Little Susitna River Water Quality Sampling as Related to Petroleum Hydrocarbon Pollution

Quality Assurance Project Plan: Version1.1

Prepared on March 20, 2014 for:

The Alaska Department of Environmental Conservation

By:

ARRI
Aquatic Restoration & Research Institute

Cover Photograph. Boat launching at the Little Susitna River Public Use Facility, with inset of sample bottles being removed from the VOC sampler.

A1. Little Susitna River—Water Quality Investigations Related to Petroleum Hydrocarbon Pollution

Aquatic Restoration and Research Institute

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Quality Assurance Officer: gay a davis **Date:** 4/9/2014
Gay A. Davis

Alaska Department of Environmental Conservation

Project Manager: Laura K. Eldred **Date:** 4/11/14
Laura Eldred

Quality Assurance Officer: ______________________ **Date:** 4/14/14
Dr. Douglas Kolwaite

Effective Date:______________________

A2. Table of Contents

A3. Distribution List

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A4. Project/Task Organization

Laura Eldred, DEC Project Manager. Ms. Eldred will oversee the project for DEC; provide technical support, QAPP review and approval, and the review of all field, draft, and final reports.

Dr. Douglas Kolwaite, DEC Division of Water QA Officer. Dr. Kolwaite will be responsible for the review/approval of the QAPP. He will work with the DEC project manager to provide recommendations and requirements for sample collection and analyses to the DEC Project Manager.

Jeffrey C. Davis, ARRI Project Manager. The Project Manager (Figure 1) listed below will be responsible for all project components including data collection, entry, analyses, and reports. Mr. Davis will make sure that all field data are collected as specified in the QAPP. He will oversee testing and maintenance of all equipment prior to use and perform the review of data entry and analyses. He will be responsible for preparing all reports.

Gay A. Davis, ARRI Quality Assurance Officer. Ms. Davis will be responsible for making sure that all data are collected, replicate samples taken and analyzed, and all data entered and analyzed correctly. She will be the primary contact for the contracting laboratory.

AM Test, Inc.—AM Test, Inc. Laboratories, 13600 NE 126th Place, Suite C, Kirkland, WA, 98034. AM Test, Inc. will be responsible for analyzing all collected water samples for TAH and providing quality control and quality assurance reports relative to parameters tested.

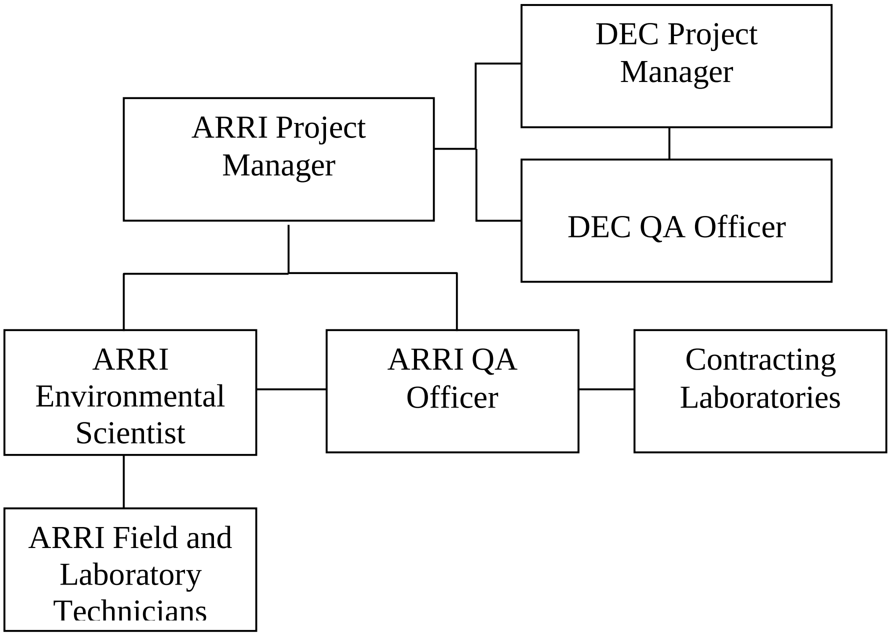

Figure 1. Relationship and lines of communication among personnel and organizations.

A5. Problem Definition/Background

The Little Susitna River, located in Southcentral Alaska, supports all five species of Pacific salmon. Primary use of the Lower Little Susitna River, from its mouth upstream 63 miles to the Parks Highway, is related to the salmon sport fishery. This part of the river is also a popular recreational area for motorized and non-motorized boating and camping. The primary motorized boat access point to the lower Little Susitna River is the state operated Public Use Facility (PUF) boat launch located approximately 40 km (25 miles) upstream from Cook Inlet. Sport fishing use of the river is concentrated near the PUF.

Historic DEC Weekly Sampling

Starting in 2007, weekly water samples for TAH analyses were collected at sites distributed from 1 km (0.6 miles) upstream to 0.5 km (0.3 miles) downstream of the PUF boat launch to evaluate the influence of motorized boat use on water quality. Subsequent sampling through June 2011 was designed to verify the magnitude, exposure duration, and frequency of the TAH exceedances. Additional sample sites were added as the project progressed in order to determine the longitudinal extent of TAH pollution from upstream to downstream of the PUF. Downstream sites extended to 32 km (20 miles) below the PUF and upstream to 12 km (6 miles). From July 2007-June 2011, the majority of the sampling was conducted once per week on either Saturday or Sunday (generally the highest use days of the week) between 12:00 and 16:00 during May – September.

Historic DEC Intensive Sampling

Along with determining the longitudinal extent of TAH in the river, DEC conducted intensive sampling to determine the temporal variability of the TAH pollution over two and three day sample periods. This intensive sampling occurred on anticipated heavy-use weekends with samples taken every three hours between 06:00 and 21:00 at the sample site located immediately downstream of the PUF boat launch (LS-0). The two (2)-day intensive sample events were conducted in June 2010 and June 2011 coinciding with the king salmon fishery. The three (3)-day intensive sample events were conducted in August 2009 and August 2010 during the more popular silver salmon fishery. A 96-hour sampling event took place in August 2012 to determine a 4-day average concentration of TAH. However, poor fish returns led to the Alaska Department of Fish and Game (ADFG) closing the fishery and no further TAH sampling occurred.

Historic DEC Sample Collection

Representative samples at multiple sample sites upstream and downstream of the PUF boat launch were collected to determine the spatial extent of the TAH pollution along the river corridor. Water samples were collected mid-depth in the water column adjacent to the thalweg using a volatile organic compound (VOC) sampler and methods developed by the United States Geological Survey. All sampling followed a DEC-approved QAPP and sampling plan. Samples were analyzed for benzene, ethyl-benzene, toluene, and xylene (BTEX) at a certified laboratory using EPA method 624. TAH was calculated as the sum of the concentration of these four compounds, excluding values below method detection limits. Maximum and average TAH values were compared against state water quality criteria (WQC) of 10 µg/L described in 18 AAC 70.

TAH exceedances were observed primarily in the months of June and August. TAH exceedances ranged from slightly over 10 µg/L to over 75 µg/L (recorded below the PUF in spring 2008) (Table 1). TAH concentrations were highest downstream from the PUF boat launch. TAH concentrations greater than 10 µg/L were recorded at sites located from 4 km (2.5 miles) upstream from the PUF boat launch to 12 km (7.5 miles) downstream. The source of the petroleum hydrocarbons in the Little Susitna River is from motorized boats.

The 2007-2012 cumulative data report, as well as each individual year's detailed report, are available on the Department's web site:
http://dec.alaska.gov/water/wnpspc/protection_restoration/LittleSusitnaWQ/index.htm

DEC is in the process of developing a petroleum hydrocarbon impairment listing methodology. This listing methodology outlines how DEC determines persistent exceedances of the water quality criteria including benchmarks for determining frequency, duration and magnitude of water quality exceedances. This proposed listing methodology is available from DEC.

Table 1. Summary of previous TAH sampling results.

WQS	Max Observed Value (µg/L)	# Samples Exceeding WQS	Total # Samples	Sampling Period
10 µg/L	10.17	1	15	July – Sept 2007
	75.2	29	72	May - Aug 2008
	12.7	2	49	May - June 2009
	27.2	11	70	July - Sept 2009
	15.8	4	52	May - June 2010
	30.4	14	40	Aug-10
	20.5	5	12	Jun-11*
	4.4	0	50	Aug-12*
Total	75	65	362	

* The Chinook fishery was closed in June 2011 and the coho fishery closed in August 2012 due to low returns.

A6. Project/Task Description Total Aromatic Hydrocarbons

State Water Quality Standards (WQS, 18 AAC 70) for "petroleum hydrocarbons, oils, and grease for freshwater uses," are based on the observation of a visible sheen on the water or shoreline for designated uses (water supply for drinking, culinary, and food processing; agriculture; and water recreation) and numeric criteria for water supply for aquaculture and the growth and propagation of fish (Table 2). The numeric criteria for total aromatic hydrocarbons is 10 µg/L (DEC 2011).

State WQS's do not specify whether the numeric criteria for petroleum hydrocarbons are due to acute or chronic effects. The lighter, more volatile hydrocarbons tend to have toxic rather than mutagenic or carcinogenic chronic effects (Scannell et al. 2005). Current numeric criteria were based upon studies of acute toxicity and sublethal effects on Alaska species (Scannell et al. 2005); however, results from an extensive literature review documented both acute and chronic effects.

The water quality criterion for TAH is based on chronic effects. Therefore, measures of 4-day average concentrations are necessary to evaluate potential Category 5 listing.

The purpose of this project is to obtain additional measures of hydrocarbon concentrations in order to assist DEC in determining whether a Category 5 water quality listing is warranted. Three project objectives have been developed by DEC.

1. To collect water quality information on the Lower Little Susitna River for evaluating concentrations of total aromatic hydrocarbons (TAH) during the spring Chinook fishery in late May -early June and the coho fishery during the month of August.
2. To correlate motor craft numbers with TAH concentrations by gathering motorized boat usage information from the Department of Natural Resources Little Susitna River Public Use Facility entrance booth.
3. To provide the Department with a project report of the monitoring results. The project report will provide a discussion of the results and conclusions.

Table 2. Alaska Water Quality Standards (18 AAC 70) for Petroleum Hydrocarbons.

Designated Use	Water Quality Standard
(5) PETROLEUM HYDROCARBONS, OILS AND GREASE, FOR FRESH WATER USES	
(A) Water Supply **(i) Drinking, Culinary, and Food Processing**	May not cause a visible sheen upon the surface of the water. May not exceed concentrations that individually or in combination impart odor or taste as determined by organoleptic tests.
(ii)Agriculture, including irrigation and stock watering	May not cause a visible sheen upon the surface of the water.
(iii) Aquaculture	Total aqueous hydrocarbons (TAqH) in the water column may not exceed 15 µg/l (see note 7). Total aromatic hydrocarbons (TAH) in the water column may not exceed 10 µg/l (see note 7). There may be no concentrations of petroleum hydrocarbons, animal fats, or vegetable oils in shoreline or bottom sediments that cause deleterious effects to aquatic life. Surface waters and adjoining shorelines must be virtually free from floating oil, film, sheen, or discoloration.
(iv) Industrial	May not make the water unfit or unsafe for the use.
(B) Recreation **(i) Contact**	May not cause a film, sheen, or discoloration on the surface or floor of the waterbody or adjoining shorelines. Surface waters must be virtually free from floating oils.
Recreation **(ii) Secondary**	Same as (5)(B)(i).
(C) Growth and Propagation of Fish, Shellfish, Other Aquatic Life, and Wildlife.	Same as (5)(A)(iii).

Sampling locations

DEC scope of work has identified 7 sampling locations (Table 3). Sampling locations extend from 4 km above to 12 km below the Public Use Facility (PUF) boat launch. Previous sampling has documented TAH concentrations above 10 µg/L at each of these sampling locations on at least 1 sampling date. Sampling locations upstream from the PUF, while not expected to exceed the WQC provide values that can be used to estimate downstream transport. That is, using upstream TAH concentrations, flow times, and loss rates, one can estimate the portion of TAH at the PUF coming from upstream (upstream loading).

The sampling site at the PUF provides a location with easy access that can be used to monitor TAH concentrations over time. Samples collected immediately below the PUF are a combination of upstream loading and inputs at the boat launch. Motor inefficiencies (fuel discharged/fuel burned) are higher when motors are idling. Even though fuel use rates are low during idling, high inefficiencies and direct inputs from fueling, and runoff from the boat ramp due to removing drain plugs can result in high TAH loading at this location.

Sampling locations distributed downstream from the PUF are necessary to determine the longitudinal extent of exceedances. Downstream TAH concentrations are a combination of downstream transport within the water column plus additional boat inputs minus loss. Loss rates vary with initial concentration; however, at a flow time of 1.65 km/hr, and using loss rates measured on Big Lake, at an initial concentration of 30 µg/L, approximately 10 µg/L would be lost from the PUF to LS 12 km dn. TAH loss is lower at a lower initial concentrations, and with moderate inputs could result in cumulative downstream increases. That is, if inputs exceed loss rates, concentrations will increase downstream. The limited boat activity downstream of LS 12 km dn reduces the likelihood that 4-day average concentrations will exceed WQC below this sampling location.

Table 3. TAH 2014 sampling locations and frequency.

Sampling Locations	Sampling Frequency
LS 4 km up	Once per day between 13:00 – 16:00
LS 1 km up	Once per day between 13:00 – 16:00
LS 0, PUF	Five times per day: 07:00 10:00 13:00 16:00 20:00
LS 1 km dn	Once per day between 13:00 – 16:00
LS 4 km dn	Five times per day: 07:00 10:00 13:00 16:00 20:00
LS 8 km dn	Once per day between 13:00 – 16:00
LS 12 km dn	Once per day between 13:00 – 16:00

Sampling Dates

Sampling will be conducted over 96-hour or 120 hour periods on the dates specified in Table 4. The use of bait during the coho sport fishery opens on August 6. There is generally a large amount of boating activity on the Little Susitna when the use of bait is authorized. Other sampling dates may shift in consultation with the DEC project manager.

Table 4. Sampling dates identified within the scope of work. Asterisk denotes proposed modification to include the opening of bait fishing.

Month	Days
May	23 - 26
May	30, 31
June	1, 2
Aug	1 – 4
Aug	6 – 10*
Aug	14 – 18
Aug	21 - 25

Sampling Frequency

Proposed sampling frequency is shown in Table 3. At the intensive sampling locations (LS 0, and LS 4 km dn) will be collected 5 samples per day for a total of 20 samples per 4-day sampling event. The first sample time will be at 07:00. TAH concentrations in previous sampling at 05:00 were below detection limits and before most boat use, which starts around 06:00. The 07:00 sample will document inputs from initial daily boat activity. Three sampling events will occur during the most active portion of the day: 10:00, 13:00, and 16:00. The final sample will be collected at 20:00. The 20:00 sample will document the declining limb of daily TAH concentrations. Sampling will begin at LS 0 followed by LS 4 km dn. Therefore, sampling at LS 4 km dn will occur approximately 30 minutes later than at LS-0.

All other sites be sampled once each day between 13:00 and 16:00. Daily sampling at the additional sampling locations will provide information necessary to confidently assess the spatial extent of exceedances. In addition, daily longitudinal samples from 4 km up to 12 km dn will allow us to evaluate cumulative increase or decrease in concentrations downstream relative to boat activity and estimate the number of boats necessary for inputs to exceed TAH loss rates.

Additional Data Collection

Stream discharge will be measured on each day samples are collected at LS 1 km up. This will allow for calculation of total daily hydrocarbon flux and for evaluation of dilution due to changes in water volume. Measures of stream discharge will provide average water velocity that can be used to calculate flow times between sampling sites. In addition, average velocity can be used to estimate the distance and rate of flushing from upstream waters where concentrations were previously found to be below or very near detection limits. This information may be necessary to develop management options.

Stream water temperature will be measured concurrent with water sample collection. Water temperature will be used to evaluate potential differences in evaporative TAH loss. Water temperature will be measured with a temperature specific thermistor and meter at 0.5 x depth at each sampling location. In addition, water temperature loggers (Pro V2) will be deployed at LS-

0. LS 4 km dn and LS 12 km dn on the first sampling date and removed on the final sampling date. Water temperature loggers will record every 30 minutes.

Boat Use Surveys

Boat use data is necessary in order to calculate TAH discharge per boat and to investigate relationships between TAH discharge and boat motor type. ARRI will coordinate with Dan Amyot (DNR/DPOR Chief Ranger) to ensure that boat use data including motor type will be recorded at the PUF entrance booth. ARRI will check with the booth staff on a daily basis to ensure that they are recording information accurately. ARRI will make arrangements with booth staff to scan or photocopy records at the end of each day or before they are transferred to the State Parks Finger Lake office. DNR/DPOR information on boats passing the entrance booth, motor size and type (2-cycle, 2-cycle direct inject, and 4-cycle) during the time period the booth is open (~ 08:00 to 17:00) will provide an approximation of the total number of boats by motor type operating within the sampling reach for each sampling period.

ARRI will augment booth count data with stop action photography of the boat launch. The entrance booth usually is not operated prior to 08:00 or after 17:00. Boat activity prior to 08:00 could influence TAH concentrations in the 07:00 sample and activity following 17:00 could influence TAH concentrations in the 20:00 sample. Therefore, we recommend augmenting the booth data using stop action photography. A camera will be installed with a view of the boat launch and mooring area but out of view of the general public. The camera will be set to take an exposure every 5 minutes. The camera will be downloaded at the end of each day. Boat use counts can be obtained rapidly by viewing the series of photographs as a video in the ARRI laboratory following field sampling.

Project Reporting

A field sampling report will be provided to the DEC project manager following each sampling event, and draft and final monitoring reports will be provided following the summer field season. The ARRI project manager, with support from ARRI staff will develop a draft monitoring report for DEC. The draft report will contain an introduction summarizing previous sampling results, and evaluate project results relative to projective objectives. The draft report will clearly describe sampling collection methods and analyses and reference the DEC approved sampling plan and QAPP. The draft report will present the project results including tables and figures as appropriate. A table of sampling results will provide values for benzene, ethyl-benzene, toluene, and total xylene. TAH will be calculated as the sum of these molecules. When analytical results are below detection limits, a value of 0.5 x detection limit will be used to calculate TAH. For intensive sampling locations, daily averages will be calculated as the mean of the 5 samples. ARRI also will calculated weighted means for comparison, and in order to account for the differences in time between samples, including overnight. Averages over each 96-hour sampling event also will be calculated for each sampling location and evaluated for compliance with WQC as described in the draft listing methodology and in consultation with the DEC project manager. ARRI will use the 4-day average values for all sampling locations and the change in TAH concentrations downstream to provide recommendations to DEC regarding spatial extent of any exceedances if present. Two 4-day average values will be calculated from data collected during 5-day sampling events and the highest average will be used to evaluate compliance with WQS.

The project report will summarize boat use data collected by DNR/DPOR at the entrance booth supplemented with video counts. Boat use data will be used to calculate the percentage of boat motor use by motor type and size. The boat use data will be compared to previous years to determine if there is a change in the number of carbureted 2-stroke motors being used. The relationship between TAH concentrations, boat use numbers, boat motor size, and motor type will be analyzed. In addition, ARRI will attempt to model TAH concentrations using data from the intensive sampling locations, TAH loss rates, discharge, and boat use between sampling events in order to calculate TAH loading. These analyses will be used to assist DEC in the development of potential management options, if warranted.

The draft project report will discuss project results relative to previous sampling results within the Little Susitna River. The relationships between TAH concentration and boat use will be discussed relative to previous findings in the Little Susitna River and other similar published results. ARRI will provide a discussion of data results relative to proposed Category 5 listing including spatial and longitudinal extent. Any recommendations for future monitoring will be provided.

ARRI will distribute the draft report to the DEC project manager. ARRI will meet with the DEC project manager to discuss the draft report including any DEC comments. ARRI will incorporate these comments into a second draft for DEC review. ARRI will incorporate DEC comments into the second draft report and prepare a Final Report. ARRI will work with DEC to ensure that all data entry into Ambient Water Quality Monitoring System (AWQMS) is accurate and complete. ARRI will provide DEC with electronic and hard copies of reports, field data, project photographs, AWQMS spreadsheets. See Table 4 for a summary of sampling and reporting dates.

Table 5. Summary of project measures schedule and products.

Task	Measures	Start Date	End Date	Product
QAPP and Sampling Plan	None	March 4, 2014	April 30, 2014	QAPP and Sampling Plan
TAH Sampling	Water Samples collected 5 times each day for BTEX analyses	May 23, 2014	August 30, 2014	Laboratory Reports of BTEX; Field Sampling Reports
Boat Surveys	Entrance Booth Counts and Photographic Records.	May 23, 2014	August 30, 2014	Boat use during TAH sampling
Water Temperature	Point measures and data recording at 30 minute intervals.	May 23, 2014	August 30, 2014	Water temperature throughout the sampling period.
Discharge	Grab samples concurrent with TAH sampling.	May 23, 2014	August 30, 2014	Daily flow measures during the sampling periods.
Project Report	None	Sept 2014	Jan 2015	Formatted data for AWQMS, Draft and final Report of project results.

A7. Quality Objectives and Criteria for Measurement of Data

Project Data Quality Objectives

The overall data quality objective for this monitoring project is to determine whether the concentrations of petroleum hydrocarbons, oils and grease exceed state water quality standards (18 AAC 70). State water quality criteria for petroleum hydrocarbons require that the 4-day average concentration of total aromatic hydrocarbon not exceed 10µg/L. Temperature and discharge are secondary measures. Discharge measures will be used to evaluate the volume of water for dilution of hydrocarbon inputs. Water temperature will be measured to evaluate effects to TAH evaporative losses. Boat counts are used to interpret the differences in TAH concentrations.

Criteria for Measurement of Data

Measurement Quality Objectives (MQOs) are a subset of DQOs. MQOs are derived from the monitoring project's DQOs. MQOs are designed to evaluate and control various phases (sampling, preparation, and analysis) of the measurement process to ensure that total measurement uncertainty is within the range prescribed by the project's DQOs. They define the acceptable quality of the field and laboratory data for the project. MQOs are defined in terms of precision, bias, representativeness, detectability, completeness and comparability.

The parameters in Table 6 will be measured at the listed performance level. TAH is critical to meeting project objectives. These critical criteria are to be met to ensure that the project's data quality objectives are met. Other measures are important for project completion but not critical for completion.

Table 6. Project Specific Measurement Quality Objectives (MQOs).

Parameter	Method	Detectability (MDL/RL)	Expected Range	Accuracy	Precision	Completeness
TAH (µg/L)	EPA 624	1.5/1.5	1.0 to 50	70 - 130	20%	90%
Benzene (µg/L)	EPA 624	0.5/0.5	1.0 to 20	70 - 130	20%	90%
Toluene (µg/L)	EPA 624	0.5/0.5	1.0 to 20	70 - 130	20%	90%
Ethyl Benzene (µg/L)	EPA 624	0.5/0.5	1.0 to 20	70 - 130	20%	90%
Total Xylene (µg/L)	EPA 624	1.0/1.0	1.0 to 20	70 - 130	20%	90%
Discharge (cfs)	Measure	1.0	100 to 400	N/A	10%	90%
Temperature (°C) Thermometric	SM 2550 B	0.1	4 to 25	85 to 115	10%	90%
Boat Counts	Booth Survey: video photos	1	0 to 20	N/A	5%	90%

Quality Assurance Definitions

Detectability

Detectability is defined as the lowest value that a method procedure can reliably discern a measured response above background noise.

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.

$$Accuracy = \frac{MeasuredValue}{TrueValue} \times 100$$

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 between two measurements (A and B).

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

Representativeness

Representativeness is the extent to which measurements actually represent the true condition. Measurements that represent the environmental conditions are related to sample frequency and location relative to spatial and temporal variability of the condition one wishes to describe.

Comparability

Comparability is the degree to which data can be compared directly to similar studies. Standardized sampling and analytical methods and units of reporting with comparable sensitivity will be used to ensure comparability.

Completeness

Completeness is the comparison between the amounts of usable data collected versus the amounts of data called for.

Quality Assurance for Measurement Parameters

Detectability

Detectability is defined as the lowest value that a method procedure can reliably discern a measured response above background noise. In other words, detectability is the level below which the instrument cannot reliably discriminate from zero. Because there is always variation in any measurement process (precision uncertainty), the level of detectability depends on how much precision error is in the process. Two aspects of detectability are used to characterize the level at which data is reported with confidence:

- Method detection limit (MDL)

- Reporting limit or practical quantitation limit (RL or PQL).

The MDL is the minimum value which the instrument can discern above background. For field measurements the manufacturer's listed instrument detection limit (IDL) can be used.

The RL or PQL is the minimum value that can be reported with confidence (usually some multiple of the MDL).

Parameter specific detectability limits (MDL and RL) are listed in Table 6.

Accuracy

The percent accuracy for the acceptance of data is shown for each parameter in Table 6. Accuracy will be determined for those measurements where actual values are known. Measurements of accuracy will be determined for each sampling event. Contract laboratories will provide the results of accuracy measures along with chemical analytical reports. Accuracy will not be determined for discharge where true values are unknown: However, for discharge, the velocity meter will be spin tested as per manufacturer's recommendation prior to each use.

Precision

Table 6 shows the precision value for the acceptance of data. Precision will be determined for all chemical measures by processing a duplicate for every 10 samples. A discharge measure will be repeated every 10th measurement to determine measurement precision.

Representativeness

The monitoring sampling locations, sampling frequency, and timing will ensure that the measurement parameters adequately describe and represent actual stream conditions for the sampling period.

Comparability and Completeness

The use of standard collection and analytical methods will allow for data comparisons with previous or future studies and data from other locations. We expect to collect all of the samples, ensure proper handling, and ensure that they arrive at the laboratory and that analyses are conducted. Our objective is to achieve 90 to 95% completeness for all measures. Sample collection will be repeated if problems arise such as equipment malfunction or lost samples.

The following equation is used to calculate completeness:

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

Where T = Total number of expected measurements.
I = Number of invalid results.
NC = Number of results not produced (e.g. spilled sample, etc.).

A8. Special Training Requirements/Certification Listed

All ARRI staff working on this project have been trained to collect and preserve water samples using the VOC sampler and using the “clean hands” method to avoid sample contamination. Staff have been trained to measure water velocity and calculate stream discharge. Staff have been trained to operate the Omega meter and launch and deploy temperature loggers. ARRI staff will be required to demonstrate their proficiency to the ARRI project manager. The date staff complete their training and demonstrate their proficiency to the ARRI project manager will be recorded on field data sheets.

Jeffrey C. Davis (Project Manager) has a B.S. degree in Biology from University of Alaska Anchorage and a M.S. degree in Aquatic Ecology from Idaho State University. He has 20 years of experience in stream research. Mr. Davis has managed 10 projects that involved the collection of water samples for hydrocarbon analyses. Mr. Davis has experience in all of the assessment techniques outlined in this document.

Gay A. Davis (Quality Assurance Officer) has a B.S. degree In Wildlife and Fisheries Biology from the University of Maine. She has over 20 years of experience in stream evaluation and restoration. Ms. Davis has over 15 years of experience in stream ecological field assessment methods and water quality sampling.

Chemical analyses will be conducted through AM Test, Inc., in Kirkland, Washington. AM Test, Inc. has been accredited by Washington State Department of Ecology for drinking water, waste water and solid matrix chemical analyses. AM Test is certified through the National Environmental Laboratory Accreditation Program (Appendix B).

With the combined experience of these investigators, no additional training will be required to complete this project.

A9. Documentation and Records

Field data, including replicates measures for quality assurance, will be recorded in Rite-in-the-Rain field books. Upon returning to the laboratory, the field book will be photocopied (daily or weekly). The field data book will be stored by the project manager and the quality assurance officer will store the photocopies. ARRI will maintain records indefinitely. The final data report will include, as appendices, results of QC checks. Laboratory reporting and requested laboratory turn around times of 6 to 10 days are discussed in section B4. Laboratory reports will be received as paper and electronic files.

The project reporting requirements are as follows:

Field sampling reports: Field sampling reports will be prepared and submitted to the DEC project manager following each 4-day sampling event as email summaries. These reports will review all activities, any problems with data collection, and comments on observations.

Laboratory Reports: AM Test will submit laboratory reports as signed pdf documents and Excel spreadsheets that comply with the electronic reporting rule 2 or 3. ARRI will forward all laboratory reports to the DEC project manager when received.

Draft Monitoring Report: ARRI will prepare a draft monitoring report detailing sampling objectives, the sampling plan, analyses and results. The results will be discussed relative to WQS's, previously published literature, and previous sampling results.

Data in AWQMS: All field data will be entered into AWQMS or STORET compatible format as directed by DEC.

Photographs and Video: ARRI will prepare a CD containing project photographs, video clips of the launch, and time-lapse photographs of the launch during high use periods.

Final Monitoring Report: ARRI will incorporate all DEC project manager comments to produce a final project report. Printed and electronic copies of the report will be delivered to the DEC project manager.

At the conclusion of the project, the QA project officer will provide to Project Management and DEC an end of year/season summary of Quality Assurance for the project. This will include an assessment of precision, accuracy and data completeness compared to the Project's stated Measurement Quality Objectives, problems found, corrective actions taken, how problems were finally resolved as well as any exceedances of Alaska's Water Quality Standards. This will be included in the final monitoring report.

B1. Sampling Process Design

Project sampling design including sampling locations, sampling dates, sampling frequency, and sampling parameters is described in Section A6.

Sampling locations

Sampling locations are shown in Table 7 and Figures 2 and 3. Sampling locations extend from 4 km above to 12 km below the Public Use Facility (PUF) boat launch.

Sampling Dates

ARRI proposes to conduct sampling on the dates specified in Table 4. Samples will be collected over 4- or 5-day sampling events during the Chinook fishery in late May and early June and the coho fishery in August.

Table 7. Sampling site names, latitude, longitude, and description.

Site ID	Description	Distance from PUF Launch km/mi*	Latitude	Longitude
LS 4 km up	Sampling location 4.0 km upstream from PUF. Upper extent of detectable levels of TAH during previous sampling.	4.0/2.5	61.45642	-150.14433
LS 1 km up	Sampling station 1.0 km upstream from the PUF. Location where discharge is measured. Site located upstream of My Creek.	1.15/0.71	61.44245	-150.15931
PUF or LS 0 km	Sampling location located just downstream from the PUF boat launch. Intensive sampling site.	0.00	61.43783	-150.17386
LS 1 km dn	Sampling location 1.0 km downstream PUF.	-1.35/-0.84	61.43345	-150.17239
LS-4 km dn	Sampling location 4.0 km downstream from the PUF. Intensive sampling site.	-3.87/-2.40	61.42389	-150.18958
LS-8nkm dn	Sampling location 8 km downstream from the PUF.	-8/-4.97	61.41125	-150.20590
LS-12 km dn	Water quality sampling location 12 km downstream from the PUF. Lower extent of TAH exceedances in during previous sampling.	-12/-7.5	61.39647	-150.20579

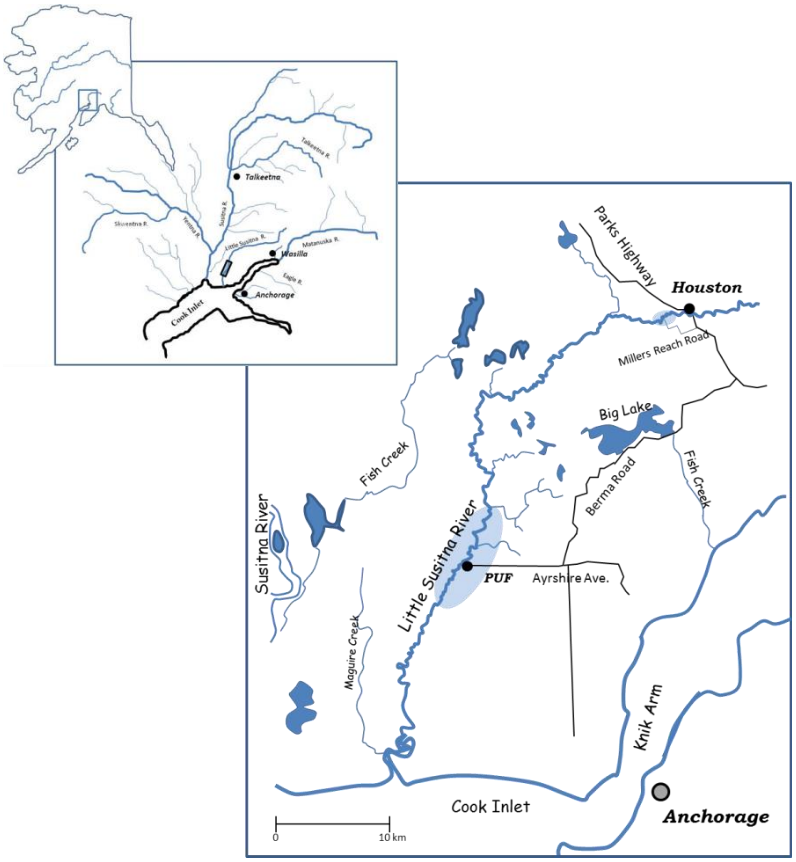

Figure 2. Drawing of Southcentral Alaska showing location of the Little Susitna River and approximate sampling reach (shaded oval).

Figure 3. Aerial photograph showing sampling locations.

Sampling Frequency

Proposed sampling frequency is shown in Table 3. At the intensive sampling locations (LS 0, and LS 4 km dn) we propose to collect 5 samples per day for a total of 20 samples per 4-day sampling event. The first sample time will be at 07:00. TAH concentrations in previous sampling at 05:00 were below detection limits and before most boat use, which starts around 06:00. The 07:00 sample will document inputs from initial daily boat activity. Three sampling events will occur during the most active portion of the day: 10:00, 13:00, and 16:00. The final sample will be collected at 20:00. The 20:00 sample should document the declining limb of daily TAH concentrations. Sampling will begin at LS 0 followed by LS 4 km dn. Therefore, sampling at LS 4 km dn will occur approximately 30 minutes later than at LS-0. All other sites be sampled once each day between 13:00 and 16:00 working from upstream to downstream. Daily sampling at the additional sampling locations will provide information necessary to confidently assess the spatial extent of exceedances. In addition, daily longitudinal samples from 4 km up to 12 km dn will allow us to evaluate cumulative increase or decrease in concentrations downstream relative to boat activity and estimate the number of boats necessary for inputs to exceed TAH loss rates.

Additional Data Collection

Stream discharge will be measured on each day samples are collected at a site located upstream of the boat launch (LS 1 km up). This will allow for calculation of total daily hydrocarbon flux (concentration x discharge) and for evaluation of dilution due to changes in water volume. Measures of stream discharge will provide average water velocity that can be used to calculate flow times between sampling sites. In addition, we can estimate the distance and rate of flushing from upstream waters where concentrations were previously found to be below or very near detection limits. This information may be necessary to develop management options.

Stream water temperature will be measured concurrent with water sample collection. Water temperature will be measured with a temperature specific thermistor and meter at 0.5 x depth at each sampling location during each sampling event. In addition, water temperature loggers (Pro V2) will be deployed at LS-0, LS 4 km dn, and LS-12 km dn, on the first sampling date and removed on the final sampling date. Water temperature loggers will record every 30 minutes.

Boat Use Surveys

Boat use data is necessary in order to calculate TAH discharge per boat and to investigate relationships between TAH discharge and boat motor type. ARRI will coordinate with Dan Amyot (DNR/DPOR Chief Ranger) to ensure that boat use data including motor type will be recorded at the PUF entrance booth. ARRI will check with the booth staff regularly to ensure that they are recording information accurately. ARRI will make arrangements with booth staff to scan or photocopy records at the end of each day or before they are transferred to the State Parks Finger Lake office. DNR/DPOR information on boats passing the entrance booth, motor size and type (2-cycle, 2-cycle direct inject, and 4-cycle) during the time period the booth is open (~ 08:00 to 17:00) will provide an approximation of the total number of boats by motor type operating within the sampling reach for each sampling period.

Booth count data will be augmented with stop action photography of the boat launch. The entrance booth usually is not operated prior to 08:00 or after 17:00. Boat activity prior to 08:00 could influence TAH concentrations in the 07:00 sample and activity following 17:00 could influence TAH concentrations in the 20:00 sample. A camera will be installed with a view of the boat launch and mooring area but out of view of the general public. The camera will be set to take an exposure every 5 minutes. The camera will be downloaded at the end of each day. Boat use counts can be obtained rapidly by viewing the series of photographs as a video in the ARRI laboratory following field sampling.

External Data

Discharge data for the Little Susitna at Hatcher Pass will be obtained from the USGS web site (http://nwis.waterdata.usgs.gov/ak/nwis/dv/?site_no=15290000&agency_cd=USGS) and weather data will be downloaded from the National Climate Data Center (http://www.ncdc.noaa.gov/oa/ncdc.html).

B2. Sampling Methods Requirements

Field Data Collection

Field data collection will be conducted by ARRI staff. The latitude and longitude of sampling locations will be recorded and photographs taken upstream, downstream and across the channel at each site. ARRI staff will look for the presence of oil sheens. If sheens are present they will be evaluated to determine if they fracture on disturbance, indicating a natural source. If they do not fracture, their presence will be recorded and photographed. Samples will be collected from a well-mixed area at each sampling site. TAH sampling will be conducted using the sampler and methods described below, and samples preserved, held in a cooler, kept between 1 °C and 6°C, and shipped overnight for laboratory analyses.

Total Aromatic Hydrocarbons (TAH)

Samples will be collected in accordance with the USGS report "Field guide for collecting samples for analysis of volatile organic compounds in stream water for the national Water Quality Assessment Program (USGS Open File Report 97-401)." This report contains detailed instructions on sample collection procedures (Appendix A) using the USGS-designed VOC sampler distributed by Wildco. Prior to sample collection, the VOC sampler will be decontaminated in Alconox (or similar detergent) and rinsed thoroughly.

Samples will be collected in sample bottles obtained from the contract laboratory. One sample to be analyzed for TAH will be collected (2 vials) from each lowering of the sampler. Samples will be collected at least 12 cm below the water surface and away from any observable sheen. Sampling locations will be accessed by boat or foot. When sampling from the boat, the boat will be anchored, the motor turned off for 5 minutes prior to a sample being collected. The samples will be collected adjacent to the thalweg. A rope will be attached to the sampler cables and the sampler lowered into the flowing water off of the bow of the boat, upstream of the motor, until the sampler opening is at 0.5 stream depth. The attached rope and weighted sampler will be used to keep the sampler upright. HCl acid, provided by the contract laboratory, will be added to each vial after sample collection for preservation and capped (~1 drop). Clean exam gloves will be worn at all times when handling sampling bottles. The samples will be checked to ensure that there are no air bubbles after capping. The sample bottles will be dried, labeled using adhesive labels, placed within a cooler on frozen gel-paks and shipped to the contract laboratory. Sample temperatures will be recorded by the contract laboratory upon receipt using an in-certification NIST traceable laser thermometer readable to 0.01°C and accurate to at least 0.2°C. Trip blanks provided by the contract laboratory will accompany the sample bottles during collection, shipping, and analyses. Field blanks will be collected at the end of each sampling event by submerging the sampler in a stainless steel pot filled with artesian well (hydrocarbon-free) water. This well has been sampled previously by ARRI and has been found to be hydrocarbon free.

Materials Required: Sample bottles, trip blank, labels, gloves, hydrochloric acid, dropper, Alconox, VOC sampler, rope and carabineer, gel-paks, cooler, thermometer, and laboratory chain-of-custody forms.

Water Temperature

Point measures of water temperature will be measured concurrent with hydrocarbon sampling and recorded every 30 minutes at three locations using temperature data loggers. Point measures of temperature will be measured with an Omega HH801A temperature logger with thermistor. Onset ProV2 temperature loggers will be deployed at LS-0 and LS-4km dn.

Materials Required: Omega meter and thermistor. ProV2 loggers (2) with cable. Onset Shuttle.

Discharge

Discharge will be measured directly using a velocity meter and summing of individual components (Rantz et al. 1982). Velocity will be measured using a Swoffer 3000 velocity meter and wading rod or YSI Flow tracker. Lateral distance will be measured using a distance finder or meter tape.

Materials Required: Velocity meter and wading rod, and distance finder or 50-meter tape.

B3. Sample Handling and Custody Requirements

Water samples will be labeled in the field. Sample labels will record the date, time, location, preservation, and initials of collector. Chain of custody forms will be initiated in the field and completed each time samples are transferred to a laboratory, or other carrier. Sample preservation and holding times are shown in Table 8. Samples will be placed within a cooler and the cooler sealed closed using plastic packing tape. Samples will be shipped to the laboratory where they will be placed in a secure location until analyses are completed.

Table 8. Preservation and Holding Times for Sample Analysis.

Analyte/ Method	Method	Matrix	Container	Necessary Volume	Preservative	Holding Time
Discharge	USGS Sum of Components	Surface Water	In Situ	In situ measurement	N/A	N/A
Temperature	EPA 170.1	Surface Water	In Situ	In situ measurement	N/A	N/A
TAH	EP 624	Surface Water	G, FP lined septum	40 ml each (2 bottles)	HCl to pH <2, Cool≤6°C, do not freeze, 0.008% $Na_2S_2O_3$ if oxidant present (e.g., chlorine, etc).in sample	14 days

G = glass, FP = flouropolymer

B4. Analytical Methods Requirements

Sample analytical methods are shown in Table 8 and 9. Field samples will be collected by ARRI staff and delivered to the commercial laboratory for subsequent analyses by the identified standard method. Temperature will be measured in the field.

Corrective Action

ARRI will be responsible for ensuring that all samples are collected and delivered to the laboratory. The QA officer will make sure all samples are labeled and stored correctly and that all equipment has been calibrated and accuracy tests completed as needed. The project manager will be informed of any errors and will be responsible for corrective action including repeating sample collection or analyses (for metered measures). If any samples are lost or are determined to be contaminated by the laboratory or if there are any laboratory problems, the project manager will be responsible for collecting new samples and delivering them to the laboratory or working with the DEC project manager to determine the appropriate corrective action.

Table 9. List of Analytical methods and detection limits for study parameters.

Measurement	Collection/ Analyses	Method	Method Detection Limits	Turnaround Time (days)
Temperature	ARRI	Omega Thermister Onset ProV2	0.1 °C	Direct Measure
Total Aromatic Hydrocarbons	ARRI/ AM Test Inc	EPA 624	0.001 mg/L	14 days hold time
Discharge	ARRI	Swoffer 3000 Velocity Meter	0.1 cfs	Direct Measure

B5. Quality Control Requirements

Quality control of field activities will include adherence to the QAPP and other documented procedures associated with the collection of *in-situ* measurements and TAH samples. This includes maintaining field notebooks and data sheets, COCs, and following EPA CWA approved analytical methods.

This section defines the quality control activities that will be used to control the monitoring process to validate sample data. The following tables define field QC measurements and Lab QC measurement and their criteria for accepting/rejecting project specific water quality measurement data.

B.5.1 Field Quality Control (QC) Measures

Quality Control measures in the field include but are not limited to:

- Adherence to documented procedures in this QAPP;
- Proper cleaning of sample containers and sampling equipment;
- Maintenance, cleaning and calibration of field equipment/ kits per the manufacturer’s and/or laboratory’s specifications, and field Standard Operating Procedures (SOPs);
- Chemical reagents and standard reference materials are used prior to expiration dates;
- Proper field sample collection and analysis techniques;
- Correct sample labeling and data entry to ensure consistency and accuracy;
- Proper sample handling and shipping/transport techniques;
- Field replicate Blind (to the laboratory) samples (1 replicate/10 samples) and
- Field replicate measurements (1 replicate measurement/10 field measurements).

Table 10 below defines the field QC types, frequency and acceptance criteria limits.

Table 10. Field Quality Control Samples

Field Quality Control Sample	Measurement Parameter	Frequency		QC Acceptance Criteria Limits
		Frequency of Occurrence	Total # of QC Type Samples	
Field Blank	TAH (BETX)-	Per EPA 624 Method Requirements	1/day, 4 per sampling event	≤ BETX MDL
Trip Blank	TAH (BETX)	1/cooler	1/sampling event	≤ BETX MDL
Temperature Blank	Temperature	1/cooler	1/sampling event	
Field Replicate (Blind to Lab)	TAH (BETX)	14% and at least 1/sampling day event	1/day, 4 per sampling event	See BETX precision criteria listed in section A7 Table 3
Field Replicate Measurement	Boat Count	N/A	N/A	N/A
Field Replicate Measurement	Discharge	1/every 10th sampling date	1	See Discharge precision criteria listed in section A7 Table 3

B.5.2 Laboratory Quality Control (QC) Measures

Quality Control in laboratories includes the following (see Table 11):

- Laboratory instrumentation calibrated with the analytical procedure,
- Laboratory instrumentation maintained in accordance with the instrument manufacturer's specifications, the laboratory's QAP and Standard Operating Procedures (SOPs),
- Matrix spike/matrix spike duplicates, sample duplicates, calibration verification checks, surrogate standards, external standards, etc. per the laboratories QAP and SOPs.
- Specific QC activities prescribed in the project's QAPP.
- Laboratory data verification and validation prior to sending data results to the project Grantee/ADEC.

Sub-contracted laboratories will provide analytical results after verification and validation by the laboratory QA Officer. The laboratory must provide all relevant QC information with its summary of data results so that the project manager and project QA officer can perform field data verification and validation, and review the laboratory reports. QC specific to TAH/BETX samples analyzed will requested from the lab and reported as part of this project. The project manager reviews these data to ensure that the required QC measurement criteria have been met. If a QC concern is identified in the review process, the Project Manager and Project QA Officer will seek additional information from the sub-contracted laboratory to resolve the issue and take appropriate corrective action/s.

Table 11. Laboratory Quality Control Samples

Field/Lab Quality Control Sample	**Measurement Parameter**	**Frequency**		**QC Acceptance Criteria Limits**
		Frequency of Occurrence	Total # of QC Type Samples	
Field Blank	All method 624 analytes	One per each cooler shipment	1/sampling event (4 total)	Field Blank ≤ BETX MDL
Trip Blank	Temp (C°)	1 per each cooler shipment	1/sampling event (4 total)	Temp blank ≤ 6°C, no indication of freezing
Field Replicate	All method 624 analytes	14% and at least 1/sample day event	4/sampling event (16 total)	See BETX precision criteria listed in section A7 Table 3
Lab Blank	All method 624 analytes	1 per batch		< detection limit (1)
Lab Fortified Blank	All method 624 analytes	1 per curve		
Calibration Verification Check Standard	All method 624 analytes and surrogates	1 per calibration curve		%RSD ≤ 30%
Continuing Calibration Verification Check Standard	All method 624 analytes and surrogates	1 every 12 hrs		%RSD ≤ 20%
Matrix Spike/Matrix Spike Duplicate	All method 624 analytes	1 per 12 hr shift		See below
Lab Duplicate Sample	All method 624 analytes			
External QC Check Standard	See Lab Fortified Blank	1 per curve		See below
Surrogate Standard	Identify surrogate Std	All samples, blanks and spikes		See below

Spike Control Limits	**Low%**	**High%**
Benzene	48.7	153
Toluene	50.5	135
Ethyl Benzene	39.7	148
Total Xylene	43.7	117

QC Check Standards	**Std. Dev.**	**Average Recovery of 20μg/L QC Std**	**% Recovery**
Benzene	6.9	15.2-26.0	76%-130%
Toluene	4.8	16.6-26.7	83%-134%
Ethyl Benzene	7.5	17.4-26.7	87%-134%

Xylene not tested

Surrogate Standard Recovery Limits	**%R Water**	**%R Soil**
Toluene-d8	82.2-116	72-121
Bromofluorobenzene	85.8-104	69-115
1, 2 – Dichloroethane-d4	75.6-151.1	70-134

B6. Instrument/Equipment Testing, Inspection, and Maintenance Requirements

Instruments and meters will be tested for proper operation as outlined in respective operating manuals. Inspections and calibration will occur prior to use at each site. Equipment that does not calibrate or is not operating correctly will not be used. In the case of complete equipment failure, new equipment will be purchased. We currently have 2 VOC samplers on loan from the State of Alaska. The sampler is of simple and sturdy construction. The project manager will be responsible for calibrating, testing and storing equipment and completing log sheets. All calibrating, testing and storage will follow the manufacturer's recommendations. The QA officer will inspect the log sheets.

B7. Instrument Calibration and Frequency

The velocity meter will be calibrated and checked for accuracy following the manufacturer's recommendation. Calibration will be checked monthly. The accuracy of the temperature loggers will be checked at 3 temperatures prior to deployment and the thermistor prior to the May/June and August sampling events. Accurate water temperature will be determined using a NIST calibrated thermometer. Accuracy will be determined at three temperatures: ~0 C, 10 C, and 20 C.

If accuracy and precision are not met for the analyses ARRI is conducting, the meters will be recalibrated and measures will be repeated or meters or probes will be replaced. Data measurements that do not meet the limits described in A7 may or may not be used in the final report depending on degree to which limits are not met. However, the report will clearly state if there are any questions regarding used data.

B8. Inspection/Acceptance Requirements for Supplies and Consumables

Sample containers will be obtained from AM Test Inc. Any needed standards for equipment calibration will be purchased directly from the equipment manufacturer if possible or from a well established chemical company. The QA officer will be responsible for ensuring that standards are not outdated and for the purchase of replacements. The date and source of all purchased materials will be recorded within a separate file for each piece of equipment and kept on file by ARRI along with equipment calibration records.

B9. Data Acquisition Requirements for Non-Direct Measurements

Discharge data for Little Susitna at Hatcher Pass will be obtained from the USGS web site (http://nwis.waterdata.usgs.gov/ak/nwis/dv/?site_no=15290000&agency_cd=USGS) and weather data will be downloaded from the National Climate Data Center (http://www.ncdc.noaa.gov/oa/ncdc.html) for the Anchorage Airport. Data from both of these sources will be assumed accurate for the locations where collected. Flow data from the USGS site located near Hatcher Pass will be compared with direct measures to determine whether it is representative of sampling locations.

B10. Data Management

The success of this monitoring project relies on the collection and interpretation of data. It is critical that data be available to users and that these data are:

- Of known quality,
- Reliable,
- Aggregated in a manner consistent with their prime use, and
- Accessible to a variety of users.

To ensure that date meets these criteria, the following flow chart (Figure 4) depicts how data will be collected, processed, QA/QC, and distributed.

Field data will be entered into rite-in-the-rain books. The quality assurance officer will copy the field books and review the data to ensure that it is complete and check for any errors. Field and laboratory data sheets will be given to the project manager. The project manager will enter data into Excel spreadsheets. The quality assurance officer will compare approximately 10% of the field and laboratory data sheets with the Excel files. If any errors are found they will be corrected and the project manager will check all of the field and laboratory data sheets with the Excel files. The quality assurance officer will then verify correct entry by comparing another 10% of the sheets. This process will be repeated until all errors are eliminated. The project manager will then summarize and compare the data for review or analyses. The quality control officer will review any statistical or other comparisons made. The project manager will write the final report, which will be proofed by the quality assurance officer and the DEC project manager. The DEC project manager will distribute the report for peer review. The quality assurance officer will check the results in the report and associated statistical error (i.e. standard deviation and confidence interval) against those calculated with computer programs. Any errors found will be corrected by the project manager. Any errors will be corrected.

Along with presenting project data in easy to understand tables and graphs in the final project report, the water quality data will be provided to DEC in a modernized STORET compatible format. Data will be formatted into AWQMS compatible files as described at the following DEC web site (http://dec.alaska.gov/water/wqsar/awq_data_info.htm.

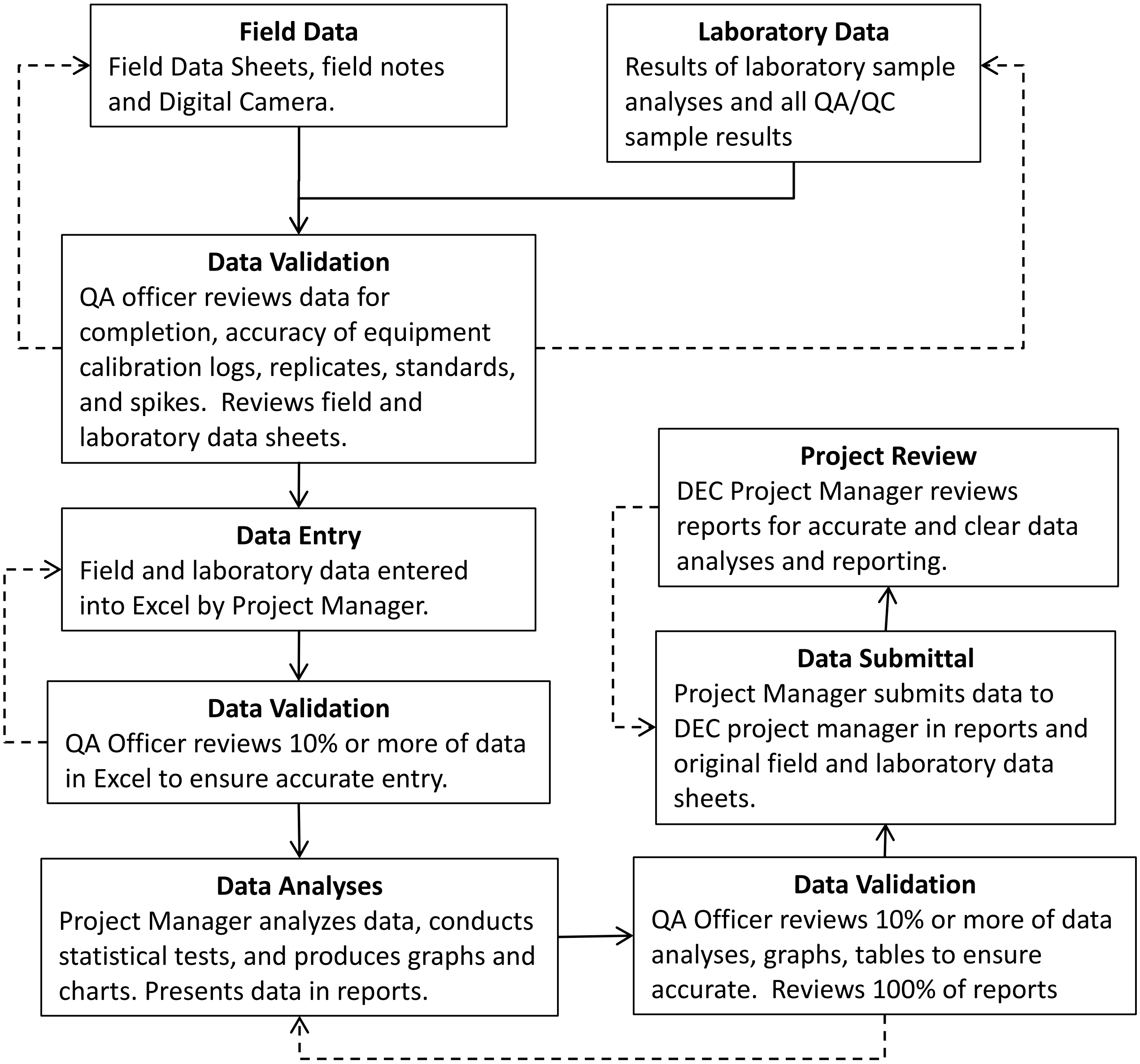

Figure 4. Data management flowchart.

C1. Assessments and Response Actions

Project assessment will primarily be conducted through the preparation of reports for DEC by the project manager. Section A6 contains more information on the type and date of each required report. At that time the project manager will review all of the tasks accomplished against the approved workplan to ensure that all tasks are being completed. The project manager will review all data sheets and entered data to make sure that data collection is complete. Data collection processes or data entry will be modified, as necessary. Any modifications of the data collection methods will be reviewed against the processes described within the QAPP to determine whether the document needs to be updated.

The quality assurance officer will check on field sampling and the contractor's laboratory practices to ensure that samples are handled correctly and consistently (see Data Management Section B10). The final report will contain an appendix that will detail all of the QA procedures showing precision, accuracy and completeness. Representativeness and comparability will be discussed in the body of the report as applicable. Any QA problems will be outlined and discussed relative to the validity of the conclusions in the report. Any corrective actions will be discussed as well as any actions that were not correctable, if any.

The QA officer will report to ARRI management any problems in data collection, analyses, or entry identified either internally or through a 3rd party audit. ARRI management will be responsible for developing and implementing a course of action to correct these problems. Where problems may have affected project validity, these will be identified and reported to the DEC project manager and DEC Water QA Officer directly and included in project reports as directed.

C2. Reports to Management

Reports will be prepared by the ARRI project manager and distributed to the DEC project manager. Any QA problems will be identified and specific corrective actions taken to resolve the problems. Any QA problems will be identified and reported in the quarterly reports or more often if necessary. The project manager will prepare all of the reports. Reports will be reviewed by the quality assurance officer for errors. The final report also will be submitted in electronic format along with the data tables and photo log. Any potential problems with data due to QA will be identified and reported in all submitted reports.

<u>Field sampling reports</u>: Field sampling reports will be prepared and submitted to the DEC project manager following each 4-day sampling event. These reports will review all activities, any problems with data collection, and comments on observations.

<u>Laboratory Reports</u>: ARRI will forward all laboratory reports to the DEC project manager when received.

<u>Draft Monitoring Report</u>: ARRI will prepare a draft monitoring report detailing sampling objectives, the sampling plan, analyses and results. The results will be discussed relative to WQS's, previously published literature, and previous sampling results.

<u>Data in AWQMS</u>: All field data will be entered into AWQMS or STORET compatible format.

<u>Photographs and Video</u>: ARRI will prepare a CD containing project photographs, video clips of the launch and from aerial surveys, and time-lapse photographs of the launch during high use periods.

Final Monitoring Report: ARRI will incorporate all DEC project manager comments to produce a final project report. Printed and electronic copies of the report will be delivered to the DEC project manager.

D. Data Validation and Usability

The purpose of this section is to define the criteria used to review and validate monitoring data-that is, accept, reject or qualify data in an objective and consistent manner. Data review, verification and validation is a way to decide the degree to which each data item has met its quality specifications (i.e. analyte specific QC criteria and overall project measurement quality objectives).

D1. Data Review, Validation, and Verification

Analytical results will be reviewed and validated in accordance with United States Environmental Protection Agency (USEPA) documents, including the *USEPA Guidance on Environmental Data Verification and Validation* (EPA QA/G-8), 2002b. The project manager and the quality assurance officer will conduct data review and validation. Data errors can occur during collection, laboratory analyses, data entry, and reporting. The QA officer will review all field data sheets to ensure that field measures and sample collection followed the QAPP and sampling plan procedures. The QA officer will ensure that all field replicate samples and measures were collected. The QA officer will review and store copies of all chain of custody forms to ensure proper sample handling and delivery.

The QA officer will be responsible for reviewing data received from contract laboratories. The review will include an evaluation of the laboratory quality control measures including laboratory controls, duplicates, and spikes and ensure method/analyte—specific QC criteria limits were met to ensure validity of laboratory analytical method QC requirements as well as project data precision and accuracy criteria. The review will check to make sure the proper analytical methods were used. Site names and dates will be compared to field notes.

For samples analyzed by ARRI, the QA officer will check to make sure that all meters are calibrated and operating correctly and that the calibration and measures of standards is being recorded.

The QA officer will conduct reviews of data entry, analyses, and reporting to ensure that there are no errors in data entry and reporting.

Data that are obtained using equipment that has been stored and calibrated correctly and that meets the accuracy and precision limits will be used. Data that does not meet the accuracy and precision limits may be used; however, we will clearly identify these data and clearly indicate the limitations.

D2. Validation and Verification Methods

Data Validation

Data validation is the sample-specific process that extends the evaluation of data beyond method, procedural, or contractual compliance to determine the analytical quality of the specific data set to ensure that the reported data values meet the quality goals of the project. The QA officer will be responsible for quality control from all contract laboratories. This will include review of sample labeling, analytical method used, turnaround time, and whether all required method/analyte—specific laboratory quality control criteria have been met. The QA officer will work with the contract laboratory to correct or clarify any errors. Analytical results that are below the method detection limit will be reported as such with no numeric value. Data that is below the PQL but above the method detection limit will be reported as estimated (usually flagged with a J) and identified as being below the PQL.

The QA officer will review data values for accuracy and precision. For laboratory data, the QA officer will review all analytical method required QC including field duplicates, laboratory duplicates, matrix spikes, and standard values and using equations in section A-7 determine if laboratory analyses met quality assurance goals for accuracy and precision. If not, the QA officer will request that the laboratory repeat the analyses. Data that repeatedly does not meet QA goals, will not be used in the project analyses or report unless strong justification substantiates its proposed use and it supports the project’s overall data quality goals.

Data Verification

Data verification is the process of evaluating the completeness, correctness, and conformance of the specific data set against the method requirements. The project manager will be responsible for field physical and biotic measures and water sampling and handling. The project manager will review methods to ensure that field data collection is conducted as described in the approved sampling plan and QAPP. Any variation in methods or problems in data collection will be reported to the DEC project manager. The project manager will ensure that the samples for laboratory analyses are identified by the correct site location name, date, and sampling personnel. The project manager will ensure proper sample storage and handling and will fill out and sign all chain of custody forms. Copies of chain of custody forms will be turned over to the QA officer. A log of sampling locations, personnel, labeling, and handling will be kept within the field data book. The project manager will be responsible for final review of data and calculating completeness of data collection.

Data Review

The project manager will enter all data from laboratory and field data sheets into Excel worksheets. The project manager will double-check all entries to ensure that they are correct. The quality assurance officer will compare 10% of the laboratory and field data sheets with the Excel worksheets. The project manager will enter all formulas for calculation of parameters and basic statistics. All of these formulas will be checked by the quality assurance officer. If any errors are found, the project manager will correct the errors and then check all entries. The quality assurance officer will then repeat a check of 10% of the data entry and all of the formulas and statistics. This process will be repeated until any errors are eliminated.

The project manager will organize and write the final report. The quality assurance officer will check the results in the report and associated statistical error (i.e. standard deviation and confidence interval) against those calculated with computer programs. Any errors found will be corrected by the project manager. The project manager will review and respond or incorporate all comments received from the DEC project manager and other reviewers. The QA officer will check the final report to ensure that all review comments were addressed

D3. Reconciliation with User Requirements

The project results and associated variability, accuracy, precision, and completeness will be compared with project objectives. If results do not meet criteria established at the beginning of the project, this will be explicitly stated in the final report. Based upon data accuracy some data may be discarded. If so the problems associated with data collection and analysis, or completeness, reasons data were discarded, and potential ways to correct sampling problems will be reported. In some cases accuracy project criteria may be modified. If this occurs, prior approval is required by both the DEC project manager and DEC Water QA Officer and the justification for modification, problems associated with collecting and analyzing data, as well as potential solutions will be reported in the project final report.

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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

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

U.S. GEOLOGICAL SURVEY
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CONTENTS

FIGURES

TABLES

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\x11km2).

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 km2 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.

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 2.

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

CAS number	PCODE	Compound
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

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 then 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 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
```

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
```

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:
PNSP Publications
USGS Water Resources of California
NAWQA Program

For questions concerning this document, contact: Larry Shelton <lshelton@usgs.gov>
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Appendix B. AM Test Proficiency Certification