

# BIG LAKE WATER QUALITY MONITORING QUALITY ASSURANCE PROJECT PLAN

April 2009



## A. PROJECT MANAGEMENT ELEMENTS

### A.1. Title Page and Approvals

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<b>OASIS Project Manager – Ben Martich</b>	<b>Date</b>
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<b>OASIS Quality Assurance Officer – Tom Beckman</b>	<b>Date</b>
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<b>ADEC Project Manager – Laura Eldred</b>	<b>Date</b>
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<b>ADEC Water Quality Assurance Officer – Richard Heffern</b>	<b>Date</b>
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## A.2. Table of Contents

<b>A. PROJECT MANAGEMENT ELEMENTS.....</b>	<b>1</b>
A.1. Title Page and Approvals.....	1
A.2. Table of Contents .....	3
A.3. Distribution List .....	5
A.4. Project/Task Organization .....	5
A.5. Problem Definition/Background .....	7
A.6. Project/Task Description.....	8
A.6.1. Public Information Session.....	8
A.6.2. Sampling and Quality Assurance Project Plan.....	8
A.6.3. Field Data Collection .....	8
A.6.4. Draft Report.....	8
A.6.5. Final Report.....	9
A.7. Data Quality Objectives and Criteria for Measurement of Data.....	9
A.7.1. Project Data Quality Objectives .....	9
A.7.2. Criteria for Measurement of Data.....	10
A.7.3. Accuracy .....	10
A.7.4. Precision .....	10
A.7.5. Representativeness .....	10
A.7.6. Comparability .....	11
A.7.7. Completeness .....	11
A.8. Training and Certifications .....	11
A.9. Documents and Records .....	11
<b>B. DATA GENERATION AND ACQUISITION.....</b>	<b>13</b>
B.1. Sampling Process Design.....	13
B.2. Sampling Methods .....	16
B.3. Sample Handling and Custody .....	18
B.4. Analytical Methods.....	19
B.5. Quality Control.....	19
B.6. Instrument/Equipment Testing, Inspection, and Maintenance.....	21
B.7. Instrument/Equipment Calibration and Frequency .....	21
B.8. Inspection/Acceptance of Supplies and Consumables.....	21
B.9. Non-Direct Measurements.....	22
B.10. Data Management .....	22
<b>C. ASSESSMENT AND OVERSIGHT .....</b>	<b>25</b>
C.1. Assessments and Response Actions .....	25
C.2. Reports to Management .....	25
<b>D. DATA VALIDATION AND USABILITY.....</b>	<b>27</b>
D.1. Data Review, Validation, and Verification Requirements.....	27
D.2. Validation and Verification Methods .....	27

D.2.1. Review of Sample Handling .....	27
D.2.2. Laboratory Blank Samples .....	28
D.2.3. Laboratory Control Samples .....	28
D.2.4. Matrix Spike and Matrix Spike Duplicates .....	28
D.2.5. Surrogates.....	29
D.2.6. Field Duplicate Samples .....	29
D.2.7. Reporting Limits .....	29
D.2.8. Data Qualification.....	29
D.2.9. Completeness .....	30
D.3. Reconciliation with User Requirements .....	30

**TABLES**

Table 1: Parameter PQLs and Levels of Concern .....	9
Table 2: Sample Sites .....	13
Table 3: Sample Schedule .....	14
Table 4: Sampling Program for Standard Sample Days .....	14
Table 5: Sampling Program for Intensive Sample Days .....	15
Table 6: Analytical Program .....	15
Table 7: Preservation and Holding Times for Sample Analysis .....	18
Table 8: Analytical Methods, Precision and Accuracy .....	19
Table 9: Quality Control Samples .....	20
Table 10: Analytical Summary .....	20
Table 11: Data Qualifiers .....	30

**FIGURES**

Figure 1: OASIS Organization Chart.....	6
Figure 2: ADEC Organization Chart.....	7
Figure 3: Data Management Chart.....	23

**APPENDICES**

- A: Map of Sample Sites that Exceeded TAH Water Quality Standard in 2004 and 2005
- B: 2009 Sample Locations
- C: OASIS Observer and Interviewer Forms
- D: USGS Sampling Protocols for VOC Sampler
- E: Water Sampling Log Sheet
- F: EPA 624
- G: Laboratory Accreditation

### A.3. Distribution List

This list includes the names and addresses of those who receive copies of this approved quality assurance project plan (QAPP) and subsequent revisions. It is not the list of those who receive data reports.

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### A.4. Project/Task Organization

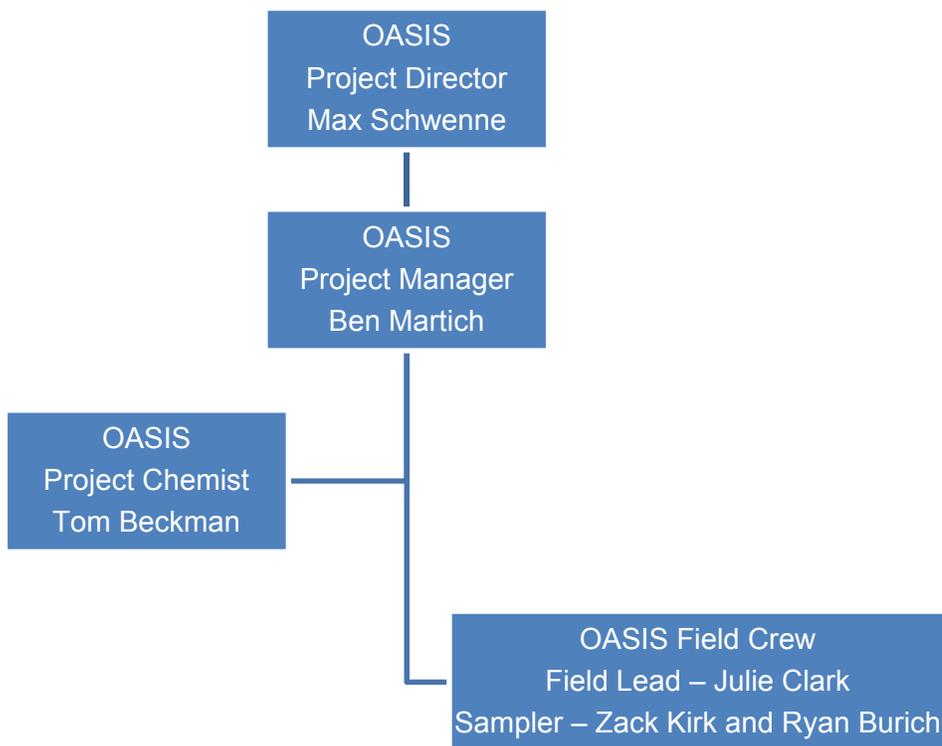
OASIS Environmental, Inc. (OASIS) has been contracted to conduct petroleum hydrocarbon sampling on Big Lake during the summer of 2009. The data will to be used to compare to past results from 2004 and 2005; to compare to Alaska water quality standards; to estimate the volume of water that may be impaired in the lake; and to estimate the loading of petroleum hydrocarbons in the lake. Tasks to be performed include field sampling on 13 different days during the summer, submitting a draft report by October 30, 2009, and submitting a final report by December 15, 2009. Contractual and Alaska Department of Environmental Conservation (ADEC) staff duties and responsibilities for completing these tasks are described below.

The project will be performed by the following staff and subcontractors. See the organization charts for OASIS and ADEC below (Figures 1 and 2). Additional, approved staff may support the project as needed.

- Max Schwenne is the Project Director. He will provide overall senior review and direction for the project.
- Ben Martich will be the Project Manager. He will serve as the primary contact for communications with ADEC and will organize the sampling events and reporting responsibilities. Mr. Martich also will provide on-site coordination for sampling, including direct participation in nearly one-half of the sample days. He has

extensive sampling experience and previous experience managing water quality projects for the ADEC Division of Water.

- Julie Clark will be an alternate field team leader in lieu of Mr. Martich. Ms. Clark is experienced in leading field events for ADEC.
- Zack Kirk and Ryan Burich will be other members of the field team.
- Tom Beckman will serve as the Project Chemist. Mr. Beckman will oversee data validation.
- The project laboratory will be OnSite Environmental (OnSite) with facilities in Redmond, Washington.



**FIGURE 1: OASIS ORGANIZATION CHART**

The following ADEC staff will assist in the review and approval of the sampling plan and QAPP and will interface with contractor staff for this project:

- Laura Eldred is the ADEC Project Manager. Ms. Eldred will provide overall direction of this project.
- Richard Heffern is the ADEC Quality Assurance Officer. Mr. Heffern will be responsible for quality assurance (QA)/quality control (QC) procedures.
- Cindy Gilder is the ADEC Contract Manager.

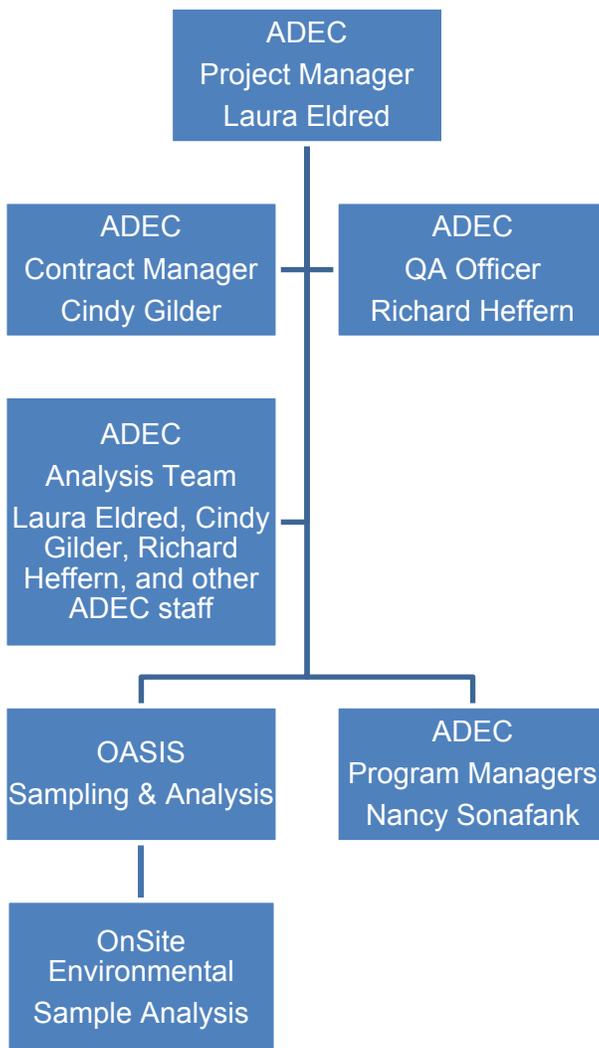


FIGURE 2: ADEC ORGANIZATION CHART

### A.5. Problem Definition/Background

The purpose of this project is to determine the level of impairment from petroleum hydrocarbons in Big Lake, Alaska, and the effect motorized watercraft may have on concentrations of petroleum hydrocarbons. The primary tasks that will be undertaken to accomplish the project purpose are collecting water samples, analyzing the lake's structure, and counting motorized watercraft.

ADEC previously conducted hydrocarbon sampling in Big Lake during 2004 and 2005. A total of 122 samples for analysis of benzene, toluene, ethylbenzene, and xylenes (BTEX) were collected to assess the concentrations of total aromatic hydrocarbons (TAH). Nineteen samples at six different sample sites exceeded the TAH water quality standard for aquatic life (10 micrograms per liter [ $\mu\text{g/L}$ ]). These persistent exceedances led ADEC to list Big Lake as impaired for petroleum hydrocarbons. Specifically, the

areas of impairment were an estimated 1,250 acres and are seasonal in nature, i.e., from May 15 to September 15. The impairment areas include the traffic lane between the east and west basins and heavily used regions near harbors and marinas, launch ramps, and traffic lanes in the east basin, except for the area directly north of Long Island. Appendix A contains a figure showing the sample locations that exceeded the TAH standard. Complete project history is available at:

[http://www.dec.state.ak.us/water/wnpspc/protection\\_restoration/biglakewq/index.htm](http://www.dec.state.ak.us/water/wnpspc/protection_restoration/biglakewq/index.htm)

## **A.6. Project/Task Description**

The proposed work elements to meet the project objective are summarized below by task. Each task summary includes the products to be produced and delivered for that task and the task schedule.

### **A.6.1. Public Information Session**

ADEC will host an informational meeting in the community of Big Lake to seek comments from the public regarding the project.

- **Deliverable:** Project summary fact sheet and PowerPoint presentation
- **Schedule:** April 21, 2009

### **A.6.2. Sampling and Quality Assurance Project Plan**

This sample plan and QAPP will be reviewed by ADEC and potentially other agencies and organizations with technical expertise.

- **Deliverable:** Sampling plan and QAPP
- **Schedule:** Completed by May 1, 2009

### **A.6.3. Field Data Collection**

OASIS will perform field data collection on 13 days beginning in May and ending in September. Table 1 includes the parameters for which sampling will occur; Table 3 lists when sampling will occur; and Appendix B includes the locations where samples will be collected. Water samples will be collected using ADEC's Wildco® hydrocarbon sampler. Data obtained over the course of the fieldwork, including analytical results, water quality parameters, and motorized watercraft counts will be compiled and managed for production in a project report as well as for inclusion into the STORET database. ADEC data management guidance will be followed as described at <http://www.dec.state.ak.us/water/wqsar/storetdocumentation.htm>.

- **Deliverable:** Project updates following each sample day via e-mail or verbal correspondence with ADEC project manager

### **A.6.4. Draft Report**

A draft report will be prepared after the completion of the final field event on September 7, 2009. The report will include analytical sampling results from the laboratory, field measured parameters, and motorized watercraft usage data. Analytical results will be

compared to 18 AAC 70 Water Quality Standards. QA/QC will be assessed as detailed in Section D.

- **Deliverable:** Draft report
- **Schedule:** Completed by October 30, 2009

### A.6.5. Final Report

A final report will be prepared following ADEC review of the draft report and will incorporate comments from that review. Photographic records and the project database will be submitted with the final report.

- **Deliverable:** Final report
- **Schedule:** Completed by December 15, 2009

## A.7. Data Quality Objectives and Criteria for Measurement of Data

### A.7.1. Project Data Quality Objectives

The overall data quality objective of this QAPP is to ensure that data generated from field activities are of sufficient quality to make decisions regarding the impairment of Big Lake.

In order to meet the data quality objective, detection limits for the analytical methods must be comparable to the levels of concern. The levels of concern used for this project are the water quality criteria in 18 AAC 70 for TAH. A summary of the parameters, their associated analytical methods with method detection limits, practical quantitation limits (PQLs), and the levels of concern are provided in Table 1. PQLs are defined by the US Environmental Protection Agency (EPA) as "the lowest concentration of an analyte that can be reliably measured within specified limits of precision and accuracy during routine laboratory operating conditions."

TABLE 1: PARAMETER PQLS AND LEVELS OF CONCERN

Analyte	Method	Method Detection Limit	Practical Quantitation Limit	Levels of Concern
Benzene	EPA 624	0.152 µg/L	0.2 µg/L	TAH 10 µg/L
Toluene	EPA 624	0.0988 µg/L	1.0 µg/L	TAH 10 µg/L
Ethylbenzene	EPA 624	0.0771 µg/L	0.2 µg/L	TAH 10 µg/L
Xylene	EPA 624	0.320 µg/L	0.6 µg/L	TAH 10 µg/L
pH	In situ (electronic probe)	NA	+/- 0.01 pH units	<6.5 or >8.5 pH units
Dissolved oxygen	In situ (electronic probe)	NA	+/- 0.01 mg/L	<7 or >17 mg/L
Temperature	In situ (electronic probe)	NA	+/- 1°C	13°C
Conductivity	In situ (electronic probe)	NA	0.1 (mS/cm)	NA

Notes:  
mS/cm – Millisiemens per centimeter  
NA - Not applicable

### A.7.2. Criteria for Measurement of Data

Criteria for measurements of data are the following data quality indicators: accuracy, precision, comparability, representativeness, and completeness of the tests. These criteria must be met to ensure that the data are verifiable and that project quality objectives are met.

OASIS' objectives for accuracy, precision, comparability, representativeness, and completeness are summarized in this section.

### A.7.3. Accuracy

Accuracy is a measure of confidence that describes how close a measurement is to its "true" value. Methods to ensure accuracy of field measurements include instrument calibration and maintenance procedures discussed in Section B of this QAPP. Sample handling procedures are also discussed in Section B, and a review of these procedures for verification of data is included in Section D.

Laboratory accuracy is normally determined by the percent recovery (%R) of the target analyte in spiked samples and also by the recoveries of the surrogates in all samples and QC samples. Laboratory accuracy ranges depend on the parameter being measured. Accuracy is calculated as follows:

$$\%R = \frac{\text{Analyzed value} \times 100}{\text{True value}}$$

Laboratory accuracy will be ensured by evaluating %R values specified by EPA methods listed in Section B.4.

### A.7.4. Precision

Precision is the degree of agreement among repeated measurements of the same characteristic, or parameter, and gives information about the consistency of methods. Precision is expressed in terms of the relative percent difference (RPD) between two measurements (A and B), and is computed as follows:

$$RPD = \frac{(A - B) \times 100}{(A+B)/2}$$

Field and lab precision is measured by collecting blind (to the laboratory) field duplicate samples. Field duplicates will be collected at a rate of 10% of project samples.

Laboratory precision will be evaluated by the analysis of laboratory duplicate samples, laboratory control sample (LCS) and a laboratory control sample duplicates (LCSD). Precision will also be evaluated in the laboratory using matrix spike/matrix spike duplicate (MS/MSD) samples. One set of MS/MSD, LCS/LCSD, and laboratory duplicate samples will be analyzed per batch of samples. RPDs specific to the EPA method listed in Section B.4 will be used for each sample parameter.

### A.7.5. Representativeness

Representativeness is the extent to which measurements actually represent the true environmental condition. Representativeness of data collected is part of the sampling

program developed by OASIS. This project is focused on determining the timing, frequency, locations, and specific causes of TAH exceedances. The sampling strategy is designed to obtain representative samples that address this concern. The selection of sample sites, days, depths, and collection times are based on an evaluation of past sampling results and an approach to meet current project objectives.

All samples will be analyzed for BTEX for the determination of TAH. OASIS will ensure the representativeness of the data using consistent sampling methods and ensuring quality during sample collection, handling, and transport (see Sections B.2 and B.3).

#### **A.7.6. Comparability**

Comparability is the degree to which data can be compared directly to similar studies. Standardized sampling techniques, analytical methods, and units of reporting will be used to ensure comparability. Analytical sample analysis will be performed by OnSite and will follow EPA-approved procedures.

The methods used for this sampling program will be compared to field sample collection methods used previously at Big Lake by OASIS for ADEC.

#### **A.7.7. Completeness**

Completeness is the comparison between the amount of usable data collected versus the amount of data called for in the scope of work. OASIS will determine completeness by comparing sampling and analyses completed with the requirements in the scope of work. The goal is to complete 90%+ of required monitoring. The following equation is used to calculate completeness:

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

Where T = Total number of expected measurements

I = Number of invalid results

NC = Number of results not produced (e.g., spilled sample, etc.) or rejected during data validation.

#### **A.8. Training and Certifications**

Sampling personnel are trained in field measurements, sample handling, chain-of-custody, and sample transport. Personnel analyzing and reporting data are qualified to conduct these tasks per their experience with hydrocarbon sampling on various contaminated sites in Alaska and 18 AAC 70 water quality criteria. Resumes of all project personnel are on file with ADEC as part of the Water Quality Term Contract. OASIS maintains documentation of training for field procedures and equipment usage.

#### **A.9. Documents and Records**

Field notebooks will be filled out using *Write in the Rain* ink or pencil, and should not be erased. Changes are made by crossing out errors, initialing, and adding correct information. Field notebooks will be bound with numbered pages.

Laboratory data results are recorded on laboratory data sheets, bench sheets, and/or in laboratory logbooks for each sampling event. These records as well as control charts; logbook records of equipment maintenance records; calibration and quality control checks, such as preparation and use of standard solutions; inventory of supplies and consumables; and check in of equipment, equipment parts, and chemicals are kept on file at the laboratory.

Any procedural or equipment problems are recorded in the field notebooks. Any deviation from this QAPP will also be noted in the field notebooks. Data results returned to ADEC will include information on field and/or laboratory QA/QC problems and corrective actions.

Chain-of-custody and/or transmission forms will be kept with the sample during transport and will accompany data results back to ADEC. All sample analysis and reporting will be performed under standard turnaround.

Training records and data review records will be kept on file by ADEC and the contractor and will be available on request by ADEC. All sample analysis records and documents will be kept by the contractor and will be available to EPA and ADEC for inspection at any time.

In addition to any written report, data collected for a project will be provided electronically to ADEC via a CD-ROM or e-mail ZIP file. Both the original application file and a comma delimited text file will be provided. The text file will be an ASCII (text) file, with fields separated by commas, comma delimited, often "CSV" (comma separated value), text enclosed in quotes. Spaces will not be used between fields. Blank lines will not be used permitted in the file. All dates will be formatted as "MM-DD-YYYY."

All records will be retained by the contractor for five years. All project records at ADEC are retained permanently.

## B. DATA GENERATION AND ACQUISITION

### B.1. Sampling Process Design

The sample plan is designed so that water samples are collected from key sample sites based on the 2004 and 2005 assessments. Table 2 lists the sample sites and the rationale for sampling each site. Appendix B contains a figure of the sample sites and locational data.

**TABLE 2: SAMPLE SITES**

Site	Description and Rationale
BL-1	Historic U.S. Geological Survey sampling site at the deepest area of the west basin. Serves as a control site for the project.
BL-2	Existing sample site that is a major traffic lane between the two basins. This site has previously exceeded the water quality standard for TAH.
BL-3	Historic U.S. Geological Survey sampling site at the deepest area of the east basin. Serves as a control site for the project. There is boat traffic in this area.
BL-4	Existing sample site near the South Shore State Recreation Area. This area is the most heavily used basin in the lake.
BL-5	Existing sample site that is a traffic lane for the bay to the southwest. This site has previously exceeded the water quality standard for TAH.
BL-6	Existing sample site near Southport Marina. This site has previously exceeded the water quality standard for TAH.
BL-7	Existing sample site located at the mouth of Fish Creek. This is a popular fishing area as well as a high use traffic lane. This site has previously exceeded the water quality standard for TAH.
BL-8	Existing sample site located near Burkeshore Marina. This site has previously exceeded the water quality standard for TAH.
BL-10	Existing sample site near the North Shore State Recreation Area. This area is heavily used for launching boats, swimming, camping, and personal watercraft operation. This site has previously exceeded the water quality standard for TAH.
BL-11	Existing sample site in the east basin near the mouth of Meadow Creek.
BL-26	New sample site located in the middle of the bay near North Shore State Recreation Area and west of location BL-10. Location will assess attenuation of hydrocarbons commonly detected at sample site BL-10.
BL-27	New sample site located in the main traffic lane for users leaving North Shore State Recreation Area. Location will assess the area between the north bay and east basin.

The sample plan also includes a sample schedule to collect samples on days that should represent a variety of watercraft usage patterns. These sample dates are divided into “standard” sample days and “intensive” sample days to reflect the frequency of sampling that will occur for each day. There will be seven intensive sample days: four days over Memorial Day weekend and three days over Independence Day weekend. Table 3 presents the planned sample days, the type of sampling that will occur, and the reasoning for sampling on each day.

**TABLE 3: SAMPLE SCHEDULE**

Sample Date	Type	Reason
May 9, 2009 (approximate – date will occur soon after ice goes out)	Standard	Low watercraft activity – Establish baseline lake conditions for the summer and determine hydrocarbon accumulation from winter activities
May 23, 2009	Intensive	High watercraft activity – Memorial Day weekend
May 24, 2009	Intensive	High watercraft activity – Memorial Day weekend
May 25, 2009	Intensive	High watercraft activity – Memorial Day
May 26, 2009	Intensive	Low watercraft activity – Monitor lake conditions following holiday
June 17, 2009	Standard	Low watercraft activity – Mid-week sample date
June 27, 2009	Standard	Moderate to high watercraft activity – Weekend day
July 4, 2009	Intensive	High watercraft activity – Independence Day
July 5, 2009	Intensive	High watercraft activity – Independence Day weekend
July 6, 2009	Intensive	High watercraft activity – Independence Day weekend
July 25, 2009	Standard	Moderate to high watercraft activity – Weekend day
August 15, 2009	Standard	Moderate to high watercraft activity – Weekend day
September 7, 2009	Standard	High watercraft activity – Labor Day

A “standard” sample day will entail a single sample event for each sample site. Samples will be collected for analysis of BTEX and measurement of water quality parameters. This approach will provide a discrete snapshot of water quality in Big Lake for each “standard” sample day. The order for sampling and the depths at which samples will be collected are presented in Table 4.

**TABLE 4: SAMPLING PROGRAM FOR STANDARD SAMPLE DAYS**

Sample Site Order	Sample Depth
BL-4	0.15 meters and 0.5 meters
BL-7	0.15 meters
BL-8	0.15 meters and 0.5 meters
BL-27	0.15 meters
BL-26	0.15 meters
BL-10	0.15 meters and 0.5 meters
BL-11	0.15 meters
BL-1	0.15 meters
BL-2	0.15 meters
BL-3	0.15 meters
BL-5	0.15 meters
BL-6	0.15 meters

Water quality parameters will be collected to determine the location and thickness of the lake’s thermocline and to assess influence from incoming water at Meadow Creek. Data for the thermocline will be used with the analytical results for BTEX samples to assess

the depth and resulting volume of water that may be impaired, and data for influence from incoming waters will be used with analytical results for BTEX samples to assess the contribution of hydrocarbons from upgradient in the watershed.

An “intensive” sample day will include multiple sample events for sample sites BL-10, BL-26, and BL-27, as well as single sample events for the other sample sites. Samples will be collected for analysis of BTEX and measurement of water quality parameters. This plan will allow for an analysis of the trend of TAH concentrations during the boating day at the intensive sample sites. In addition, the sample design, combined with watercraft usage observations, will yield the necessary contaminant concentrations, lake characteristics, and watercraft data to estimate loading of petroleum hydrocarbons in Big Lake. The order and schedule for sampling and the depths at which samples will be collected are presented in Table 5.

**TABLE 5: SAMPLING PROGRAM FOR INTENSIVE SAMPLE DAYS**

Sample Site	Sample Time	Sample Depth
BL-1	Any	0.15 meters
BL-2	Any	0.15 meters
BL-3	Any	0.15 meters
BL-4	Any	0.15 meters and 0.5 meters
BL-5	Any	0.15 meters
BL-6	Any	0.15 meters
BL-7	Any	0.15 meters
BL-8	Any	0.15 meters and 0.5 meters
BL-10	09:00, 12:00, 15:00, 18:00, 21:00	0.15 meters and 0.5 meters
BL-11	Any	0.15 meters
BL-26	09:00, 12:00, 15:00, 18:00, 21:00	0.15 meters
BL-27	09:00, 12:00, 15:00, 18:00, 21:00	0.15 meters

The 13 combined “standard” and “intensive” sample days will yield the total number of samples as presented in Table 6.

**TABLE 6: ANALYTICAL PROGRAM**

Sample Day	Number of Sample Days	Number of Primary Samples Per Day	Number of Primary Samples Per Program
Standard	6	16	96
Intensive	7	32	224

Motorized watercraft activity also will be monitored on four of the intensive sampling days: May 24, May 25, July 5, and July 6. The purpose is to gather watercraft usage data that will be used in conjunction with sample analytical data to estimate daily loading of petroleum hydrocarbons to Big Lake. The calculated loading estimates for these four “intensive” sample days will be extrapolated to “standard” sample days to assess loading

throughout the summer season. The strategy for monitoring watercraft involves the placement of an observer on the shore near sample site BL-2 and the placement of an interviewer at the North Shore State Recreation Area.

The observer near sample site BL-2 will count the number of motorized watercraft during each hour for a 12-hour period from 09:00 to 21:00 hours. Each watercraft will only be counted once per hour. The observer, who will be experienced in visual determination of engine types, will identify, if possible, the type of engine (2-stroke or 4-stroke) on each motorized watercraft. Possible errors made in the visual identification of engine type will be cross-checked against the survey results of the interviewer, which are discussed below, to ascertain the quality of the data. Appendix C contains the form that the observer will use for recording observations.

The interviewer located at the North Shore State Recreation Area will conduct brief, voluntary surveys of each user at the public boat launch. For lake users who are launching, the interviewer will count the watercraft, note the time of launch, and ask the user what type and size of engine is being used. For lake users returning to the launch area, the interviewer will verify the number of hours the user was on the lake. In addition, the interviewer will count any other motorized watercraft visible in the north bay area that were not launched from the North Shore Recreation Area and note what type of engine likely is powering the watercraft. Appendix C contains the form that the interviewer will use for recording observations.

The field team collecting water samples also will make general use observations at each sample site for all sample days to augment watercraft usage data. In addition, OASIS will cross-check its watercraft counts against launch fees collected by the Alaska Department of Natural Resources at the North Shore and South Shore State Recreation Areas.

## **B.2. Sampling Methods**

Field personnel will conduct water sampling from a 22-foot, v-hull boat powered with a 4-stroke engine. The field team will navigate to the sample sites using an onboard GPS unit with stored waypoints. When the boat is approximately 100 feet from the sample site, the boat operator will turn off the engine to allow the boat to coast to the sample site. When the boat reaches the sample site, the field team will deploy an anchor to maintain sample position.

When the field team reaches the initial sample site each day, a sample will be collected off the stern of the boat directly adjacent to the outboard to assess potential hydrocarbon contribution from the sample watercraft. The sample will be collected by placing three uncapped 40-milliliter amber sample vials in the Wildco® hydrocarbon sampler and lowering the sampler so that inlet ports on the top of the sampler are at a depth of 0.15 meters (m). The sampler will release air bubbles as it fills, and when the bubbles cease the sampler will be brought to the surface. At this point, the sample bottles will be retrieved from inside the sampler where they are immersed in water. The bottles will be field-preserved with hydrochloric acid (HCl) and capped so that no headspace remains

in the bottles. Sample protocol will follow the United States Geological Survey report "Field Guide for Collecting Samples for Analysis of Volatile Organic Compounds in Stream Water for the National Water Quality Assessment Program," which is presented in Appendix D. During this initial sample, the field team will document the number of other motorized watercraft on the water in order to assess potential hydrocarbon contribution from other watercraft.

For sampling at all sample sites, the following activities will occur:

- Lower weighted, graduated polyethylene tubing that is connected to a peristaltic pump to a depth of 0.15 m below water surface. Use the peristaltic pump to draw water through a flow cell and measure pH, temperature, specific conductivity, and dissolved oxygen using the YSI® multi-probe meter, which will be calibrated according to Section B.7. Parameters will be recorded when readings stabilize.
- Perform the first step again at 0.5 m, and then at 1 m increments beginning at 1 m and ending at 10 m or the bottom of the water body, whichever is less.
- Collect samples for analysis of BTEX by placing three uncapped 40-milliliter amber sample vials in the Wildco® hydrocarbon sampler and lowering the sampler using one of the manual pot pullers attached to each side of the boat. The sampler should be lowered so that the inlet ports on top of the sampler are at a depth of 0.15 m. The sampler will release air bubbles as it fills, and when the bubbles cease the sampler will be brought to the surface using the manual pot puller. At this point, the sample bottles will be retrieved from inside the sampler where they are immersed in water. The bottles will be field-preserved with HCl and capped so that no headspace remains in the bottles. Sample protocol will follow the United States Geological Survey report "Field Guide for Collecting Samples for Analysis of Volatile Organic Compounds in Stream Water for the National Water Quality Assessment Program," which is presented in Appendix D.
- For sample sites BL-4, BL-8, and BL-10, also perform the previous step at a depth of 0.5 m.

For the collection of field duplicate samples, place four uncapped 40-milliliter amber sample vials in the Wildco® hydrocarbon sampler and lower the sampler so that inlet ports on the top of the sampler are at the required sample depth (0.15 m or 0.5 m). The sampler will release air bubbles as it fills, and when the bubbles cease the sampler will be brought to the surface. At this point, the sample bottles will be retrieved from inside the sampler where they are immersed in water. The bottles will be field-preserved with HCl and capped so that no headspace remains in the bottles. Two vials will be labeled as the primary sample, and the other two vials will be labeled as the blind duplicate sample.

For the collection of MS/MSD samples, place four uncapped 40-milliliter amber sample vials in the Wildco® hydrocarbon sampler and lower the sampler so that inlet ports on the top of the sampler are at the required sample depth (0.15 m or 0.5 m). The sampler will release air bubbles as it fills, and when the bubbles cease the sampler will be

brought to the surface. At this point, the sample bottles will be retrieved from inside the sampler where they are immersed in water. The bottles will be field-preserved with HCl and capped so that no headspace remains in the bottles. All four vials will be labeled as a single sample.

The Wildco® hydrocarbon sampler will be decontaminated between samples by rinsing the device with lake water. If a sheen is visible at a sample site, or if the field team believes significant hydrocarbon concentrations may be present at a sample site, or if the sampler is placed in an area with visible organic matter, then the field team will conduct a thorough flushing of the sampler at a location that is not a sample site and removed from observed contamination.

Lastly, during sampling at each sample site, field personnel will count or make an estimate of the number of motorized watercraft that are present in the area during sampling activities. This data and all other sampling data will be recorded on a sample data sheet, which is included in Appendix E.

### B.3. Sample Handling and Custody

Individual samples for analysis will be placed in the appropriate pre-cleaned sample containers as shown in Table 7. To ensure sample integrity, specific sampling and documentation procedures will be followed. These procedures will include labeling containers prior to sampling, extensive sample and site information recording, appropriate sample handling, and comprehensive chain-of-custody procedures. Sample and site information will be recorded in the field notebooks. Quality control samples or additional sample volume for laboratory QC will be collected as appropriate and are discussed in more detail in Section B.5. All samples will be immediately placed in coolers and packed with gel ice after sampling and will remain chilled to 4°C during transportation to the approved laboratory. Samples will be transported by vehicle or by air shipment to the analytical laboratory. All samples shipped will be accompanied with completed chain-of-custody forms, and coolers will be sealed with signed and dated fiber tape for shipment. Holding times and sample preservation requirements are described in Table 7. Holding times for each sample analysis type will be met.

**TABLE 7: PRESERVATION AND HOLDING TIMES FOR SAMPLE ANALYSIS**

Analyte/ Method	Matrix	Container	Preservative	Holding Time
BTEX/ EPA 624	Water	3 x 40 mL vials	HCL to <2 pH, chill to 4°C	14 days

Sample documentation procedures will include project field notebooks, chain-of-custody forms, and sample labels. Specific information such as site identification, sample identification numbers, sampling observations, and sample collection time and date will be recorded in field notebooks and data sheets. Additionally, photographic documentation will be collected during each sampling event.

Unique sample IDs will be based on the following format:

09-BL-DATE-XX-YY-AA

Where: 09 = year

BL = Big Lake

DATE = month and day (i.e., 0523)

XX = sample site (i.e., 01)

YY = sample depth (i.e., 15 or 50)

AA = sample designator (i.e., SW or TB)

For example, a water sample collected on May 23 at sample site BL-01 from a depth of 0.15 meters would have the following sample ID: 09-BL-0523-01-15-SW.

## B.4. Analytical Methods

Water quality analytical methods that will be used throughout this project are outlined in Table 8. All analysis methods used for this program are EPA approved. Appendix F contains the analytical method for EPA 624.

**TABLE 8: ANALYTICAL METHODS, PRECISION AND ACCURACY**

Analyte	Method	Method Detection Limit	Precision (RPD) <sup>1</sup>	Accuracy (%R) <sup>1</sup>
Benzene	EPA 624	0.152 µg/L	30%	70-130%
Toluene	EPA 624	0.0988 µg/L	30%	79-121%
Ethylbenzene	EPA 624	0.0771 µg/L	30%	82-120%
Xylene	EPA 624	0.320 µg/L	30%	81-121%

1- For a discussion of Precision (RPD) and Accuracy (%R), see Section A.7.

OnSite Environmental of Redmond, Washington, will perform the analyses. Their Quality Management Plan (QMP) is on file with the ADEC QA Officer.

## B.5. Quality Control

Quality control activities in the field will include adherence to documented procedures and the comprehensive documentation of sample collection information included in the field notebooks and data sheets. A rigidly enforced chain-of-custody program will ensure sample integrity and identification. The chain-of-custody procedure documents the handling of each sample from the time the sample was collected to the arrival of the sample at the laboratory.

Analytical methods in use on the program have been approved and documented by the EPA. These methods will be used as project-specific protocols to document and guide analytical procedures. Adherence to these documented procedures will ensure that analytical results are properly obtained and reported.

Quality control activities in the field will consist of the following items:

- Adherence to documented procedures in this QAPP
- Cross-checking of field measurements and recording to ensure consistency and accuracy

- Comprehensive documentation of field observations, sample collection, and sample identification information

Internal laboratory quality control checks will include the use of surrogate solutions and quality control samples such as procedural (or method) blanks, LCS, MS/MSD, standard reference materials (SRMs) or EPA QC check samples, and duplicates as specified in the EPA-approved analytical procedures. Surrogate compounds will be spiked into the samples as appropriate to measure individual sample matrix effects associated with sample preparation and analysis.

In addition to laboratory QC samples, multiple field quality control samples will also be collected. One field duplicate sample will be collected for every ten project samples and sent to the lab blind to test for precision of analytical procedures. A trip blank will be submitted to the lab during each sampling event to ensure that equipment handling and transport procedures do not introduce contamination. A list of the quality control samples and their collection frequency is included in Table 9.

**TABLE 9: QUALITY CONTROL SAMPLES**

Quality Control Sample	Frequency
Method Blanks	per EPA 624 Method Requirements
Laboratory Control Sample/Laboratory Control Sample Duplicate	1 per SDG
Surrogate Compounds	3 per EPA 624 Method Requirements
Matrix Spike/Matrix Spike Duplicates	1 per 20 samples
Field Duplicate	1 per 10 samples
Trip Blank	one per cooler

Table 10 presents an estimate of the complete analytical summary for the Big Lake water quality monitoring project.

**TABLE 10: ANALYTICAL SUMMARY**

Parameter/ Analytical Method	Sample Day	Number of Primary Samples Per Program	Number of Duplicate Samples Per Program	Number of Trip Blanks Per Program	Number of MS/MSD Samples Per Program	Total Number of Samples Per Program
BTEX/EPA 624	Standard	96	12	6	6	120
	Intensive	224	28	7	14	273

Laboratory duplicates and the blind field duplicate will be compared to the RPD criteria for the methods provided in Table 8. Spiked QC samples including surrogates, MS, and LCS will be compared to the %R values in Table 8. Concentrations of contaminants of concern reported in method blanks will be compared to reported values in the analytical samples. If analytical sample results are less than five times the concentration reported in the method blank, then results will be reported as a laboratory contaminant.

Concentrations of contaminants of concern reported in trip blanks will be compared to reported values in the analytical samples. If analytical sample results are less than ten times the concentration reported in the trip blank, then results will be reported as not-detected at the concentration in the analytical sample.

Results from quality control samples allow the assessment of quality assurance parameters such as accuracy and precision of the data. Any data falling outside the acceptable criteria as defined in the methods will be appropriately investigated and qualified as described in Section D.2.

## **B.6. Instrument/Equipment Testing, Inspection, and Maintenance**

Field equipment used for collection, measurement, and testing will be subject to a strict program of control, calibration, adjustment, and maintenance. Analytical samples for BTEX will be collected for laboratory analysis in the field using a Wildco VOC sampler, described in Appendix D. Routine maintenance of the VOC sampler will be conducted prior to each sampling event. Maintenance will include a visual inspection that all parts are present, attached correctly, and devoid of any obvious contamination. The sampler will be submerged in lake water for ten seconds with bottles inside the sampler to check that all four copper tubes are not blocked and are sampling correctly.

Water quality parameters including pH, temperature, conductivity, and dissolved oxygen will be measured in the field during each sampling event using a YSI 556 field meter. Routine maintenance on the meters will be conducted according to schedules described in the manual provided by the manufacturer and recorded in the maintenance log stored in its carrying case. In case of instrument failure, a spare YSI meter will either be on-site or available within a few hours.

## **B.7. Instrument/Equipment Calibration and Frequency**

The YSI meter will be calibrated and adjusted prior to each sample day using required instrument procedures with known standards for pH and standard conductivity. The dissolved oxygen probe will be calibrated using a saturated atmosphere and current barometric pressure. All calibration measurements will be recorded on the appropriate field forms or in field logbooks and will be available for review by ADEC upon request.

## **B.8. Inspection/Acceptance of Supplies and Consumables**

All buffer solutions used for field instrument calibration will be checked for expiration date, sufficient quantity, and discoloration. All calibration information is documented in the project field notebook and on a calibration sheet that accompanies the instrument.

Qualified field staff will check all field equipment and supplies required for this project to ensure their technical specifications before use. Evaluation criteria that will be used are listed below:

- Ensure that equipment and supplies have been cleaned if they are reusable or are sterile if they are packaged.
- Equipment is in serviceable condition.

- The appropriate chain-of-custody procedures have been taken if equipment or supplies were shipped.
- Cooler temperature will be maintained at 4°C +/- 2°C.

Extra sample containers will be available in the event re-sampling becomes necessary.

## **B.9. Non-Direct Measurements**

Non-direct measurements collected for this project include the following:

- Weather data
- Alaska State Parks launch fees collected at the two state recreation areas

Weather data will be obtained from NOAA weather station 503731 in Houston, Alaska, from the National Weather Service website. A record of launch fees will be provided by Alaska State Parks.

## **B.10. Data Management**

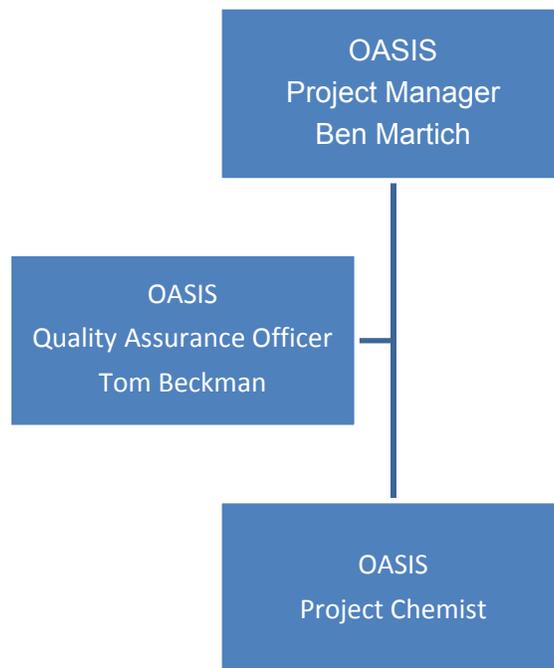
Data obtained during sampling activities will be entered into field notebooks or field data sheets.

The following is a list of possible data information that will be kept in OASIS' or OnSite's files for ADEC review upon request:

- Field equipment and chemicals maintenance, cleaning, and calibration records
- Field notebooks
- Photographs of sampling stations and events
- Chain-of-custody forms
- Laboratory equipment maintenance, cleaning, and calibration records
- Laboratory bench sheets, control charts, and SOPs
- Records of QA/QC problems and corrective actions (field and/or laboratory)
- Laboratory data QC records
- Records of data review sheets
- Duplicate, performance evaluation, and other QA/QC control records (field and laboratory)
- Data review, verification, and validation records

Field data will be validated according to the procedures of Section D. The project manager will direct a project chemist, under supervision of the Quality Assurance Officer, to review laboratory data reports. The Quality Assurance Officer will provide oversight and approval of the review process. After review of data, the Project Manager will oversee the transcription of data for reporting purposes. Analytical data will be transcribed electronically from electronic data deliverables. A minimum 10%-percent check of transcriptions will be performed to assess potential errors.

Figure 3 presents a flow chart for managing data.



**FIGURE 3: DATA MANAGEMENT CHART**

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## **C. ASSESSMENT AND OVERSIGHT**

### **C.1. Assessments and Response Actions**

Assessments of field procedures may be performed by either the Quality Assurance Officer or the ADEC Water Quality Assurance Officer, or their designees. Assessments may include field audits, lab audits, data audits, peer reviews and/or systems audits.

Should the sampling staff, laboratory personnel, or Quality Assurance Officer find errors in sampling or analysis, the Quality Assurance Officer will notify the Project Manager and the party responsible for the error or deficiency and recommend methods of correcting the deficiency. The responsible party will then take action to correct the problem and will report corrections to the QA Officer and Project Manager.

The Quality Assurance Officer will review the QA/QC procedures used for the sampling and analytical program. Procedures for this review are included in Section D.2 to meet the data quality criteria specified in Section D.7. The Quality Assurance Officer will report these assessment records in the draft and final reports.

OnSite Environmental performs analytical methods based on established procedures such as those published by the EPA, the Washington State Department of Ecology, and ADEC. OnSite Environmental maintains current certifications for the ADEC Contaminated Sites Program and Washington Department of Ecology Laboratory Accreditation (Appendix G). ADEC Division of Water does not have an accreditation program; therefore, no certification of Onsite Environmental is required to run the proposed analytical method for this project, EPA 624.

### **C.2. Reports to Management**

Sampling results will be summarized in the draft and final reports completed for this project. These reports will include the results of project assessments listed above. Reports will be submitted to the ADEC Project Manager.

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## D. DATA VALIDATION AND USABILITY

### D.1. Data Review, Validation, and Verification Requirements

Analytical results will be reviewed and validated in accordance with United States Environmental Protection Agency (USEPA) documents, including the *USEPA Environmental Data Verification and Validation (EPA QA/G-8)*, August 1999; the *USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (EPA 540/R-94/012)*, 1994; and the *USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (EPA 540/R-94/013)*, 1994. In addition, an ADEC laboratory data review checklist will be completed for each laboratory report.

OASIS will conduct data review and validation using the following methods for project samples, including their associated quality control duplicates and laboratory quality control samples.

- Review of sample handling and analytical and field data for completeness, accuracy, holding time compliance, and QC sample frequency compliance
- Evaluation of laboratory blank samples
- Evaluation of the accuracy and precision of field duplicate samples, LCS/LCSD, and MS/MSD samples
- Assignment of data qualifiers, when necessary, to reflect limitations identified in the data assessment process
- Estimation of completeness

### D.2. Validation and Verification Methods

The following procedures will be used to determine if data meets the data quality objectives and criteria specified in Section A.7. If data QA/QC procedures do not meet the specified criteria, the Quality Assurance Officer will review all field and laboratory records to determine the cause. If equipment failures are limiting the usability of the data, calibration and maintenance procedures will be reviewed and changed as needed. If sampling or analytical procedures are causing the failures, methods will be reviewed to resolve the errors. Any changes or modifications to quality control procedures will be approved by ADEC prior to inclusion in the QAPP.

#### D.2.1. Review of Sample Handling

Proper sample handling techniques are required to ensure sample integrity. During data review, the sample handling procedures identified below are evaluated to determine potential effects on data quality:

- Review of field sample collection and preservation procedures to determine whether they were completed in accordance with the requirements specified by the analytical methods.
- Review of chain-of-custody documentation to ensure control and custody of the samples were maintained.
- Review of sample holding times between sample collection, extraction, and analysis (see Table 7 in Section B.3).

- Review of sample conditions upon receipt at the laboratory.
- Review of QA/QC samples. Specific procedures for review of QA/QC samples are included in the sections below.

### **D.2.2. Laboratory Blank Samples**

Laboratory blank samples (method and instrument blanks) are laboratory-prepared, analyte-free samples used to detect the introduction of contamination or other artifacts into the laboratory sample handling and analytical process. These blanks play an especially important role in sampling programs involving trace-level analyses or analytes that are common solvents found in a laboratory. None of the analytes of concern for this project are common laboratory contaminants. If a contaminant is discovered in an analytical sample at less than five times the concentration it is found in a laboratory blank, the contaminant will be considered a laboratory contaminant and all results for that contaminant in the batch will be flagged as such. Otherwise, the contaminant will be reported as an environmental contaminant. Similarly, if a contaminant is discovered in an analytical sample at less than five times the concentration it is found in a trip blank, the contaminant will be considered a field contaminant and all results for that contaminant in the sample shipment will be flagged as such. Otherwise, the contaminant will be reported as an environmental contaminant.

### **D.2.3. Laboratory Control Samples**

LCS are used to assess analytical performance under a given set of standard conditions. Synthetic samples, containing some or all of the analytes of interest at known concentrations, are prepared independently from calibration standards. The samples consist of LCS and LCSD. LCS will be analyzed with each analytical batch and may be used to estimate analytical accuracy and precision by comparing measured results to actual concentrations. LCS/LCSD percent recoveries will be checked on laboratory reports to ensure they are within the limits set by the EPA methods listed in Table 8 in Section B.4.

LCS are also duplicated in the laboratory and then analyzed in an identical manner by the laboratory to assess the laboratory's internal precision. The analytical precision is expressed by the RPD (see calculation in Section A.7). Analytical precision and accuracy should meet the method criteria listed in Table 8 in Section B.4.

### **D.2.4. Matrix Spike and Matrix Spike Duplicates**

MS samples are actual field samples to which known amounts of select compounds (one, or more, of the analytes of interest) are added. Both spiked and unspiked aliquots are analyzed. The difference between the concentration of the spike compound(s) in the spiked and unspiked aliquots is compared to the amount of spike added before the extraction process. Since actual samples are used for the recovery determination, the matrix effects can be evaluated. Usually expressed as a percentage of the mass of the spiked amount, spike recovery is the measurement of accuracy anticipated for the sample matrix. Percent recoveries will be compared to EPA method-specific recoveries listed in Table 8.

MS samples are also duplicated in the laboratory and then analyzed in an identical manner by the laboratory to assess sample reproducibility and the laboratory's internal precision. The analytical precision is expressed by the RPD between the measurement results of the two duplicate samples. Analytical precision and accuracy should meet the criteria provided in Table 8. MS/MSD samples will be run on each batch of samples.

#### **D.2.5. Surrogates**

Surrogate compounds will be added to all samples being analyzed for TAH to evaluate analytical accuracy for each individual sample. Surrogate compounds are chemically similar to the analytes of interest but are not expected to be present in the field samples. Recovery of these surrogate compounds gives an estimate of the effectiveness of the extraction and analysis for each individual sample. Surrogate recoveries (%R) should meet the criteria provided in Table 8 for each analyte.

#### **D.2.6. Field Duplicate Samples**

Field duplicate samples will be collected simultaneously with a primary project sample. Duplicates are treated in the same manner as the primary sample during all phases of sample collection, handling, and analysis. Duplicate sample results are used to assess precision, including variability associated with both the laboratory analysis and the sample collection process (i.e., QC purposes). One duplicate field sample will be collected for each ten project samples and will be submitted blind to the laboratory.

Analytical results will be reviewed for agreement with each other or their respective reporting limits and evaluated for comparability. Estimated results quantified below the reporting limit and qualified with a "J" flag are not considered significant for the purpose of data agreement. The comparison between project and field duplicate sample results should meet RPD criteria for each method listed in Table 8.

#### **D.2.7. Reporting Limits**

The reporting limits are the lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory conditions. For many analytes, the reporting limit analyte concentration is selected by the laboratory as the lowest non-zero standard in the calibration curve. Sample reporting limits vary based on sample matrix and dilution of the samples during analysis. Reporting limits should be equal to or below the PQLs provided in Table 1 for each method.

#### **D.2.8. Data Qualification**

Qualifiers will be applied to QC samples when acceptance criteria are not met and corrective action is not performed or is unsuccessful. These same qualifiers will be applied to the associated sample data. Table 11 defines the data qualifiers.

**TABLE 11: DATA QUALIFIERS**

Qualifier	Description
J	The analyte was positively identified, the quantitation is an estimate or was below the analytical reporting limit.
U	The analyte was analyzed for, but not detected. The associated numerical value is at or below the method detection limit.
R	The data are unusable due to deficiencies in the ability to analyze the sample and meet QC criteria.
B	The analyte was found in an associated blank, as well as in the sample.
M	A matrix effect was present.
H	Analysis was performed outside of the recommended holding time.

### D.2.9. Completeness

Completeness is calculated after the QC data have been evaluated and the qualifiers have been applied to the sample data. Invalid results, broken or spilled samples, and samples that are unable to be analyzed for other reasons are included in the assessment of completeness. The criteria and calculation to determine completeness are provided in Section A.7. If data cannot be qualified to meet completeness goals, OASIS will consult with the ADEC Project Manager to determine if additional sampling should be performed to accomplish data quality objectives.

### D.3. Reconciliation with User Requirements

The Project Manager will review all data deliverables upon receipt from the lab. Laboratory results will be checked for data qualifiers entered by the lab to ensure that sample collection and preservation procedures were adequate and that laboratory analysis procedures met quality assurance objectives. Any outstanding issues will be addressed immediately with the lab and/or sampling staff to ensure that project quality assurance objectives are met.

The Project Manager and Quality Assurance Officer will review and validate the data during the draft and final reporting stages. If there are any problems with quality sampling and analysis, these issues will be addressed immediately and methods will be modified to ensure that data quality objectives are being met. Modifications to monitoring will require notification to ADEC and subsequent edits to the approved QAPP.

## **APPENDIX A**

**Map of Sample Sites that Exceeded TAH Water Quality Standard in 2004 and 2005**

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MAP OF SAMPLE SITES THAT EXCEEDED TAH WATER QUALITY STANDARD IN 2004 AND 2005



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## **APPENDIX B**

### **2009 Sample Locations**

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# MAP OF SAMPLE LOCATIONS



SAMPLE ID	WGS 84		NAD 83 STATE PLANE ZONE 4	
	X	Y	X	Y
BL-01	-149.92967	61.53072	1652695.27717	2751423.37519
BL-02	-149.89617	61.53106	1658541.86327	2751553.04699
BL-03	-149.87358	61.53725	1662478.92468	2753824.52612
BL-04	-149.83703	61.53236	1668861.33925	2752051.02556
BL-05	-149.85022	61.53167	1666559.98647	2751792.05248
BL-06	-149.84409	61.53154	1667630.32085	2751748.25520
BL-07	-149.83455	61.53997	1669287.47464	2754834.13422
BL-08	-149.84628	61.54042	1667240.83908	2754992.41389
BL-10	-149.85555	61.54795	1665616.95687	2757742.69463
BL-11	-149.87758	61.54981	1661772.68247	2758414.94679
BL-26	-149.85976	61.54891	1664881.70067	2758091.97646
BL-27	-149.86712	61.54818	1663598.67437	2757822.43091

## **APPENDIX C**

### **OASIS Observer and Interviewer Forms**

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# Big Lake - Observer Form

Date: \_\_\_\_\_

Hour	Watercraft Vessel Count	2-stroke	4-stroke	Unknown	Photos
9:00					
10:00					
11:00					
12:00					
13:00					
14:00					
15:00					
16:00					
17:00					
18:00					
19:00					
20:00					



## **APPENDIX D**

### **USGS Sampling Protocols for VOC Sampler**

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**FIELD GUIDE FOR COLLECTING SAMPLES FOR  
ANALYSIS OF VOLATILE ORGANIC  
COMPOUNDS IN STREAM WATER FOR THE NATIONAL  
WATER-QUALITY ASSESSMENT PROGRAM**

*By* Larry R. Shelton  
U.S. GEOLOGICAL SURVEY  
Open-File Report 97-401  
Sacramento, California  
1997

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U.S. DEPARTMENT OF THE INTERIOR  
BRUCE BABBITT, Secretary  
U.S. GEOLOGICAL SURVEY

Gorden P. Eaton, Director

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**CONTENTS**

[Glossary](#)

[Abstract](#)

[Introduction](#)

[Overview](#)

[Preparation for sample collection](#)

Site selection

Sampling Equipment

Sampler

Support Equipment

[Equipment cleaning](#)

[Sample collection procedures](#)

Preparation

Routine sampling

Dip sampling

[Sample processing procedures](#)

[Field measurements](#)

[Quality assurance and quality control](#)

Field blanks

Trip blanks

Field-matrix spikes

Replicate samples

[Documentation](#)  
[Sample identification](#)  
[Shipping](#)  
[References cited](#)  
[Appendix - Selected technical memorandums](#)

## FIGURES

[1. Schematic of the volatile organic compound \(VOC\) sampler.](#)

## TABLES

[1. List of volatile organic compound analytes for the National Water-Quality Assessment Program](#)

[2. List of equipment and supplies for collecting and processing stream-water volatile organic compound \(VOC\) samples](#)

## CONVERSION FACTORS, ABBREVIATIONS, AND ACRONYMS

### Conversion Factors

---

Multiply By To obtain

---

foot (ft) 0.3048 meter  
gallon (gal) 3.785 liter  
inch (in.) 25.4 millimeter

---

Temperature is given in degrees Celsius (C), which can be converted to degrees Fahrenheit (F) by the following equation:  $F=1.8(C)+32$

### Abbreviations

L, liter  
mg/L, microgram per liter  
mL, milliliter  
lb, pound  
ASR, analytical services request  
DIW, deionized water  
FS, field spike  
FSR, field-spike replicate  
HCL, hydrochloric acid  
ID, identification  
QA, quality assurance  
QC, quality control  
VBW, pesticide/volatile blank water  
VG, VOC grade blank  
VOC, volatile organic compound

### Acronyms

NAWQA, National Water-Quality Assessment  
NWQL, National Water Quality Laboratory  
USGS, U.S. Geological Survey  
WRD, Water Resources Division

### GLOSSARY

Environmental Setting -- Land areas characterized by a unique, homogeneous combination of natural and human-related factors, such as row-crop cultivation on glacial-till soils.

Gaging station -- A fixed site on a stream or river where hydrologic and environmental data are collected.

Indicator Sites -- Stream sampling sites located at outlets of drainage basins with relatively homogeneous land use and physiographic conditions. Basins are as large and representative as possible, but still encompassing primarily one Environmental Setting (typically 50 to 500\ x 11 km<sup>2</sup>).

Integrator Site -- Stream sampling sites located downstream from drainage basins that are large and complex and commonly contain multiple Environmental Settings. Most Integrator Sites are on major streams with drainage basins that include a substantial portion of the Study Unit area (typically, 10 to 100 percent).

Point sample -- A sample collected at a single point in the stream cross section and at a single point in the stream vertical.

Study Unit -- A major hydrologic system of the United States in which NAWQA studies are focused. NAWQA Study Units are geographically defined by a combination of ground- and surface-water features and usually encompass more than 10,000 km<sup>2</sup> of land area. The NAWQA design is based on assessment of these Study Units, which collectively cover a large part of the Nation, encompass the majority of population and water use, and include diverse hydrologic systems that differ widely in natural and human factors that affect water quality.

Water-Column Studies -- Assessment of physical and chemical characteristics of stream water, including suspended sediment, dissolved solids, major ions and metals, nutrients, organic carbon, and dissolved pesticides, in relation to hydrologic conditions, sources, and transport.

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## **Field Guide For Collecting Samples For Analysis of Volatile Organic Compounds In Stream Water For The National Water-quality Assessment Program**

*By* Larry R. Shelton

### **Abstract**

For many years, stream samples for analysis of volatile organic compounds have been collected without specific guidelines or a sampler designed to avoid analyte loss. In 1996, the U.S. Geological Survey's National Water-Quality Assessment Program began aggressively monitoring urban stream-water for volatile organic compounds. To assure representative samples and consistency in collection procedures, a specific sampler was designed to collect samples for analysis of volatile organic compounds in stream water. This sampler, and the collection procedures, were tested in the laboratory and in the field for compound loss, contamination, sample reproducibility, and functional capabilities. This report describes that sampler and its use, and outlines field procedures specifically designed to provide contaminant-free, reproducible volatile organic compound data from stream-water samples.

These guidelines and the equipment described represent a significant change in U.S. Geological Survey instructions for collecting and processing stream-water samples for analysis of volatile organic compounds. They are intended to produce data that are both defensible and interpretable, particularly for concentrations below the microgram-per-liter level. The guidelines also contain detailed recommendations for quality-control samples.

### **INTRODUCTION**

One of the goals of the National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey (USGS) (Hirsch and others, 1988) is to establish a network of comprehensive and integrated urban water-quality studies to develop an understanding of the occurrence, significance, sources, movement, and fate of environmental chemicals in urbanized hydrologic

systems (Lopes and Price, 1997; Squillace and Price, 1996). The occurrence of many contaminants, including volatile compounds, are being assessed in urban areas. For the information to be comparable among studies in different parts of the Nation, consistent procedures and equipment specifically designed to produce contaminant-free, reproducible volatile organic compound (VOC) data from stream-water samples are critical.

The assessment of VOCs in stream water is part of the Water-Column Studies (Gilliom and others, 1995), which focus on assessing the occurrence, concentrations and seasonal distribution of VOCs (Lopes and Price, 1997). The purpose of this report is to describe the equipment used to sample VOCs in streams and the procedures for using the VOC sampler. Companion reports by Koterba and others (1996) outline the procedures used for collecting VOC samples in ground-water, and Majewski and Capel (1995) discuss sampling of pesticides in the atmosphere.

The glossary at the front of this report includes brief definitions of some terms used in this report. Key terms used to describe the NAWQA Program are capitalized. Trade names used in connection with equipment or supplies do not constitute an endorsement of the product.

## **OVERVIEW**

The sampling designs for stream-water studies rely on coordinated sampling of varying intensity and scope at two general types of sites, Integrator Sites and Indicator Sites. Integrator Sites are chosen to represent water-quality conditions of streams and rivers in the large basins affected by complex combinations of land-use settings, point sources, and natural influences. Indicator Sites, in contrast, are chosen to represent water-quality conditions of streams with relatively homogeneous land use and, usually, are associated with smaller basins in specific Environmental Settings. Most, but not all VOC samples will be collected at urban Indicator Sites located in residential and commercial areas. Site selection and sampling strategies for urban Indicator Sites are described in Lopes and Price (1997).

Two primary sampling strategies are used at the selected Integrator and Indicator Sites: (1) fixed interval sampling (usually monthly) characterizes the spatial and temporal distribution of contaminants in relation to hydrologic conditions and contaminant sources, and (2) intensive sampling characterizes seasonal and short-term temporal variability of contaminant transport during high flows and at more frequent fixed intervals.

Most VOCs are man-made compounds that are components of gasoline, by-products of chlorinating drinking water, or solvents. Laboratory analysis is done by the purge-and-trap technique to separate the VOCs from the water matrix, and the quantitation is done by capillary-column gas chromatography/mass spectrometry. Results are reported in micrograms per liter.

The USGS National Water Quality Laboratory (NWQL) VOC analysis schedule 2020 will be used. The analytes are summarized in table 1.

## **PREPARATION FOR SAMPLE COLLECTION**

### **Site Selection**

All VOC sampling sites should be at or near streamflow gaging stations because stream discharges associated with contaminant concentrations are needed to evaluate relations between streamflow and water-quality characteristics (Gilliom and others, 1995; Lopes and Price, 1997).

The sample collection site should not be more than a few hundred feet from the station.

Collection sites should be located in relatively straight channel reaches where the flow is uniform. Collecting samples directly in a ripple, or from ponded or sluggish water, should be avoided. Sites directly upstream or downstream of confluences or direct sources of contamination also should be avoided to minimize problems caused by backwater effects or poorly mixed flows. In addition, samples collected downstream from a bridge can be

contaminated by runoff from the road surface. Proper field judgement is crucial to achieve a sample representative of the typical environmental conditions.

Samples should be collected at the centroid of the stream in the same cross section throughout the project. This will eliminate many of the potential problems that might arise during the interpretation of the data. This does not mean that the same section used during the low-water wading stage must be used during higher stages that require the use of a bridge or cableway. However, the flow characteristics at different cross sections can result in incomparable data if the cross sections are not located near each other or in the same flow regime. Rapidly changing stage, discharge, and constituent concentrations dictate that sampling schemes and techniques be planned carefully in advance to ensure that representative samples are obtained.

**Table 1.** List of volatile organic compound analytes for the National Water-Quality Assessment Program.

[CAS, Chemical Abstract Service number; PCODE, USGS Parameter Code]

-----  
Laboratory analyses: Schedule Number 2020  
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CAS number PCODE Compound  
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Halogenated Alkanes

630-20-6 77562 1,1,1,2-Tetrachloroethane  
71-55-6 34506 1,1,1-Trichloroethane  
79-34-5 34516 1,1,2,2-Tetrachloroethane  
76-13-1 77652 1,1,2-Trichloro-1,2,2-trifluoroethane  
79-00-5 34511 1,1,2-Trichloroethane  
75-34-3 34496 1,1-Dichloroethane  
96-18-4 77443 1,2,3-Trichloropropane  
96-12-8 82625 1,2-Dibromo-3-chloropropane  
106-93-4 77651 1,2-Dibromoethane  
107-06-2 32103 1,2-Dichloroethane  
78-87-5 34541 1,2-Dichloropropane  
142-28-9 77173 1,3-Dichloropropane  
594-20-7 77170 2,2-Dichloropropane  
74-97-5 77297 Bromochloromethane  
75-27-4 32101 Bromodichloromethane  
74-83-9 34413 Bromomethane  
124-48-1 32105 Chlorodibromomethane  
75-00-3 34311 Chloroethane  
74-87-3 34418 Chloromethane  
74-95-3 30217 Dibromomethane  
75-71-8 34668 Dichlorodifluoromethane  
75-09-2 34423 Dichloromethane  
67-72-1 34396 Hexachloroethane  
74-88-4 77424 Iodomethane  
56-23-5 32102 Tetrachloromethane  
75-25-2 32104 Tribromomethane  
75-69-4 34488 Trichlorofluoromethane  
67-66-3 32106 Trichloromethane

Halogenated Alkenes

75-35-4 34501 1,1-Dichloroethene  
563-58-6 77168 1,1-Dichloropropene  
107-05-1 78109 3-Chloro-1-propene

593-60-2 50002 Bromoethene  
75-01-4 39175 Chloroethene  
87-68-3 39702 Hexachlorobutadiene  
127-18-4 34475 Tetrachloroethene  
79-01-6 39180 Trichloroethene  
156-59-2 77093 cis-1,2-Dichloroethene  
10061-01-5 34704 cis-1,3-Dichloropropene  
156-60-5 34546 trans-1,2-Dichloroethene  
10061-02-6 34699 trans-1,3-Dichloropropene  
110-57-6 73547 trans-1,4-Dichloro-2-butene

#### Aromatic Hydrocarbons

71-43-2 34030 Benzene  
91-20-3 34696 Naphthalene  
100-42-5 77128 Styrene

#### Alkyl Benzenes

488-23-3 49999 1,2,3,4-Tetramethylbenzene  
527-53-7 50000 1,2,3,5-Tetramethylbenzene  
526-73-8 77221 1,2,3-Trimethylbenzene  
95-63-6 77222 1,2,4-Trimethylbenzene  
95-47-6 77135 1,2-Dimethylbenzene  
108-67-8 77226 1,3,5-Trimethylbenzene  
108-38-3 85795 1,3-Dimethylbenzene  
106-42-3 --- 1,4-Dimethylbenzene  
611-14-3 77220 2-Ethyltoluene  
100-41-4 34371 Ethylbenzene  
98-82-8 77223 Isopropylbenzene  
108-88-3 34010 Methylbenzene  
104-51-8 77342 n-Butylbenzene  
103-65-1 77224 n-Propylbenzene  
99-87-6 77356 p-Isopropyltoluene  
135-98-8 77350 sec-Butylbenzene  
98-06-6 77353 tert-Butylbenzene

#### Halogenated Aromatics

87-61-6 77613 1,2,3-Trichlorobenzene  
120-82-1 34551 1,2,4-Trichlorobenzene  
95-50-1 34536 1,2-Dichlorobenzene  
541-73-1 34566 1,3-Dichlorobenzene  
106-46-7 34571 1,4-Dichlorobenzene  
95-49-8 77275 2-Chlorotoluene  
106-43-4 77277 4-Chlorotoluene  
108-86-1 81555 Bromobenzene  
108-90-7 34301 Chlorobenzene

#### Ethers and other Oxygenated Compounds

78-93-3 81595 2-Butanone  
591-78-6 77103 2-Hexanone  
108-10-1 78133 4-Methyl-2-pentanone  
67-64-1 81552 Acetone  
60-29-7 81576 Diethyl ether  
108-20-3 81577 Diisopropyl ether

637-92-3 50004 Ethyl tert-butyl ether  
1634-04-4 78032 Methyl tert-butyl ether  
109-99-9 81607 Tetrahydrofuran  
994-05-8 50005 tert-Amyl methyl ether

#### Others

107-02-8 34210 2-Propenal  
107-13-1 34215 2-Propenenitrile  
75-15-0 77041 Carbon disulfide  
97-63-2 73570 Ethyl methacrylate  
96-33-3 49991 Methyl acrylate  
126-98-7 81593 Methyl acrylonitrile  
80-62-6 81597 Methyl methacrylate

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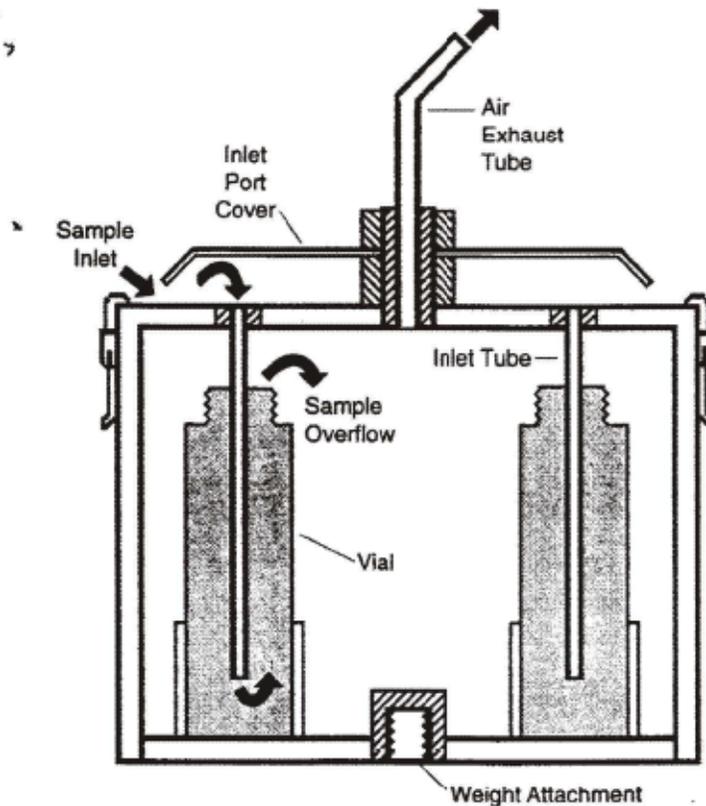
## **Sampling Equipment**

### **Sampler**

Obtaining representative VOC samples in flowing streams is a difficult task. Of critical importance is the design and operation of the equipment and the sampling procedure (Brown and others, 1970). Samplers must be designed to collect an unbiased sample of environmental conditions. One important process is to flush atmospheric gases from the sampler before collecting a stream sample (Kilpatrick and others, 1989).

A newly developed VOC sampler designed by the USGS and built by Wildco (fig. 1) will be used to collect stream-water samples for VOC analysis. This sampler has been tested for analyte loss, reproducibility, and carryover contamination in the laboratory and in field settings. The sampler, which is made of noncontaminating materials (stainless steel and refrigeration-grade copper) that will not sorb the analytes of interest, can collect a sample representative of environment conditions in most streams. An important function of the sampler design is to evacuate air and other gases from the sampler before collecting a sample. The VOC sampler weighs 11 lb and can be suspended, by hand, from a short rope or chain while wading a stream. However, when sampling during periods of high flow, 10-lb weights can be added to keep the sampler vertical when it is suspended from a bridge or cableway.

The sampler is designed to collect a sample at a single point in the stream. The stainless-steel sampler holds four 40-mL vials. Copper tubes extend to the bottom of each vial from the inlet ports on top of the sampler. The vials fill and overflow into the sampler body, displacing the air in the vials and in the sampler through the exhaust tube. The total volume of the sampler is eight times larger than the vials; therefore, the vials are flushed seven times (removing the air) before the final volume is retained in the vial. The small (1/16-in. inside diameter) copper inlet ports results in a slow (3 to 4 minutes) filling time. This important design feature helps to produce a representative sample and allows sufficient time to place the sampler at the desired depth. The sampler begins to fill as soon as it enters the stream; however, the final sample is retained in the vial during the last 15 to 20 seconds of the filling process. A cover over the inlet ports prevents contamination from surface oil and debris when the sampler is removed from the stream.



**Figure 1.** Schematic of volatile organic compound (VOC) sampler. The sampler body is made of stainless steel, weighs 11 pounds, and is 6 inches in diameter and 6 inches high. It has an air exhaust tube extending above the sampler, and four copper inlet tubes that extend into four 40-milliliter sample vials.

**Figure 1.** Schematic of volatile organic compound (VOC) sampler. The sampler body is made of stainless steel, weighs 11 pounds and is 6 inches high. It has an air exhaust tube extending above the sampler, and four copper inlet tubes that extend into four 40-milliliter sample vials.

#### Support Equipment

Field vehicles are commonly used for more than one purpose (such as streamflow measurements, gaging station maintenance, construction, stream sampling, and sample processing). Sample contamination is more likely to occur when these multiuse vehicles are used to collect and process water samples. Glues and adhesives used in vehicles, and the cabinet construction, can contaminate samples for VOCs. Therefore, it is important that the processing area be free of contaminants, plastics, dirt, fumes, and oil residue. Samples should be removed from the sampler, processed, and capped streamside to avoid possible contaminants in the vehicles. Each vehicle should have a separate storage area for the VOC sampling equipment and supplies. A complete equipment list is given in table 2.

**Table 2.** List of equipment and supplies for collecting and processing stream-water volatile organic compound (VOC) samples.

*[Sources for some items are listed to maintain quality standards. OCALA, USGS Water-Quality Service Unit at Ocala, Florida; NWQL, National Water Quality Laboratory; VG, VOC grade blank; VBW, pesticide/volatile blank water]*

### **Sampling equipment and supplies**

Volatile organic compound (VOC) sampler (Wildco 990-J98)  
Vial, glass, amber septum, 40 milliliter (NWQL and OCALA 333FLD)  
Rope, nylon, 1/4-inch diameter (OCALA 84FLD)

### **Cleaning and storing equipment and supplies**

Gloves, vinyl, powderless (OCALA 155HWS)  
Detergent, phosphate free, 0.2 percent by volume (OCALA 62FLD)  
Methanol, pesticide grade  
Deionized water  
VOC grade blank water (VG or VBW) (NWQL)  
Bottles, wash, plastic, for detergent (OCALA 357FLD)  
Bottles, wash, Teflon, for VG water (OCALA 377FLD)  
Bottles, wash, Teflon, for methanol (OCALA 377FLD)  
Basins, wash, plastic (2)  
Brush, scrub, soft metallic  
Bag, plastic, sealable, medium (OCALA 23FLD)  
Storage container, sealable, 8 inches x 8 inches x 12 inches  
Foil, aluminum, heavy duty  
Container, waste, solvent, 5 gallons

### **Processing equipment and supplies**

Cannister, stainless steel, 8 quarts with cover (for field blanks)  
Flask tongs  
Gloves, vinyl, powderless (OCALA 155HWS)  
Hydrochloric acid 1:1 acid, in Teflon vials (NWQL)  
Kit, matrix spike (NWQL)  
pH paper (alkacid test ribbon)  
Bottle labels (OCALA 84FLD)  
Sleeves, foam (OCALA 358FLD)  
Coolers, shipping, 1 gallon  
Coolers, shipping, 5 gallon s  
Bags, plastic, 5 gallons  
Ice

### **Miscellaneous equipment and supplies**

Boots, hip  
Waders, chest  
Tools  
First aid kit  
Highway emergency kit  
Forms, field documentation (OCALA)  
Forms, analytical request (NWQL)  
Tissues, laboratory  
Pens, marking, permanent, (OCALA 77FLD)  
Field meters, conductance, pH, dissolved oxygen  
Supplies for field measurements

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## **EQUIPMENT CLEANING**

All equipment that will come in contact with the sample should be soaked in a dilute phosphate-free detergent solution; rinsed with tap water, VOC grade blank (VG) water, and methanol; and then air dried prior to each field trip and between sites (Shelton, 1994). Detergents and methanol should be used with care to avoid the possibility of the residue contaminating the sample. A thorough native-water rinse is required at each field site before sampling to remove any remaining cleaning agents and to equilibrate the equipment to the sampling conditions. A list of

the supplies needed for equipment cleaning is given in table 2, and detailed procedures for cleaning the VOC sampler are outlined below.

1. Open sampler.
2. Submerge top and base in a 0.2-percent solution of phosphate-free detergent. Scrub the sampler thoroughly with a nylon brush. Use a small squeeze bottle, filled with the detergent, to flush the copper tubing.
3. Rinse the sampler thoroughly with warm tap water or deionized water (DIW) to remove all soap residue.
4. Using a Teflon squeeze bottle, rinse with a minimum amount of methanol. Place the used methanol in a waste container for proper disposal (see Water Resources Division [WRD] memorandum 94.07, Appendix).
5. Allow to air dry (cover loosely with aluminum foil to avoid airborne contamination). If complete air drying is not possible, rinse three times with VG water.
6. Wearing vinyl gloves, reassemble the sampler.
7. Wrap areas that will come in contact with the sample with aluminum foil, and place in a sealable plastic bag. Use a large sealed container to protect the sampler in storage and during transport.
8. Rinse the sampler (without the vials) with 2 to 3 L of native water prior to sampling.

## **SAMPLE COLLECTION PROCEDURES**

### **Preparation**

The timing of the VOC sampling should be planned to avoid possible contamination by other collection and processing activities (such as procedures and equipment that use methanol). Before beginning any other activity collect and process the VOC samples at the site. The entire sampling and processing procedure (removing it from the storage container, loading the sampler, sampling, and acidifying the sample) should be done at streamside, well away from other processing activities.

### **Routine Sampling**

VOC samples should be collected where the stream velocity represents the average flow, which is typically near mid-channel in the cross section. The following procedure is designed to produce a single-vertical point sample. When collecting samples for VOC analyses, special care must be taken to avoid contamination from any oily film and debris floating on the stream surface. The samples should be collected directly into the prebaked 40-mL amber-glass vials as follows:

1. Reclean the sampler, if necessary (see 'Equipment Cleaning' section).
2. Transport the sampler to the collection site and rinse three times with native water or submerge it in the stream for several minutes.
3. In a protected area, away from any direct source of contamination and wearing vinyl gloves, uncap four 40-mL unlabeled vials and place them in the sampler. Secure and lock the sampler top in position. Store the vial caps in a protected area.
4. Lower the sampler into the stream near mid-channel to about one half of the total depth at that vertical. Add weights if the stream velocity is great enough to pull the sampler downstream.

5. Collect a sample by holding the sampler in one position until the sampler is full. Air bubbles will rise to the surface while the sampler is being filled, but may be difficult to see. This takes about 3 to 4 minutes. The sample will be retained in the vial during the last 15 to 20 seconds of sampling.
6. Remove the sampler when bubbles are no longer present or after about 5 minutes, and return to a protected area at the side of the stream for processing.

### **Dip Sampling**

In very shallow streams where the VOC sampler cannot be submerged, a representative sample usually can be obtained manually by immersing an open vial (dip sample) near the centroid of flow. Wearing vinyl gloves, lower a 40-mL vial to about one half of the stream depth. Point the vial into the stream current, remove the cap, allow the vial to fill, then slowly bring it to the surface. Add hydrochloric acid (HCL), carefully cap the vial, and check for air bubbles that may be trapped in the vial. A dip sample should never be taken when it is possible to use the sampler. Consistent procedures will avoid the possibility of a sampling bias.

### **SAMPLE PROCESSING PROCEDURES**

Biodegradation and chemical reactions, such as oxidation and volatilization, can change many of the compounds present in natural waters before analyses in a laboratory. Therefore, samples must be preserved as soon as possible after collection. The method of preserving VOCs includes the addition of 1:1 HCL and refrigeration to 4°C to arrest microbiological activity and to minimize volatilization. Great care must be exercised in the field to prevent compound loss or sample contamination. Because exhaust fumes and adhesives in field vehicles may be a source of contamination, processing samples streamside can best prevent contamination. Evaluate trip and field blanks to confirm that the processing area is appropriate.

To preserve the samples, add 1:1 HCL to lower the pH to 2 or less, and immediately place the vials on ice. To determine the volume of acid to add, collect a hand dipped test sample in a used 40-mL vial. Add HCL to the test sample to lower the sample pH to less than 2.0. Two drops of HCL should be adequate for most conditions; however, some environmental samples may require additional HCL. At no time should you use more than six drops of HCL. Alkacid test ribbons can be used to estimate the pH.

By following this sequence for sample preservation, the risk of contaminating a sample is reduced. Acid should be stored and transported properly (see WRD memorandum 94.06, Appendix). These procedures are summarized below.

1. Wearing vinyl gloves, open the sampler carefully at streamside.
2. Using metal tongs, slowly lift each vial from the sampler reservoir. Do this carefully to avoid losing the convex meniscus.
3. Add drops (usually two, but no more than six) of 1:1 HCL to lower the pH to less than 2, and cap the vial.
4. Agitate the vial and check for air bubbles. Discard if bubbles are present.
5. Three vials from the same sampler set are required for one complete sample. Resample completely, if necessary.
6. Label the samples, wrap each with a foam sleeve, and place them on ice.
7. Clean the sampler and store it properly (see 'Equipment Cleaning' section).

The minimum information required on each vial is the site identification (ID) number, date and time sampled, preservation, and schedule number, as shown on the example below:

09498500  
04-24-1997 @ 1200  
HCL to <2.0 pH  
SCH - 2020

## **FIELD MEASUREMENTS**

Water temperature, specific conductance, pH, dissolved oxygen, and alkalinity could change dramatically within minutes or hours after sample collection. Immediate analysis in the field is required if the results are to be representative of in-stream conditions.

Water temperature and dissolved oxygen should be measured directly from the stream, and several readings are required in the cross section to obtain a stream average. A composite stream sample should be collected for specific conductance, pH, and alkalinity. A single field meter that measures specific conductance, water temperature, pH, and dissolved oxygen directly in the stream may be used. Detailed information on the procedures, equipment, and supplies necessary for the field analyses is presented in reports by Shelton (1994) and Wilde and Radtke (in press).

## **QUALITY ASSURANCE AND QUALITY CONTROL**

The sources of variability and bias introduced by sample collection and processing affect the interpretation of water-quality data. Quality-assurance (QA) plans ensure that the data collected are compatible and of sufficient quality to meet program objectives. These guidelines and the Study Unit design guidelines for NAWQA should be used when preparing QA plans. Specific details for QA plans are described by Shampine and others (1992).

Investigators in each Study Unit must document the quality of their data by collecting quality-control (QC) samples. A series of QC samples (blanks, replicates, and spikes) must be obtained during VOC investigations because the quality of the data collected, and the validity of any interpretation, cannot be evaluated without QC data. Detailed procedures for preparing QC samples for VOCs, and the recommended frequencies, are described in Mueller and others (1997).

### **Field Blanks**

Field blanks are used to determine whether (1) equipment-cleaning protocols adequately remove residual contamination from previous use, (2) sampling and sample-processing procedures result in contamination, and (3) equipment handling and transport periods of sample collection do not introduce contamination. Field blanks for VOCs are collected immediately before processing a routine environmental sample. Load four 40-mL vials into the sampler. Pour VG water into a clean (see 'Equipment Cleaning' section) stainless-steel cannister, and then collect two 40-mL vials from the cannister for the cannister-blank sample. Submerge the sampler containing four 40-mL vials in the cannister and allow to fill. Remove the vials and process the field and cannister blanks in the same manner as the environmental sample. Process the samples using the NWQL analytical schedule for environmental samples. If analytical results indicate carryover of residues, perform additional field tests to determine the source of the contamination. A more rigorous cleaning procedure might be necessary. Field blanks produce the most valuable QC data to evaluate potential contamination.

### **Trip Blanks**

Trip blanks are used to determine whether external VOCs from bottle handling and analytical processes, independent of the field sample processing scheme, are contaminating the samples. Trip blanks are provided upon request and are prepared and distributed to each Study Unit by the

NWQL. These trip blanks bottles should be stored and transported with the other bottles used for collecting the environmental sample, and then submitted for analysis in the same manner. Trip blanks should never be opened in the field. If analytical results indicate that samples have been contaminated, additional blanks should be processed to identify the source. Trip blanks should only be prepared with field blanks.

### **Field-Matrix Spikes**

Field-matrix spikes are designed to (1) assess recoveries from field matrices and (2) assist in evaluating the precision of results for the range of target analytes in different matrices. Biases and interferences can result from sample matrices and from other processes that occur from the time the sample vial is preserved in the field to the time the vial is analyzed in the laboratory. After collecting the environmental sample, immediately collect a second set of four vials for the field-matrix spikes and preserve each using HCL. Add a standard spike solution using a microliter gas-tight syringe. Matrix-spike kits (solution and syringe) with instructions are available from the NWQL. Label two vials 'FS' (field spike) and two vials 'FSR' (field-spike replicate). Record the lot number and volume of the spike solution on the field notes and on the NWQL analytical services request (ASR) form. Send each set of vials-two FS and two FSR-as separate sample sets, including the environmental sample, to the laboratory for analyses.

### **Replicate Samples**

Sample replicates are designed to provide information needed to (1) estimate the precision of concentration values determined from the combined sample-processing and analytical method and (2) evaluate the consistency of identifying target analytes for VOCs. Each replicate sample is an aliquot of the environmental sample collected in the same sampler, processed at the same time, and stored and shipped in the same way. Compare the analytical results to determine if accurate, consistent data can be reproduced.

### **DOCUMENTATION**

All field activities and site information should be documented on standard surface-water-quality field notes (Shelton, 1994). A complete documentation will aid in future analyses of the collected information.

Field notes should include the following information:

1. Station name and number.
2. Date and time (1 minute earlier than environmental sample).
3. Gage height, discharge, or both; stage conditions.
4. Type of sample (single-vertical point sample).
5. Sampler (VOC sampler).
6. Sampling method (bridge, cableway, wading).
7. Depth and width of stream at sampling location.
8. Location within the cross section (midstream).
9. Depth of sampling (mid depth).
10. Field analyses and calibration (temperature, conductance, pH, alkalinity, oxygen).
11. Detailed alkalinity titration.
12. Type of samples collected (VOC, major ions, quality control, and others).
13. Name of sample collector(s).
14. Site information: color and odor of the stream, weather conditions, and others.

### **SAMPLE IDENTIFICATION**

Consistent specific identification of samples is essential for national data aggregation. For this reason, a data-coding strategy has been developed for the NAWQA Program. Use the following instructions for coding information onto the water quality field notes and on the NWQL ASR forms. The most critical codes for proper sample identification are the station ID number, sample medium, and sample type. Different sample-time coding is specified to distinguish among multiple samples collected during the same site visit. VOC samples will have a time 1 minute earlier than all other environmental samples to segregate the VOC analytical results from other analyses. For QC samples, the time codes are used to establish a rationale for associating the necessary sample codes with each individual sample. Do not use fictitious station ID numbers for routine QC samples.

#### **VOC Environmental Sample**

STATION ID - Same as other environmental sample

DATE - Same as other environmental sample

TIME - One minute earlier than the other environmental samples

SAMPLE MEDIUM - '9' (surface water)

SAMPLE TYPE - '9' (regular)

Parameter 71999 (Sample purpose) - '15' (NAWQA)

Parameter 99111 (QA data with sample) - '10' (blank)

#### **Field Blank**

STATION ID - Same as environmental sample

DATE - Same as environmental sample

TIME - Exact time of preparation (different from other blanks)

SAMPLE MEDIUM - 'Q' (QA sample, artificial)

SAMPLE TYPE - '2' (blank)

COMMENTS - 'PREVIOUS SAMPLE AT:' station ID, date/time

Parameter 71999 (Sample purpose) - '15' (NAWQA)

Parameter 99102 (Type of blank sample) - '100' (field)

Parameter 99104 (Blank lot number) - Enter first five digits

Parameter 99101 (Source of blank solution) - '10' (NWQL)

#### **Cannister Blank**

STATION ID - Same as environmental sample

DATE - Same as environmental sample

TIME - One minute earlier than field blank (different from other blanks)

SAMPLE MEDIUM - 'Q' (QA sample, artificial)

SAMPLE TYPE - 'B' (other)

COMMENTS - 'CANNISTER BLANK'

Parameter 71999 (Sample purpose) - '15' (NAWQA)

Parameter 99102 (Type of blank sample) - '100' (field)

Parameter 99104 (Blank lot number) - Enter first five digits

Parameter 99101 (Source of blank solution) - '10' (NWQL)

#### **Trip Blank**

STATION ID - Same as environmental sample

DATE - Same as environmental sample

TIME - Exact time of preparation (end of trip)

SAMPLE MEDIUM - 'Q' (QA sample, artificial)

SAMPLE TYPE - '2' (blank)

Parameter 71999 (Sample purpose) - `15' (NAWQA)  
Parameter 99102 (Type of blank sample) - `30' (trip)  
Parameter 99101 (Source of blank solution) - `10' (NWQL)  
Parameter 99109 (Start date YMMDD) - Date blanks received from NWQL  
Parameter 99110 (End date YMMDD) - Date trip blanks shipped to NWQL

### **Field-Matrix Spike**

STATION ID - Same as environmental sample  
DATE - Same as environmental sample  
TIME - `SPIKE (FS)' 6 minutes later than environmental sample (HH:X6)  
`SPIKE REPLICATE (FSR)' 7 minutes later than environmental sample (HH:X7)  
SAMPLE MEDIUM - `R' (QA surface water)  
SAMPLE TYPE - `1' (spike)  
COMMENTS - `FS or FSR', `SCH 9090 spike lot number \_\_\_\_\_'  
Parameter 71999 (Sample purpose) - `15' (NAWQA)  
Parameter 99104 (Spike lot number) - Enter first five digits  
Parameter 99105 (Replicate type) - `10' (concurrent)  
Parameter 99106 (Spike type) - `10' (field)  
Parameter 99107 (Spike source) - `10' (NWQL)  
Parameter 99108 (Spike volume) - volume used, in milliliters

### **Replicate Samples**

STATION ID - Same as environmental sample  
DATE - Same as environmental sample  
TIME - Same as VOC environmental sample  
SAMPLE MEDIUM - `9' (surface water)  
SAMPLE TYPE - `7' (replicate)  
Parameter 99111 (QA data with sample) - `30' (replicate sample)  
Parameter 99105 (Replicate type) - `10' (concurrent)  
Parameter 71999 (Sample purpose) - `15' (NAWQA)

### **SHIPPING**

Samples should be shipped by overnight express mail to the NWQL the same day of collection. A NWQL ASR form must be included with each sample. Place all glass vials in padded sleeves or pack in some other suitable manner to prevent breakage during shipment. Insulated water coolers (1 or 5 gal in volume) make good shipping containers. Chill with an adequate amount of ice to maintain the sample temperature between 0 and 4°C. The amount of ice needed depends on the length of time in transit from field to laboratory and on the season of the year. Ice should be placed inside a double plastic bag in the shipping container. Protect the NWQL ASR form and return labels from the ice by placing them in a sealable plastic bag and fastened it to the inside of the cooler lid with tape. Detailed guidelines on shipping samples are discussed in NWQL memorandum 95.04 (Appendix).

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#### **APPENDIX-SELECTED TECHNICAL MEMORANDUMS**

These Water Resources Division (WRD) and National Water Quality Laboratory (NWQL) memorandums are available in U.S. Geological Survey offices, nationwide:

WRD 94.06 SAFETY: Storage, transport, handling, and disposal of hydrochloric acid

WRD 94.07 SAFETY: Storage, transport, handling and disposal of methyl alcohol

NWQL 95.04 OPERATIONS: Shipping to the National Water Quality Laboratory

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**Back to:**

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## **APPENDIX E**

### **Water Sampling Log Sheet**

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# **APPENDIX F**

**EPA 624**

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## **APPENDIX G**

### **Laboratory Accreditation**

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