discharge logs back to the time of last discharge)
- Field notes.
- Latitude and longitude information pertaining to each sample including which overboard port the waste was discharged through and the speed the vessel was traveling (*unannounced samples only*)
- Completed sampling checklist
- Completed data review checklist

## Appendix C - 40 CFR 136 Applicable List of Approved Biological Methods for Wastewater

Parameter and units	Method <sup>1</sup>	EPA	Standard methods 18th, 19th, 20th ed.	Standard methods online	AOAC, ASTM, USGS	Other
Bacteria:						
1. Coliform (fecal), number per 100 mL or number per gram dry weight	Most Probable Number (MPN), <sup>5</sup> tube 3 dilution, or	p. 132 <sup>3</sup> 1680 <sup>12,14</sup>  1681 <sup>12,19</sup>				
	Membrane filter (MF) <sup>2</sup> , single step	p. 124 <sup>3</sup>	9221 C E  9222 D	9221 C E-99  9222 D-97		B-0050-85 <sup>5</sup>

<sup>2</sup>A 0.45 µm membrane filter (MF) or other pore size certified by the manufacturer to fully retain organisms to be cultivated and to be free of extractables which could interfere with their growth.

<sup>3</sup>USEPA. 1978. Microbiological Methods for Monitoring the Environment, Water, and Wastes. Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, OH, EPA/600/8-78/017.

<sup>5</sup>USGS. 1989. U.S. Geological Survey Techniques of Water-Resource Investigations, Book 5, Laboratory Analysis, Chapter A4, Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples, U.S. Geological Survey, U.S. Department of the Interior, Reston, VA.

<sup>12</sup>Recommended for enumeration of target organism in sewage sludge.

<sup>14</sup>USEPA. July 2006. Method 1680: Fecal Coliforms in Sewage Sludge (Biosolids) by Multiple-Tube Fermentation Using Lauryl-Tryptose Broth (LTB) and EC Medium. US Environmental Protection Agency, Office of Water, Washington, DC EPA-821-R-06-012.

<sup>19</sup>USEPA. July 2006. Method 1681: Fecal Coliforms in Sewage Sludge (Biosolids) by Multiple-Tube Fermentation using A-1 Medium. U.S. Environmental Protection Agency, Office of Water, Washington, DC EPA-821-R-06-013.

## Appendix D— 40 CFR 136 Applicable List of Approved Inorganic Test Procedures

Parameter	Methodology <sup>58</sup>	EPA <sup>35,52</sup>	Standard methods (18th, 19th)	Standard methods (20th)	Standard methods online	ASTM	USGS/AOAC /other
Alkalinity, as CaCO <sub>3</sub> , mg/L	Electrometric or Colorimetric titration to pH 4.5, manual, or		2320 B	2320 B	2320 B-97	D1067-92, 02	973.43 <sup>3</sup> , I-1030-85 <sup>2</sup>
	automatic	310.2 (Rev. 1974) <sup>1</sup>					I-2030-85 <sup>2</sup>
Ammonia (as N), mg/L	Manual, distillation (at pH 9.5) <sup>6</sup> followed by:	350.1, Rev. 2.0 (1993)	4500-NH B3	4500-NH3 B	4500-NH3 B-97		973.493
	Nesslerization		4500-NH3 C (18th only)			D1426-98, 03 (A)	973.49 <sup>3</sup> , I-3520-85 <sup>2</sup>
	Titration		4500-NH3 C (19th) and 4500-NH3 E (18th)	4500-NH3 C	4500-NH3 C-97		
	Electrode		4500-NH3 D or E (19th) and 4500-NH3 F or G (18th)	4500-NH3 D or E	4500-NH3 D or E-97	D1426-98, 03 (B)	
	Automated phenate, or	350.1 <sup>60</sup> , Rev. 2.0 (1993)	4500-NH3 G (19th) and 4500-NH3 H (18th)	4500-NH3 G	4500-NH3 G-97		I-4523-85 <sup>2</sup>
	Automated electrode						See footnote 7
	Ion Chromatography					D6919-03	
Antimony— Total, <sup>4</sup> mg/L	Digestion <sup>4</sup> followed by:						
	AA direct aspiration <sup>36</sup>		3111 B		3111 B-99		
	AA furnace		3113 B		3113 B-99		
	STGFAA	200.9, Rev. 2.2 (1994)					
	ICP/AES <sup>36</sup>	200.7, Rev. 4.4 (1994)	3120 B	3120 B	3120 B-99		
	ICP/MS	200.8, Rev. 5.4 (1994)				D5673-03	993.143

Parameter	Methodology <sup>58</sup>	EPA <sup>35,52</sup>	Standard methods (18th, 19th)	Standard methods (20th)	Standard methods online	ASTM	USGS/AOAC /other
Arsenic— Total, <sup>4</sup> mg/L	Digestion <sup>4</sup> followed by	206.5 (Issued 1978) <sup>1</sup>					
	AA gaseous hydride		3114 B 4.d		3114 B 4.d-97	D2972 -97, 03 (B)	I-3062-85 <sup>2</sup>
	AA furnace		3113 B		3113 B-99	D2972 -97, 03 (C)	I-4063-98 <sup>49</sup>
	STGFAA	200.9, Rev. 2.2 (1994)					
	ICP/AES <sup>36</sup>	200.7, Rev. 4.4 (1994)	3120 B	3120 B	3120 B-99		
	ICP/MS	200.8, Rev. 5.4 (1994)				D5673 -03	993.143
	Colorimetric (SDDC)		3500-As C	3500-As B	3500-As B-97	D2972 -97, 03 (A)	I-3060-85
Beryllium— Total, <sup>4</sup> mg/L	Digestion <sup>4</sup> followed by:						
	AA direct aspiration		3111 D		3111 D-99	D3645 -93 (88), 03 (A)	I-3095-85 <sup>2</sup>
	AA furnace		3113 B		3113 B-99	D3645 -93 (88), 03 (B)	
	STGFAA	200.9, Rev. 2.2 (1994)					
	ICP/AES	200.7, Rev. 4.4 (1994)	3120 B	3120 B	3120 B-99		I-4471-97 <sup>50</sup>
	ICP/MS	200.8, Rev. 5.4 (1994)				D5673 -03	993.143
	DCP, or					D4190 -94, 99	See footnote <sup>34</sup>
	Colorimetric (aluminon)			3500-Be D			
Biochemical oxygen demand (BOD <sub>5</sub> ), mg/L	Dissolved Oxygen Depletion		5210 B	5210 B	5210 B-01		973.44, <sup>3</sup> p. 17, <sup>9</sup> I-1578-78 <sup>8</sup>
Cadmium— Total, <sup>4</sup> mg/L	Digestion <sup>4</sup> followed by:						

Parameter	Methodology <sup>58</sup>	EPA <sup>35,52</sup>	Standard methods (18th, 19th)	Standard methods (20th)	Standard methods online	ASTM	USGS/AOAC /other
	AA direct aspiration <sup>36</sup>		3111 B or C		3111 B or C-99	D3557-95, 02 (A or B)	974.27, <sup>3</sup> p. 37, <sup>9</sup> I-3135-85 <sup>2</sup> or I-3136-85 <sup>2</sup>
	AA furnace		3113 B		3113 B-99	D3557-95, 02 (D)	I-4138-89 <sup>51</sup>
	STGFAA	200.9, Rev. 2.2 (1994)					
	ICP/AES <sup>36</sup>	200.7, Rev. 4.4 (1994)	3120 B	3120 B	3120 B-99		I-1472-85 <sup>2</sup> or I-4471-97 <sup>50</sup>
	ICP/MS	200.8, Rev. 5.4 (1994)				D5673-03	993.143
	DCP <sup>36</sup>					D4190-94, 99	See footnote <sup>34</sup>
	Voltametry <sup>11</sup> , or					D3557-95, 02 (C)	
	Colorimetric (Dithizone)		3500-Cd D				
Chemical oxygen demand (COD), mg/L	Titrimetric	410.3 (Rev. 1978) <sup>1</sup>	5220 C	5220 C	5220 C-97	D1252-95, 00 (A)	973.46 <sup>3</sup> , p. 17 <sup>9</sup> I-3560-85 <sup>2</sup>
	Spectrophotometric, manual or automatic	410.4, Rev. 2.0 (1993)	5220 D	5220 D	5220 D-97	D1252-95, 00 (B)	See footnotes <sup>13, 14</sup> . I-3561-85 <sup>2</sup>
Chlorine— Total residual, mg/L; Titrimetric	Amperometric direct, or		4500-Cl D	4500-Cl D	4500-Cl D-00	D1253-86 (96), 03	
	Amperometric direct (low level)		4500-Cl E	4500-Cl E	4500-Cl E-00		
	Iodometric direct		4500-Cl B	4500-Cl B	4500-Cl B-00		
	Back titration ether end-point <sup>15</sup> or		4500-Cl C	4500-Cl C	4500-Cl C-00		
	DPD-FAS		4500-Cl F	4500-Cl F	4500-Cl F-00		
	Spectrophotometric, DPD or		4500-Cl G	4500-Cl G	4500-Cl G-00		
	Electrode						See footnote <sup>16</sup>

Parameter	Methodology <sup>58</sup>	EPA <sup>35,52</sup>	Standard methods (18th, 19th)	Standard methods (20th)	Standard methods online	ASTM	USGS/AOAC /other	
Chromium— Total, <sup>4</sup> mg/L	Digestion <sup>4</sup> followed by:							
	AA direct aspiration <sup>36</sup>		3111 B		3111 B-99	D1687-92, 02 (B)	974.27 <sup>3</sup> , I-3236-85 <sup>2</sup>	
	AA chelation-extraction		3111 C		3111 C-99			
	AA furnace		3113 B		3113 B-99	D1687-92, 02 (C)	I-3233-93 <sup>46</sup>	
	STGFAA	200.9, Rev. 2.2 (1994)						
	ICP/AES <sup>36</sup>	200.7, Rev. 4.4 (1994)	3120 B	3120 B	3120 B-99			
	ICP/MS	200.8, Rev. 5.4 (1994)				D5673-03	993.143	
	DCP, <sup>36</sup> or					D4190-94, 99	See footnote <sup>34</sup>	
	Colorimetric (Diphenyl-carbazide)			3500-Cr D	3500-Cr B	3500-Cr B-01		
	Copper— Total, <sup>4</sup> mg/L	Digestion <sup>4</sup> followed by:						
AA direct aspiration <sup>36</sup>			3111 B or C		3111 B or C-99	D1688-95, 02 (A or B)	974.27 <sup>3</sup> p. 37 <sup>9</sup> I-3270-85 <sup>2</sup> or I-3271-85 <sup>2</sup>	
AA furnace			3113 B		3113 B-99	D1688-95, 02 (C)	I-4274-89 <sup>51</sup>	
STGFAA		200.9, Rev. 2.2 (1994)						
ICP/AES <sup>36</sup>		200.7, Rev. 4.4 (1994)	3120 B	3120 B	3120 B-99		I-4471-97 <sup>50</sup>	
ICP/MS		200.8, Rev. 5.4 (1994)				D5673-03	993.143	
DCP <sup>36</sup> or						D4190-94, 99	See footnote <sup>34</sup>	
Colorimetric (Neocuproine) or				3500-Cu D	3500-Cu B	3500-Cu B-99		
(Bicinchoninate)				3500-Cu E	3500-Cu C	3500-Cu C-99		See footnote <sup>19</sup>

Parameter	Methodology <sup>58</sup>	EPA <sup>35,52</sup>	Standard methods (18th, 19th)	Standard methods (20th)	Standard methods online	ASTM	USGS/AOAC /other
Hydrogen ion (pH), pH units	Electrometric measurement or		4500-H <sup>+</sup> B	4500-H <sup>+</sup> B	4500-H <sup>+</sup> B-00	D1293-84 (90), 99 (A or B)	973.41. <sup>3</sup> , I-1586-85 <sup>2</sup>
	Automated electrode	150.2 (Dec. 1982) <sup>1</sup>					See footnote <sup>21</sup> , I-2587-85 <sup>2</sup>
Kjeldahl Nitrogen <sup>5</sup> — Total, (as N), mg/L	Digestion and distillation followed by. <sup>20</sup>		4500-Norg B or C and 4500-NH3 B	4500-Norg B or C and 4500-NH3 B	4500-Norg B or C-97 and 4500-NH3 B-97	D3590-89, 02 (A)	
	Titration or		4500-NH3 C (19th) and 4500-NH3 E (18th)	4500-NH3 C	4500-NH3 C-97	D3590-89, 02 (A)	973.483
	Nesslerization or		4500-NH3 C (18th Only)			D3590-89, 02 (A)	
	Electrode		4500-NH3 F or G (18th) and 4500-NH3 D or E (19th)	4500-NH3 D or E	4500-NH3 D or E-97		
	Automated phenate colorimetric	351.1 (Rev. 1978) <sup>1</sup>					I-4551-78 <sup>8</sup>
Semi-automated block digester colorimetric	Manual or block digester potentiometric	351.2, Rev. 2.0 (1993)				D3590-89, 02 (B)	I-4515-91 <sup>45</sup>
	Block digester, followed by Auto distillation and Titration, or					D3590-89, 02 (A)	
	Nesslerization, or						See footnote <sup>39</sup>
	Flow injection gas diffusion						See footnote <sup>40</sup>
Lead— Total, <sup>4</sup> mg/L	Digestion <sup>4</sup> followed by:						See footnote <sup>41</sup>
	AA direct aspiration <sup>36</sup>		3111 B or C		3111 B or C-99	D3559-96, 03 (A or B)	974.27 <sup>3</sup> , I-3399-85 <sup>2</sup>
	AA furnace		3113 B		3113 B-99	D3559-96, 03 (D)	I-4403-89 <sup>51</sup>
	STGFAA	200.9, Rev. 2.2 (1994)					

Parameter	Methodology <sup>58</sup>	EPA <sup>35,52</sup>	Standard methods (18th, 19th)	Standard methods (20th)	Standard methods online	ASTM	USGS/AOAC /other
	ICP/AES <sup>36</sup>	200.7, Rev. 4.4 (1994)	3120 B	3120 B	3120 B-99		I-4471-97 <sup>50</sup>
	ICP/MS	200.8, Rev. 5.4 (1994)				D5673-03	993.143
	DCP <sup>36</sup>					D4190-94, 99	See footnote <sup>34</sup>
	Voltametry <sup>11</sup> or					D3559-96, 03 (C)	
	Colorimetric (Dithizone)		3500-Pb D	3500-Pb B	3500-Pb B-97		
Mercury— Total <sup>4</sup> , mg/L	Cold vapor, manual or	245.1, Rev. 3.0 (1994)	3112 B		3112 B-99	D3223-97, 02	977.22 <sup>3</sup> , I-3462-85 <sup>2</sup>
	Automated	245.2 (Issued 1974)					
	Cold vapor atomic fluorescence spectrometry (CVAFS)	245.7 Rev. 2.0 (2005) <sup>59</sup>					
	Purge and Trap CVAFS	1631E <sup>43</sup>					
Nickel— Total <sup>4</sup> , mg/L	Digestion <sup>4</sup> followed by:						
	AA direct aspiration <sup>36</sup>		3111 B or C		3111 B or C-99	D1886-90, 94 (98) (A or B)	I-3499-85 <sup>2</sup>
	AA furnace		3113 B		3113 B-99	D1886-90, 94 (98) (C)	I-4503-89 <sup>51</sup>
	STGFAA	200.9, Rev. 2.2 (1994)					
	ICP/AES <sup>36</sup>	200.7, Rev. 4.4 (1994)	3120 B	3120 B	3120 B-99		I-4471-97 <sup>50</sup>
	ICP/MS	200.8, Rev. 5.4 (1994)				D5673-03	993.143
	DCP <sup>36</sup> , or					D4190-94, 99	See footnote <sup>34</sup>

Parameter	Methodology <sup>58</sup>	EPA <sup>35,52</sup>	Standard methods (18th, 19th)	Standard methods (20th)	Standard methods online	ASTM	USGS/AOAC /other
	Colorimetric (heptoxime)		3500–Ni D (17th Edition)				
Nitrate-nitrite (as N), mg/L	Cadmium reduction, manual or		4500–NO <sub>3</sub> <sup>–</sup> E	4500–NO <sub>3</sub> <sup>–</sup> E	4500–NO <sub>3</sub> <sup>–</sup> E–00	D3867 – 99(B)	
	Automated, or	353.2, Rev. 2.0 (1993)	4500–NO <sub>3</sub> <sup>–</sup> F	4500–NO <sub>3</sub> <sup>–</sup> F	4500–NO <sub>3</sub> <sup>–</sup> F–00	D3867 – 99(A)	I–4545–85 <sup>2</sup>
	Automated hydrazine		4500–NO <sub>3</sub> <sup>–</sup> H	4500–NO <sub>3</sub> <sup>–</sup> H	4500–NO <sub>3</sub> <sup>–</sup> H–00		
	Ion Chromatography	300.0, Rev 2.1 (1993) and 300.1, Rev 1.0 (1997)	4110 B	4110 B	4110 B–00	D4327 –97	993.303
	CIE/UV						D6508, Rev. 2 <sup>54</sup>
Oil and grease— Total recoverable, mg/L	Hexane extractable material (HEM): n–Hexane extraction and gravimetry	1664A <sup>42</sup>		5520 B <sup>38</sup>	5520 B–01 <sup>38</sup>		
	Silica gel treated HEM (SGT–HEM): Silica gel treatment and gravimetry.	1664A <sup>42</sup>					
Organic carbon— Total (TOC), mg/L	Combustion or oxidation		5310 B, C, or D	5310 B, C, or D	5310 B, C, or D–00	D2579 –93 (A or B)	973.47, <sup>3</sup> p. 14 <sup>24</sup>
Phosphorus —Total, mg/L	Persulfate digestion followed by: <sup>20</sup>		4500–P B.5	4500–P B.5			973.553
	Manual or	365.3 <sup>1</sup> (Is sued 1978)	4500–P E	4500–P E		D515–88(A)	
	Automated ascorbic acid reduction	365.1 Rev. 2.0 (1993)	4500–P F	4500–P F			973.56 <sup>3</sup> , I–4600–85 <sup>2</sup>
	Semi–automated block digester	365.4 <sup>1</sup> (Is sued 1974)				D515–88(B)	I–4610–91 <sup>48</sup>
Residue— non–filterable (TSS), mg/L	Gravimetric, 103–105 °C post washing of residue		2540 D	2540 D	2540 D–97		I–3765–85 <sup>2</sup>

Parameter	Methodology <sup>58</sup>	EPA <sup>35,52</sup>	Standard methods (18th, 19th)	Standard methods (20th)	Standard methods online	ASTM	USGS/AOAC /other
Residue— settleable, mg/L	Volumetric, (Imhoff cone), or gravimetric		2540 F	2540 F	2540 F-97		
Selenium— Total, <sup>4</sup> mg/L	Digestion <sup>4</sup> followed by:						
	AA furnace		3113 B		3113 B-99	D3859-98, 03 (B)	I-4668-98 <sup>49</sup>
	STGFAA	200.9, Rev. 2.2 (1994)					
	ICP/AES <sup>36</sup>	200.7, Rev. 4.4 (1994)	3120 B	3120 B	3120 B-99		
	ICP/MS	200.8, Rev. 5.4 (1994)				D5673-03	993.143
	AA gaseous hydride		3114 B		3114 B-97	D3859-98, 03 (A)	I-3667-85 <sup>2</sup>
Silver— Total, <sup>4</sup> , <sup>31</sup> mg/L	Digestion <sup>4</sup> , <sup>29</sup> followed by:						
	AA direct aspiration		3111 B or C		3111 B or C-99		974.27 <sup>3</sup> , p. 37 <sup>9</sup> , I-3720-85 <sup>2</sup>
	AA furnace		3113 B		3113 B-99		I-4724-89 <sup>51</sup>
	STGFAA	200.9, Rev. 2.2 (1994)					
	ICP/AES	200.7, Rev. 4.4 (1994)	3120 B	3120 B	3120 B-99		I-4471-97 <sup>50</sup>
	ICP/MS	200.8, Rev. 5.4 (1994)				D5673-03	993.143
	DCP						See footnote <sup>34</sup>
Specific conductance, micromhos/cm at 25 °C	Wheatstone bridge	120.1 <sup>1</sup> (Rev. 1982)	2510 B	2510 B	2510 B-97	D1125-95 (99) (A)	973.40 <sup>3</sup> , I-2781-85 <sup>2</sup>
Temperature, °C	Thermometric		2550 B	2550 B	2550 B-00		See footnote <sup>32</sup>
Zinc –Total <sup>4</sup> , mg/L	Digestion <sup>4</sup> followed by:						
	AA direct aspiration <sup>36</sup>		3111 B or C		3111 B or C-99	D1691-95, 02 (A or B)	974.27 <sup>3</sup> , p. 37 <sup>9</sup> , I-3900-85 <sup>2</sup>

Parameter	Methodology <sup>58</sup>	EPA <sup>35,52</sup>	Standard methods (18th, 19th)	Standard methods (20th)	Standard methods online	ASTM	USGS/AOAC /other
	AA furnace	289.2 <sup>1</sup> (Issued 1978)					
	ICP/AES <sup>36</sup>	200.7, Rev. 4.4 (1994)	3120 B	3120 B	3120 B-99 <sup>59</sup>		I-4471-97 <sup>50</sup>
	ICP/MS	200.8, Rev. 5.4 (1994)				D5673-03	993.143
	DCP, <sup>36</sup> or					D4190-94, 99	See footnote <sup>34</sup>
	Colorimetric (Dithizone) or		3500-Zn E				
	(Zincon)		3500-Zn F	3500-Zn B	3500-Zn B-97		See footnote <sup>33</sup>

<sup>1</sup>“Methods for Chemical Analysis of Water and Wastes,” Environmental Protection Agency, Environmental Monitoring Systems Laboratory–Cincinnati (EMSL–CI), EPA–600/4–79–020 (NTIS PB 84–128677), Revised March 1983 and 1979 where applicable.

<sup>2</sup>Fishman, M. J., *et al.* “Methods for Analysis of Inorganic Substances in Water and Fluvial Sediments,” U.S. Department of the Interior, Techniques of Water-Resource Investigations of the U.S. Geological Survey, Denver, CO, Revised 1989, unless otherwise stated.

<sup>3</sup>“Official Methods of Analysis of the Association of Official Analytical Chemists,” Methods Manual, Sixteenth Edition, 4th Revision, 1998.

<sup>4</sup>For the determination of total metals (which are equivalent to total recoverable metals) the sample is not filtered before processing. A digestion procedure is required to solubilize analytes in suspended material and to break down organic-metal complexes (to convert the analyte to a detectable form for colorimetric analysis). For non–platform graphite furnace atomic absorption determinations a digestion using nitric acid (as specified in Section 4.1.3 of Methods for the Chemical Analysis of Water and Wastes) is required prior to analysis. The procedure used should subject the sample to gentle, acid refluxing and at no time should the sample be taken to dryness. For direct aspiration flame atomic absorption determinations (FLAA) a combination acid (nitric and hydrochloric acids) digestion is preferred prior to analysis. The approved total recoverable digestion is described as Method 200.2 in Supplement I of “Methods for the Determination of Metals in Environmental Samples” EPA/600R–94/111, May, 1994, and is reproduced in EPA Methods 200.7, 200.8, and 200.9 from the same Supplement. However, when using the gaseous hydride technique or for the determination of certain elements such as antimony, arsenic, selenium, silver, and tin by non–EPA graphite furnace atomic absorption methods, mercury by cold vapor atomic absorption, the noble metals and titanium by FLAA, a specific or modified sample digestion procedure may be required and in all cases the referenced method write–up should be consulted for specific instruction and/or cautions. For analyses using inductively coupled plasma-atomic emission spectrometry (ICP–AES), the direct current plasma (DCP) technique or the EPA spectrochemical techniques (platform furnace AA, ICP–AES, and ICP–MS) use EPA Method 200.2 or an approved alternate procedure (e.g., CEM microwave digestion, which may be used with certain analytes as indicated in Table IB); the total recoverable digestion procedures in EPA Methods 200.7, 200.8, and 200.9 may be used for those respective methods. Regardless of the digestion procedure, the results of the analysis after digestion procedure are reported as “total” metals.

<sup>5</sup>Copper sulfate may be used in place of mercuric sulfate.

<sup>6</sup>Manual distillation is not required if comparability data on representative effluent samples are on file to show that this preliminary distillation step is not necessary: however, manual distillation will be required to resolve any controversies.

<sup>7</sup>Ammonia, Automated Electrode Method, Industrial Method Number 379–75 WE, dated February 19, 1976, Bran & Luebbe (Technicon) Auto Analyzer II, Bran & Luebbe Analyzing Technologies, Inc., Elmsford, NY 10523.

<sup>8</sup>The approved method is that cited in “Methods for Determination of Inorganic Substances in Water and Fluvial Sediments”, USGS TWRI, Book 5, Chapter A1 (1979).

<sup>9</sup>American National Standard on Photographic Processing Effluents, April 2, 1975. Available from ANSI, 25 West 43rd st., New York, NY 10036.

<sup>10</sup>“Selected Analytical Methods Approved and Cited by the United States Environmental Protection Agency,” Supplement to the Fifteenth Edition of *Standard Methods for the Examination of Water and Wastewater* (1981).

<sup>11</sup>The use of normal and differential pulse voltage ramps to increase sensitivity and resolution is acceptable.

<sup>12</sup>Carbonaceous biochemical oxygen demand (CBOD<sub>5</sub>) must not be confused with the traditional BOD<sub>5</sub> test method which measures “total BOD.” The addition of the nitrification inhibitor is not a procedural option, but must be included to report the CBOD<sub>5</sub> parameter. A discharger whose permit requires reporting the traditional BOD<sub>5</sub> may not use a nitrification inhibitor in the procedure for reporting the results. Only when a discharger's permit specifically states CBOD<sub>5</sub> is required can the permittee report data using a nitrification inhibitor.

<sup>13</sup>OIC Chemical Oxygen Demand Method, Oceanography International Corporation, 1978, 512 West Loop, P.O. Box 2980, College Station, TX 77840.

<sup>14</sup>Chemical Oxygen Demand, Method 8000, Hach Handbook of Water Analysis, 1979, Hach Chemical Company, P.O. Box 389, Loveland, CO 80537.

<sup>15</sup>The back titration method will be used to resolve controversy.

<sup>16</sup>Orion Research Instruction Manual, Residual Chlorine Electrode Model 97–70, 1977, Orion Research Incorporated, 840 Memorial Drive, Cambridge, MA 02138. The calibration graph for the Orion residual chlorine method must be derived using a reagent blank and three standard solutions, containing 0.2, 1.0, and 5.0 mL 0.00281 N potassium iodate/100 mL solution, respectively.

<sup>17</sup>The approved method is that cited in *Standard Methods for the Examination of Water and Wastewater*, 14th Edition, 1976.

<sup>18</sup>National Council of the Paper Industry for Air and Stream Improvement, Inc., Technical Bulletin 253, December 1971.

<sup>19</sup>Copper, Biocinchonate Method, Method 8506, Hach Handbook of Water Analysis, 1979, Hach Chemical Company, P.O. Box 389, Loveland, CO 80537.

<sup>20</sup>When using a method with block digestion, this treatment is not required.

<sup>21</sup>Hydrogen ion (pH) Automated Electrode Method, Industrial Method Number 378–75WA, October 1976, Bran & Luebbe (Technicon) Autoanalyzer II. Bran & Luebbe Analyzing Technologies, Inc., Elmsford, NY 10523.

<sup>22</sup>Iron, 1,10-Phenanthroline Method, Method 8008, 1980, Hach Chemical Company, P.O. Box 389, Loveland, CO 80537.

<sup>23</sup>Manganese, Periodate Oxidation Method, Method 8034, Hach Handbook of Wastewater Analysis, 1979, pages 2–113 and 2–117, Hach Chemical Company, Loveland, CO 80537.

<sup>24</sup>Wershaw, R. L., *et al.*, “Methods for Analysis of Organic Substances in Water,” *Techniques of Water-Resources Investigation of the U.S. Geological Survey*, Book 5, Chapter A3, (1972 Revised 1987) p. 14.

<sup>25</sup>Nitrogen, Nitrite, Method 8507, Hach Chemical Company, P.O. Box 389, Loveland, CO 80537.

<sup>26</sup>Just prior to distillation, adjust the sulfuric-acid-preserved sample to pH 4 with 1 + 9 NaOH.

<sup>27</sup>The approved method is cited in *Standard Methods for the Examination of Water and Wastewater*, 14th Edition. The colorimetric reaction is conducted at a pH of 10.0±0.2. The approved methods are given on pp 576–81 of the 14th Edition: Method 510A for distillation, Method 510B for the manual colorimetric procedure, or Method 510C for the manual spectrometric procedure.

<sup>28</sup>R.F. Addison and R. G. Ackman, “Direct Determination of Elemental Phosphorus by Gas–Liquid Chromatography,” *Journal of Chromatography*, Vol. 47, No.3, pp. 421–426, 1970.

<sup>29</sup>Approved methods for the analysis of silver in industrial wastewaters at concentrations of 1 mg/L and above are inadequate where silver exists as an inorganic halide. Silver halides such as the bromide and chloride are relatively insoluble in reagents such as nitric acid but are readily soluble in an aqueous buffer of sodium thiosulfate and sodium hydroxide to pH of 12. Therefore, for levels of silver above 1 mg/L, 20 mL of sample should be diluted to 100 mL by adding 40 mL each of 2 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and NaOH. Standards should be prepared in the same manner. For levels of silver below 1 mg/L the approved method is satisfactory.

<sup>30</sup>The approved method is that cited in *Standard Methods for the Examination of Water and Wastewater*, 15th Edition.

<sup>31</sup>For samples known or suspected to contain high levels of silver (e.g., in excess of 4 mg/L), cyanogen iodide should be used to keep the silver in solution for analysis. Prepare a cyanogen iodide solution by adding 4.0 mL of concentrated NH<sub>4</sub>OH, 6.5 g of KCN, and 5.0 mL of a 1.0 N solution of I<sub>2</sub> to 50 mL of reagent water in a volumetric flask and dilute to 100.0 mL. After digestion of the sample, adjust the pH of the digestate to >7 to prevent the formation of HCN under acidic conditions. Add 1 mL of the cyanogen iodide solution to the sample digestate and adjust the volume to 100 mL with reagent water (NOT acid). If cyanogen iodide is added to sample digestates, then silver standards must be prepared that contain cyanogen iodide as well. Prepare working standards by diluting a small volume of a silver stock solution with water and adjusting the pH>7 with NH<sub>4</sub>OH. Add 1 mL of the cyanogen iodide solution and let stand 1

hour. Transfer to a 100-mL volumetric flask and dilute to volume with water.

<sup>32</sup>Stevens, H.H., Ficke, J. F., and Smoot, G. F., "Water Temperature—Influential Factors, Field Measurement and Data Presentation," *Techniques of Water-Resources Investigations of the U.S. Geological Survey*, Book 1, Chapter D1, 1975.

<sup>33</sup>Zinc, Zincon Method, Method 8009, *Hach Handbook of Water Analysis*, 1979, pages 2–231 and 2–333, Hach Chemical Company, Loveland, CO 80537.

<sup>34</sup>"Direct Current Plasma (DCP) Optical Emission Spectrometric Method for Trace Elemental Analysis of Water and Wastes, Method AES0029," 1986—Revised 1991, Thermo Jarrell Ash Corporation, 27 Forge Parkway, Franklin, MA 02038

<sup>35</sup>Precision and recovery statements for the atomic absorption direct aspiration and graphite furnace methods, and for the spectrophotometric SDDC method for arsenic are provided in Appendix D of this part titled, "Precision and Recovery Statements for Methods for Measuring Metals."

<sup>36</sup>Microwave-assisted digestion may be employed for this metal, when analyzed by this methodology. "Closed Vessel Microwave Digestion of Wastewater Samples for Determination of Metals", CEM Corporation, P.O. Box 200, Matthews, NC 28106–0200, April 16, 1992. Available from the CEM Corporation.

<sup>37</sup>When determining boron and silica, only plastic, PTFE, or quartz laboratory ware may be used from start until completion of analysis.

<sup>38</sup>Only use n-hexane extraction solvent when determining Oil and Grease parameters—Hexane Extractable Material (HEM), or Silica Gel Treated HEM (analogous to EPA Method 1664A). Use of other extraction solvents (e.g., those in the 18th and 19th editions) is prohibited.

<sup>39</sup>Nitrogen, Total Kjeldahl, Method PAI-DK01 (Block Digestion, Steam Distillation, Titrimetric Detection), revised 12/22/94, OI Analytical/ALPKEM, P.O. Box 9010, College Station, TX 77842.

<sup>40</sup>Nitrogen, Total Kjeldahl, Method PAI-DK02 (Block Digestion, Steam Distillation, Colorimetric Detection), revised 12/22/94, OI Analytical/ALPKEM, P.O. Box 9010, College Station, TX 77842.

<sup>41</sup>Nitrogen, Total Kjeldahl, Method PAI-DK03 (Block Digestion, Automated FIA Gas Diffusion), revised 12/22/94, OI Analytical/ALPKEM, P.O. Box 9010, College Station, TX 77842.

<sup>42</sup>Method 1664, Revision A " n -Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated n -Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry" EPA–821–R–98–002, February 1999. Available at NTIS, PB–121949, U.S. Department of Commerce, 5285 Port Royal, Springfield, VA 22161.

<sup>43</sup>USEPA. 2001. Method 1631, Revision E, "Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry" September 2002, Office of Water, U.S. Environmental Protection Agency (EPA–821–R–02–024). The application of clean techniques described in EPA's draft Method 1669: *Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels* (EPA–821–R–96–011) are recommended to preclude contamination at low-level, trace metal determinations.

<sup>44</sup>Available Cyanide, Method OIA–1677, "Available Cyanide by Flow Injection, Ligand Exchange, and Amperometry," ALPKEM, A Division of OI Analytical, P.O. Box 9010, College Station, TX 77842–9010.

<sup>45</sup>"Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Ammonia Plus Organic Nitrogen by a Kjeldahl Digestion Method," Open File Report (OFR) 00–170.

<sup>46</sup>"Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Chromium in Water by Graphite Furnace Atomic Absorption Spectrophotometry," Open File Report (OFR) 93–449.

<sup>47</sup>"Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Molybdenum by Graphite Furnace Atomic Absorption Spectrophotometry," Open File Report (OFR) 97–198.

<sup>48</sup>"Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Total Phosphorus by Kjeldahl Digestion Method and an Automated Colorimetric Finish That Includes Dialysis" Open File Report (OFR) 92–146.

<sup>49</sup>"Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Arsenic and Selenium in Water and Sediment by Graphite Furnace-Atomic Absorption Spectrometry" Open File Report (OFR) 98–639.

<sup>50</sup>"Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Elements in Whole-water Digests Using Inductively Coupled Plasma-Optical Emission Spectrometry and Inductively Coupled Plasma-Mass Spectrometry," Open File Report (OFR) 98-165.

<sup>51</sup>"Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Inorganic and Organic Constituents in Water and Fluvial Sediment," Open File Report (OFR) 93–125.

<sup>52</sup>All EPA methods, excluding EPA Method 300.1, are published in "Methods for the Determination of Metals in Environmental Samples," Supplement I, National Exposure Risk Laboratory-Cincinnati (NERL–CI), EPA/600/R–94/111, May 1994; and "Methods for the Determination of Inorganic Substances in Environmental Samples," NERL–CI,

EPA/600/R-93/100, August, 1993. EPA Method 300.1 is available from <http://www.epa.gov/safewater/methods/pdfs/met300.pdf>.

<sup>53</sup>Styrene divinyl benzene beads (e.g., AMCO-AEPA-1 or equivalent) and stabilized formazin (e.g., Hach StabCal™ or equivalent) are acceptable substitutes for formazin.

<sup>54</sup>Method D6508, Rev. 2, "Test Method for Determination of Dissolved Inorganic Anions in Aqueous Matrices Using Capillary Ion Electrophoresis and Chromate Electrolyte," available from Waters Corp, 34 Maple St., Milford, MA, 01757, Telephone: 508/482-2131, Fax: 508/482-3625.

<sup>55</sup>Kelada-01, "Kelada Automated Test Methods for Total Cyanide, Acid Dissociable Cyanide, and Thiocyanate," EPA 821-B-01-009, Revision 1.2, August 2001, National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, VA 22161 [Order Number PB 2001-108275]. The toll free telephone number is: 800-553-6847. Note: A 450-W UV lamp may be used in this method instead of the 550-W lamp specified if it provides performance within the quality control (QC) acceptance criteria of the method in a given instrument. Similarly, modified flow cell configurations and flow conditions may be used in the method, provided that the QC acceptance criteria are met.

<sup>56</sup>QuikChem Method 10-204-00-1-X, "Digestion and Distillation of Total Cyanide in Drinking and Wastewaters using MICRO DIST and Determination of Cyanide by Flow Injection Analysis" is available from Lachat Instruments 6645 W. Mill Road, Milwaukee, WI 53218, Telephone: 414-358-4200.

<sup>57</sup>When using sulfide removal test procedures described in Method 335.4, reconstitute particulate that is filtered with the sample prior to distillation.

<sup>58</sup>Unless otherwise stated, if the language of this table specifies a sample digestion and/or distillation "followed by" analysis with a method, approved digestion and/or distillation are required prior to analysis.

<sup>59</sup>Method 245.7, Rev. 2.0, "Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry," February 2005, EPA-821-R-05-001, available from the U.S. EPA Sample Control Center (operated by CSC), 6101 Stevenson Avenue, Alexandria, VA 22304, Telephone: 703-461-2100, Fax: 703-461-8056.

<sup>60</sup>The use of EDTA may decrease method sensitivity in some samples. Analysts may omit EDTA provided that all method specified quality control acceptance criteria are met.

<sup>61</sup>Samples analyzed for available cyanide using Methods OIA-1677 or D6888-04 that contain particulate matter may be filtered only after the ligand exchange reagents have been added to the samples, because the ligand exchange process converts complexes containing available cyanide to free cyanide, which is not removed by filtration. Analysts are further cautioned to limit the time between the addition of the ligand exchange reagents and sample analysis to no more than 30 minutes to preclude settling of materials in samples.

## Appendix E— 40 CFR 136 Applicable List of Approved Test Procedures for Non-Pesticide Organic Compounds

Parameter	<u>EPA GC<sup>2,7</sup></u>	<u>EPA GC/MS<sub>2,7</sub></u>	<u>EPA HPLC<sub>2,7</sub></u>	<u>Standard Methods</u>	<u>Standard Methods Online</u>	<u>ASTM</u>	<u>Other</u>
1. Acenaphthene	610	625, 1625B	610	6440 B [18th, 19th, 20th]		D4657-92 (99)	See footnote <sup>9</sup> , p. 27
2. Acenaphthylene	610	625, 1625B	610	6410 B, 6440 B, [18th, 19th, 20th]	6410 B-00	D4657-92 (99)	See footnote <sup>9</sup> , p. 27
3. Acrolein	603	624 <sup>4</sup> , 1624B					
4. Acrylonitrile	603	624 <sup>4</sup> , 1624B					
5. Anthracene	610	625, 1625B	610	6410 B, 6440 B [18th, 19th, 20th]	6410 B-00	D4657-92 (99)	See footnote <sup>9</sup> , p. 27
6. Benzene	602	624, 1624B		6200 B [20th] and 6210 B [18th,19th], 6200 C [20th] and 6220 B [18th,19th]	6200 B and C-97		
7. Benzidine		625 <sup>5</sup> , 1625B	605				See footnote <sup>3</sup> , p.1
8. Benzo(a)anthracene	610	625, 1625B	610	6410 B, 6440 B [18th, 19th, 20th]	6410 B-00	D4657-92 (99)	See footnote <sup>9</sup> , p. 27
9. Benzo(a)pyrene	610	625, 1625B	610	6410 B, 6440 B [18th, 19th, 20th]	6410 B-00	D4657-92 (99)	See footnote <sup>9</sup> , p. 27
10. Benzo(b)fluoranthene	610	625, 1625B	610	6410 B, 6440 B [18th, 19th, 20th]	6410 B-00	D4657-92 (99)	See footnote <sup>9</sup> , p. 27
11. Benzo(g,h,i) perylene	610	625, 1625B	610	6410 B, 6440 B [18th, 19th, 20th]	6410 B-00	D4657-92 (99)	See footnote <sup>9</sup> , p. 27
12. Benzo(k) fluoranthene	610	625, 1625B	610	6410 B, 6440 B [18th, 19th, 20th]	6410 B-00	D4657-92 (99)	See footnote <sup>9</sup> , p. 27
15. Bis(2-chloroethoxy) methane	611	625, 1625B		6410 B [18th, 19th, 20th]	6410 B-00		See footnote <sup>9</sup> , p. 27
16. Bis(2-chloroethyl) ether	611	625, 1625B		6410 B [18th, 19th, 20th]	6410 B-00		See footnote <sup>9</sup> , p. 27
17. Bis(2-ethylhexyl) phthalate	606	625, 1625B		6410 B [18th, 19th, 20th]	6410 B-00		See footnote <sup>9</sup> , p. 27
18. Bromodichloro-methane	601	624, 1624B		6200 C [20th] and 6230 B [18th, 19th], 6200 B [20th]	6200 B and C-97		

Parameter	<u>EPA GC</u> <sup>2,7</sup>	<u>EPA GC/MS</u> <sup>2,7</sup>	<u>EPA HPLC</u> <sup>2,7</sup>	<u>Standard Methods</u>	<u>Standard Methods Online</u>	<u>ASTM</u>	<u>Other</u>
19. Bromoform	601	624, 1624B		6200 C [20th] and 6230 B [18th, 19th], 6200 B [20th] and 6210 B [18th, 19th]	6200 B and C-97		
20. Bromomethane	601	624, 1624B		6200 C [20th] and 6230 B [18th, 19th], 6200 B [20th] and 6210 B [18th, 19th]	6200 B and C-97		
22. Carbon tetrachloride	601	624, 1624B		6200 C [20th] and 6230 B [18th, 19th]	6200 C- 97		See footnote <sup>3</sup> , p. 130
23. 4-Chloro-3-methyl phenol	604	625, 1625B		6410 B, 6420 B [18th, 19th, 20th]	6410 B- 00, 6420 B-00		See footnote <sup>9</sup> , p. 27
24. Chlorobenzene	601, 602	624, 1624B		6200 B [20th] and 6210 B [18th, 19th], 6200 C [20th] and 6220 B [18th, 19th], 6200 C [20th] and 6230 B [18th, 19th]	6200 B and C-97		See footnote <sup>3</sup> , p. 130
25. Chloroethane	601	624, 1624B		6200 B [20th] and 6210 B [18th, 19th], 6200 C [20th] and 6230 B [18th, 19th]	6200 B and C-97		
26. 2-Chloroethylvinyl ether	601	624, 1624B		6200 B [20th] and 6210 B [18th, 19th], 6200 C [20th] and 6230 B [18th, 19th]	6200 B and C-97		
27. Chloroform	601	624, 1624B		6200 B [20th] and 6210 B [18th, 19th], 6200 C [20th] and 6230 B [18th, 19th]	6200 B and C-97		See footnote <sup>3</sup> , p. 130
28. Chloromethane	601	624, 1624B		6200 B [20th] and 6210 B [18th, 19th] 6200 C [20th] and 6230 B [18th, 19th]	6200 B and C-97		

Parameter	<u>EPA GC<sup>2,7</sup></u>	<u>EPA GC/MS<sup>2,7</sup></u>	<u>EPA HPLC<sup>2,7</sup></u>	<u>Standard Methods</u>	<u>Standard Methods Online</u>	<u>ASTM</u>	<u>Other</u>
29. 2-Chloronaph-thalene	612	625, 1625B		6410 B [18th, 19th, 20th]	6410 B- 00		See footnote <sup>9</sup> , p. 27
30. 2-Chlorophenol	604	625, 1625B		6410 B, 6420 B [18th, 19th, 20th]	6410 B(00, 6420 B- 00		See footnote <sup>9</sup> , p. 27
31. 4-Chlorophenyl phenyl ether	611	625, 1625B		6410 B [18th, 19th, 20th]	6410 B- 00		See footnote <sup>9</sup> , p. 27
32. Chrysene	610	625, 1625B	610	6410 B, 6440 B [18th, 19th, 20th]	6410 B- 00	D4657 -92 (99)	See footnote <sup>9</sup> , p. 27
33. Dibenzo(a,h)an-thracene	610	625, 1625B	610	6410 B, 6440 B [18th, 19th, 20th]	6410 B- 00	D4657 -92 (99)	See footnote <sup>9</sup> , p. 27
34. Dibromochloro-methane	601	624, 1624B		6200 B [20th] and 6210 B [18th, 19th] 6200 C [20th] and 6230 B [18th, 19th]	6200 B and C-97		
35. 1,2-Dichloro-benzene	601, 602	624, 1625B		6200 C [20th] and 6220 B [18th, 19th], 6200 C [20th] and 6230 B [18th, 19th]	6200 C- 97		See footnote <sup>9</sup> , p. 27
36. 1,3-Dichloro-benzene	601, 602	624, 1625B		6200 C [20th] and 6220 B [18th, 19th], 6200 C [20th] and 6230 B [18th, 19th]	6200 C- 97		See footnote <sup>9</sup> , p. 27
37. 1,4-Dichloro-benzene	601, 602	624, 1625B		6200 C [20th] and 6220 B [18th, 19th], 6200 C [20th] and 6230 B [18th, 19th]	6200 C- 97		See footnote <sup>9</sup> , p. 27
38. 3,3-Dichloro-benzidine		625, 1625B	605	6410 B [18th, 19th, 20th]	6410 B- 00		
39. Dichlorodifluoro-methane	601			6200 C [20th] and 6230 B [18th, 19th]	6200 C- 97		
40. 1,1-Dichloroethane	601	624, 1624B		6200 B [20th] and 6210 B [18th, 19th], 6200 C [20th] and 6230 B [18th, 19th]	6200 B and C-97		

Parameter	<u>EPA GC<sup>2,7</sup></u>	<u>EPA GC/MS<sup>2,7</sup></u>	<u>EPA HPLC<sup>2,7</sup></u>	<u>Standard Methods</u>	<u>Standard Methods Online</u>	<u>ASTM</u>	<u>Other</u>
41. 1,2-Dichloroethane	601	624, 1624B		6200 B [20th] and 6210 B [18th, 19th], 6200 C [20th] and 6230 B [18th, 19th]	6200 B and C-97		
42. 1,1-Dichloroethene	601	624, 1624B		6200 B [20th] and 6210 B [18th, 19th], 6200 C [20th] and 6230 B [18th, 19th]	6200 B and C-97		
43. trans-1,2-Dichloro- ethene	601	624, 1624B		6200 B [20th] and 6210 B [18th, 19th], 6200 C [20th] and 6230 B [18th, 19th]	6200 B and C-97		
44. 2,4-Dichlorophenol	604	625, 1625B		6410 B, 6420 B [18th, 19th, 20th]	6410 B- 00, 6420 B-00		See footnote <sup>9</sup> , p. 27
45. 1,2-Dichloro-propane	601	624, 1624B		6200 B [20th] and 6210 B [18th, 19th], 6200 C [20th] and 6230 B [18th, 19th]	6200 B and C-97		
46. cis-1,3-Dichloro-propene	601	624, 1624B		6200 B [20th] and 6210 B [18th, 19th], 6200 C [20th] and 6230 B [18th, 19th]	6200 B and C-97		
47. trans-1,3-Dichloro- propene	601	624, 1624B		6200 B [20th] and 6210 B [18th, 19th], 6200 C [20th] and 6230 B [18th, 19th]	6200 B and C-97		
48. Diethyl phthalate	606	625, 1625B		6410 B [18th, 19th, 20th]	6410 B- 00		See footnote <sup>9</sup> , p. 27
49. 2,4-Dimethylphenol	604	625, 1625B		6410 B, 6420 B [18th, 19th, 20th]	6410 B- 00, 6420 B-00		See footnote <sup>9</sup> , p. 27
50. Dimethyl phthalate	606	625, 1625B		6410 B [18th, 19th, 20th]	6410 B- 00		See footnote <sup>9</sup> , p. 27
51. Di-n-butyl phthalate	606	625, 1625B		6410 B [18th, 19th, 20th]	6410 B- 00		See footnote <sup>9</sup> , p. 27
52. Di-n-octyl phthalate	606	625, 1625B		6410 B [18th, 19th, 20th]	6410 B- 00		See footnote <sup>9</sup> , p. 27

Parameter	<u>EPA GC<sup>2,7</sup></u>	<u>EPA GC/MS<sup>2,7</sup></u>	<u>EPA HPLC<sup>2,7</sup></u>	<u>Standard Methods</u>	<u>Standard Methods Online</u>	<u>ASTM</u>	<u>Other</u>
53. 2,3-Dinitrophenol	604	625, 1625B		6410 B, 6420 B [18th, 19th, 20th]	6410 B-00, 6420 B-00		
54. 2,4-Dinitrotoluene	609	625, 1625B		6410 B [18th, 19th, 20th]	6410 B-00		See footnote <sup>9</sup> , p. 27
55. 2,6-Dinitrotoluene	609	625, 1625B		6410 B [18th, 19th, 20th]	6410 B-00		See footnote <sup>9</sup> , p. 27
57. Ethylbenzene	602	624, 1624B		6200 B [20th] and 6210 B [18th, 19th], 6200 C [20th] and 6220 B [18th, 19th]	6200 B and C-97		
58. Fluoranthene	610	625, 1625B	610	6410 B, 6440 B [18th, 19th, 20th]	6410 B-00	D4657-92 (99)	See footnote <sup>9</sup> , p. 27
59. Fluorene	610	625, 1625B	610	6410 B, 6440 B [18th, 19th, 20th]	6410 B-00	D4657-92 (99)	See footnote <sup>9</sup> , p. 27
63. Hexachlorobenzene	612	625, 1625B		6410 B [18th, 19th, 20th]	6410 B-00		See footnote <sup>9</sup> , p. 27
64. Hexachloro-butadiene	612	625, 1625B		6410 B [18th, 19th, 20th]	6410 B-00		See footnote <sup>9</sup> , p. 27
65. Hexachlorocyclopentadiene	612	625 <sup>5</sup> , 1625B		6410 B [18th, 19th, 20th]	6410 B-00		See footnote <sup>9</sup> , p. 27
73. Hexachloroethane	612	625, 1625B		6410 B [18th, 19th, 20th]	6410 B-00		See footnote <sup>9</sup> , p. 27
74. Ideno(1,2,3-cd) pyrene	610	625, 1625B	610	6410 B, 6440 B [18th, 19th, 20th]	6410 B-00	D4657-92 (99)	See footnote <sup>9</sup> , p. 27
75. Isophorone	609	625, 1625B		6410 B [18th, 19th, 20th]	6410 B-00		See footnote <sup>9</sup> , p. 27
76. Methylene chloride	601	624, 1624B		6200 C [20th] and 6230 B [18th, 19th]	6200 C-97		See footnote <sup>3</sup> , p. 130
77. 2-Methyl-4,6-dinitrophenol	604	625, 1625B		6410 B, 6420 B [18th, 19th, 20th]	6410 B-00, 6420 B-00		See footnote <sup>9</sup> , p. 27
78. Naphthalene	610	625, 1625B	610	6410 B, 6440 B [18th, 19th, 20th]	6410 B-00		See footnote <sup>9</sup> , p. 27
79. Nitrobenzene	609	625, 1625B		6410 B [18th, 19th, 20th]	6410 B-00	D4657-92 (99)	See footnote <sup>9</sup> , p. 27
80. 2-Nitrophenol	604	625, 1625B		6410 B, 6420 B [18th, 19th, 20th]	6410 B-00, 6420 B-00		See footnote <sup>9</sup> , p. 27
81. 4-Nitrophenol	604	625, 1625B		6410 B, 6420 B [18th, 19th, 20th]	6410 B-00, 6420 B-00		See footnote <sup>9</sup> , p. 27
82. N-Nitrosodimethylamine	607	6255, 1625B		6410 B [18th, 19th, 20th]	6410 B-00		See footnote <sup>9</sup> , p. 27

Parameter	<u>EPA GC<sup>2,7</sup></u>	<u>EPA GC/MS<sup>2,7</sup></u>	<u>EPA HPLC<sup>2,7</sup></u>	<u>Standard Methods</u>	<u>Standard Methods Online</u>	<u>ASTM</u>	<u>Other</u>
83. N-Nitrosodi-n-propylamine	607	6255, 1625B		6410 B [18th, 19th, 20th]	6410 B-00		See footnote <sup>9</sup> , p. 27
84. N-Nitrosodiphenylamine	607	6255, 1625B		6410 B [18th, 19th, 20th]	6410 B-00		See footnote <sup>9</sup> , p. 27
87. 2,2'-Oxybis(2-chloropropane) [also known as bis(2-chloroisopropyl) ether]	611	625, 1625B		6410 B [18th, 19th, 20th]	6410 B-00		
98. Pentachlorophenol	604	625, 1625B		6410 B, 6630 B [18th, 19th, 20th]	6410 B-00		See footnote <sup>3</sup> , p. 140; See footnote <sup>9</sup> , p. 27
99. Phenanthrene	610	625, 1625B	610	6410 B, 6440 B [18th, 19th, 20th]	6410 B-00	D4657-92 (99)	See footnote <sup>9</sup> , p. 27
100. Phenol	604	625, 1625B		6410 B, 6420 B [18th, 19th, 20th]	6410 B-00, 6420 B-00		See footnote <sup>9</sup> , p. 27
101. Pyrene	610	625, 1625B	610	6410 B, 6440 B [18th, 19th, 20th]	6410 B-00	D4657-92 (99)	See footnote <sup>9</sup> , p. 27
104. 1,1,2,2-Tetra-chloro ethane	601	624, 1624B		6200 B [20th] and 6210 B [18th, 19th], 6200 C [20th] and 6230 B [18th, 19th]	6200 B and C-97		See footnote <sup>3</sup> , p. 130
105. Tetrachloroethene	601	624, 1624B		6200 B [20th] and 6210 B [18th, 19th], 6200 C [20th] and 6230 B [18th, 19th]	6200 B and C-97		See footnote <sup>3</sup> , p. 130
106. Toluene	602	624, 1624B		6200 B [20th] and 6210 B [18th, 19th], 6200 C [20th] and 6220 B [18th, 19th]	6200 B and C-97		
107. 1,2,4-Trichloro-benzene	612	625, 1625B		6410 B [18th, 19th, 20th]	6410 B-00		See footnote <sup>3</sup> , p. 130; See footnote <sup>9</sup> , p. 27
108. 1,1,1-Trichloro-ethane	601	624, 1624B		6200 B [20th] and 6210 B [18th, 19th], 6200 C [20th] and 6230 B [18th, 19th]	6200 B and C-97		

Parameter	<u>EPA GC</u> <sup>2,7</sup>	<u>EPA GC/MS</u> <sup>2,7</sup>	<u>EPA HPLC</u> <sup>2,7</sup>	<u>Standard Methods</u>	<u>Standard Methods Online</u>	<u>ASTM</u>	<u>Other</u>
109. 1,1,2-Trichloro-ethane	601	624, 1624B	6200 B [20th] and 6210 B [18th, 19th], 6200 C [20th] and 6230 B [18th, 19th]	6200 B and C-97		See footno te <sup>3</sup> , p. 130	
110. Trichloroethene	601	624, 1624B		6200 B [20th] and 6210 B [18th, 19th], 6200 C [20th] and 6230 B [18th, 19th]	6200 B and C-97		
111. Trichlorofluoro-methane	601	624		6200 B [20th] and 6210 B [18th, 19th], 6200 C [20th] and 6230 B [18th, 19th]	6200 B and C-97		
112. 2,4,6-Trichlorophenol	604	625, 1625B		6410 B, 6420 B [18th, 19th, 20th]	6410 B- 00, 6420 B-00		See footnote <sup>9</sup> , p. 27
113. Vinyl chloride	601	624, 1624B		6200 B [20th] and 6210 B [18th, 19th], >6200 C [20th] and 6230 B [18th, 19th]	6200 B and C-97		

<sup>1</sup>All parameters are expressed in micrograms per liter (µg/L) except for Method 1613B in which the parameters are expressed in picograms per liter (pg/L).

<sup>2</sup>The full text of Methods 601–613, 624, 625, 1624B, and 1625B, are given at Appendix A, “Test Procedures for Analysis of Organic Pollutants,” of this Part 136. The full text of Method 1613B is incorporated by reference into this Part 136 and is available from the National Technical Information Services as stock number PB95–104774. The standardized test procedure to be used to determine the method detection limit (MDL) for these test procedures is given at Appendix B, “Definition and Procedure for the Determination of the Method Detection Limit,” of this Part 136.

<sup>3</sup>“Methods for Benzidine: Chlorinated Organic Compounds, Pentachlorophenol and Pesticides in Water and Wastewater,” U.S. Environmental Protection Agency, September, 1978.

<sup>4</sup>Method 624 may be extended to screen samples for Acrolein and Acrylonitrile. However, when they are known to be present, the preferred method for these two compounds is Method 603 or Method 1624B.

<sup>5</sup>Method 625 may be extended to include benzidine, hexachlorocyclopentadiene, N-nitrosodimethylamine, and N-nitrosodiphenylamine. However, when they are known to be present, Methods 605, 607, and 612, or Method 1625B, are preferred methods for these compounds.

<sup>5a</sup>625, screening only.

<sup>6</sup>"Selected Analytical Methods Approved and Cited by the United States Environmental Protection Agency," Supplement to the *Fifteenth Edition of Standard Methods for the Examination of Water and Wastewater* (1981).

<sup>7</sup>Each analyst must make an initial, one-time demonstration of their ability to generate acceptable precision and accuracy with Methods 601–603, 624, 625, 1624B, and 1625B (See Appendix A of this Part 136) in accordance with procedures each in Section 8.2 of each of these methods. Additionally, each laboratory, on an on-going basis must spike and analyze 10% (5% for methods 624 and 625 and 100% for methods 1624B and 1625B) of all samples to monitor and evaluate laboratory data quality in accordance with Sections 8.3 and 8.4 of these methods. When the recovery of any parameter falls outside the warning limits, the analytical results for that parameter in the unspiked sample are suspect. The results should be reported, but cannot be used to demonstrate regulatory compliance. These quality control requirements also apply to the Standard Methods, ASTM Methods, and other methods cited.

<sup>8</sup>"Organochlorine Pesticides and PCBs in Wastewater Using Empore™ Disk" 3M Corporation Revised 10/28/94.

<sup>9</sup>USGS Method 0–3116–87 from "Methods of Analysis by U.S. Geological Survey National Water Quality Laboratory—Determination of Inorganic and Organic Constituents in Water and Fluvial Sediments," U.S. Geological Survey, Open File Report 93–125.

<sup>10</sup>Analysts may use Fluid Management Systems, Inc. PowerPrep system in place of manual cleanup provided that the analysis meet the requirements of Method 1613B (as specified in Section 9 of the method) and permitting authorities.

## **Appendix F— Distribution List**

A copy via electronic format of each revision will be distributed to all vessel owner organizations, regulatory agencies, quality assurance officers, project managers and laboratory managers associated with this project. Specific contact information for all companies and officials are on file.