Deshka River Total Aromatic Hydrocarbon (TAH) Sampling

August 2018 Sampling Report

Prepared on June 2019 for the:

Alaska Department of Environmental Conservation

By:

ARRI
Aquatic Restoration & Research Institute

DEPARTMENT OF ENVIRONMENTAL CONSERVATION
STATE OF ALASKA

Cover Photograph. Boat activity at the mouth of the Deshka River in August 2018.

This project has been funded wholly or in part by the United States EPA under assistance agreement number 00J84603 to the Department of Environmental Conservation (DEC) through the Alaska Clean Water Actions (ACWA) program (grant #18-06). The contents of this document do not necessarily reflect the views and policies of the EPA or DEC, nor does the EPA or DEC endorse trade names or recommend the use of commercial product mentioned in this document.

Contents

Figures

Tables

Summary

Water samples were collected and analyzed to determine total aromatic hydrocarbon (TAH) concentrations in the lower Deshka River near Willow, AK. Measures of TAH concentrations were used to test for potential chronic (96-hour) exceedances of the fresh-water criteria for petroleum hydrocarbons, oils, and grease found in the State Water Quality Standards (WQS) (18 AAC 70). Previous sampling of the lower Deshka River during the Chinook Salmon fishery in June of 2011 and 2014 documented high motorized boat activity and concentrations of total aromatic hydrocarbons (TAH) greater than WQS numeric criteria and surface sheens were observed. Sampling was conducted in August 2018 to determine if 96-hour average concentrations exceeded numeric criteria and if surface sheens were present and persistent.

In August 16 – 19, 2018, water samples were collected five times daily over a 4-day (96 hour) period and analyzed to determine TAH concentrations. Boat use surveys by motor type were conducted concurrent with water sample collection. Other water quality and physical habitat measures included turbidity, water temperature, and water depths.

Average daily TAH concentrations in August 2018 were below method detection limits on two of the four sampling days. The maximum daily average TAH concentration was 0.26 µg/L, well below previous sampling results. There were no surface sheens due to petroleum hydrocarbon at any time in August 2018 whereas in 2014 they were observed 30 % percent of the time at DR-0 and 25% of the time at DR-0.25. The number of motorized boats operating, and the percentage of boats using less-efficient 2-cycle motors (5.5%), was less than reported previously (26%) in June of 2014..

Turbidity in the lower Deshka River was below 3.0 NTU on all August 2018 sampling dates. This result is consistent with the 2014 sampling results. Average daily specific conductivity was near 30 µS/cm and dissolved oxygen was near saturation (92%) and 9.7 mg/L.

Average daily water temperatures during the sampling period (June 26 through August 19, 2018) exceeded water quality criteria (15°C) established to protect migrating adult and rearing juvenile salmon. Average daily water temperatures were > 15°C on 43 of the 50 (86%) days and > 20°C on 14 of the 50 (28%) days measured. Average water temperatures were consistent throughout the lower Deshka River, but declined with rising water surface elevations. Water surface elevations in the lower Deshka River increased with Susitna River flows.

Introduction

The Deshka River is an important Chinook and Coho Salmon producing Susitna River tributary. Approximately 30% of Chinook salmon tagged in the Susitna River at Susitna Station (downstream from the Yentna River) migrate to the Deshka River (Yanusz et al. 2013). The Deshka River is accessed by motorized boat or by plane, and most access is by motorized boat from Deshka Landing, located on the Susitna River approximately 3 miles upstream from the mouth of the Deshka River. The abundant salmon returns to a river largely accessed by motorized boat, results in high boat use and a higher probability that concentrations of TAH will exceed water quality criteria. Other influencing factors include the larger motor sizes that are used to navigate the Susitna River, concentrated fishing within the mouth of the Deshka River, the lake-like aspect of the lower Deshka River basin, the no-wake-zone within this basin, the high dissolved organic carbon concentrations, and high water temperatures. Boat fishing within the Lower Deshka River Basin primarily is conducted from anchored boats with motors off, which can reduce TAH discharge compared to fishing while trolling with the motor running.

Concentrated boat use can result in the direct discharge of hydrocarbons through accidental spills or due to incomplete gasoline ignition. Water quality sampling conducted by the DEC has documented TAH concentrations above WQS numeric criteria in rivers and lakes of Southcentral Alaska including the Little Susitna River, Kenai River, and Big Lake (Davis et al. 2014, Davis and Davis 2013, Oasis Environmental 2008). TAH concentrations are due to the discharge of fuel from boat motors, primarily, inefficient carbureted 2-cycle motors, at locations and during times of concentrated motorized boat use.

The Department of Environmental Conservation (DEC) conducted limited water sampling in June 2011 and June 2014 to determine TAH concentrations in the lower Deshka River and the potential relationship with motorized boat use during the Chinook Salmon sport fishery (see DEC 2016). Water sampling was conducted during the Chinook Salmon fishery at four lower Deshka River sampling sites on June 18, 2011, and on four dates in June of 2014 (June 7, 13, 15 and 21). In 2011 and in 2014 three sampling sites were located between the confluence of the Susitna River and 1 mile upstream, referred to as the lower Deshka River, where most of the boat use during the Chinook and Coho Salmon fishery is concentrated. The water surface was inspected during sample collection for the presence of surface sheens due to petroleum hydrocarbons. Boat use surveys were conducted concurrent with water sample collection. Surveys counted all boats and boat motor type (2-cycle, direct injection 2-cycle, 4-cycle outboard, and 4-cycle inboard) anchored or motoring within or through the sampling reach.

On June 18, 2011, the daily average TAH concentration (23.69 µg/L) was above water quality criteria (10 µg/L). Maximum TAH concentrations recorded that date were over 24 µg/L. In June 2014, average daily TAH concentrations in the Deshka River exceeded water quality criteria (DEC 2016) and the maximum average daily TAH concentration was 17.5 µg/L. Surface sheens due to petroleum hydrocarbons were observed in both 2011 and 2014.

Exceedances of state WQS (18 AAC 70) criteria for TAH can be due to a visible sheen or numeric criteria (Table 1). Identifying a water body as water quality impaired requires, in part, average concentrations to exceed numeric criteria over a 4-day period, as impairment is based upon chronic hydrocarbon effects to biota (Scannell et al. 2005) (see Water Quality Standards (DEC 2018) and Listing Methodology for determining Water Quality Impairments from Petroleum Hydrocarbons, Oils, and Grease" (DEC 2015)). TAH concentrations and the presence of sheens reported previously supported the need to conduct water sampling over a 4-day period (96 hours) in order to determine if exceedances warranted potential impairment designation.

The purpose of this project was to obtain measures of TAH concentrations over a 4-day period to determine if 96-hour average TAH concentrations exceed numeric criteria (10 µg/L). Additional field data were collected concurrently to the water sampling to determine possible TAH sources and to calculate pollutant loading and possible concentration dilution based on river water volume. These measures included surveys of boat use by motor type and receiving basin water volume and residence time. Water sampling was proposed to occur during the Chinook Salmon sport fishery in June 2018, and the Coho Salmon fishery in August 2018. However, the Chinook Salmon fishery was closed by the Alaska Department of Fish and Game prior to water sampling by emergency order (Appendix B) due to low fish escapement. Because of this emergency order, June water sampling was not conducted in 2018 nor in June 2019 due to an additional emergency order issued in January 2019. All previous Deshka River TAH concentrations had been measured during the month of June. This project collected the first August TAH concentration data.

Table 1. Alaska Water Quality Standards (18 AAC 70) for Petroleum Hydrocarbons for Fresh Water Uses.

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).

Methods

August 2018 water sampling was conducted at the three lower sampling sites established in 2014 (Table 2 and Figure 1). These sampling sites bracket the area of most motorized boat activity. The DR-1.0 mile site is upstream of most active fishing but within the transportation corridor. DR-0.25 is located between DR-1 and DR-0 and is at the upstream portion of concentrated motorized boat activity. DR-0 is at the mouth of the Deshka River at the Susitna River confluence.

Sampling Frequency

Sampling occurred over a 4-day (96-hour) period from Thursday August 16 through Sunday August 19, 2018 (Table 3). Sampling overlapped with the Coho Salmon fishery. Five samples were collected each day at approximately 2-hour intervals from 08:00 to 17:00.

Table 2. Deshka River TAH sampling locations.

Site Name	Description	Activity	Latitude	Longitude
DR – 0	Site located at the mouth of the Deshka River downstream from most boat activity but part of transportation corridor Confluence with Susitna River	Water sampling location. Site of water level and temperature logger.	61.69845	-150.31871
DR – 0.25	Site 0.25 miles upstream of the mouth of the Deshka River and just upstream from the concentrated fishing area. Part of transportation corridor.	Water sampling location. Location of water temperature logger, air pressure logger, and stop action camera.	61.70162	-150.32215
DR –0.75	Site 0.75 miles upstream from the mouth of the Deshka River	Site of water level and temperature logger.	61.70673	-150.32563
DR – 1.0	Site 1 mile upstream of the mouth and near the upper end of backwater water reach. Upper extent of concentrated motorized boat use. Part of transportation corridor	Water sampling location.	61.71241	-150.32532
DR – 1.5	Site 1.5 miles upstream at the upstream end of the lower Deshka River.	Site of water temperature logger.	61.715851	-150.326216

Table 3. Deshka River TAH sampling dates and times.

Salmon Fishery	Sampling Start Date	Sampling End Date	TAH sample Times
Coho	August 16, 2018	August 19, 2018	08:00, 10:00, 12:00, 14:00, 17:00

Water Sample Collection

Sample collection and analyses followed the methods described Shelton (1997) and are described in the attached QAPP (Appendix C.). Sampling sites were accessed by boat with a 4-cycle motor. Sampling began at the downstream sampling station and worked in an upstream direction. Upon reaching a sampling site, the boat was anchored and the motor turned off. Water samples were collected off the bow after the motor had been off for 5 minutes. A volatile organic compound (VOC) sampler was submerged to 0.5 x water depth. Samples were preserved with hydrochloric acid (HCl), sealed, labeled, and placed in a cooler with frozen gel-paks until shipped to the analytical laboratory for analyses. Cooler temperatures were kept < 6°C until received at the analytical laboratory for processing.

Water depth, dissolved oxygen, temperature, and turbidity were measured at each sampling site on each sampling date and time. Water temperature and dissolved oxygen were measured using a YSI Pro ODO meter and probe. Specific conductivity was measured using a YSI Pro 1030, and turbidity was measured with a LaMotte TC-3000we.

All water sampling followed a DEC approved Quality Assurance Project Plan (QAPP). Additional details on the sampling can be found in the QAPP attached as Appendix A.

Boat use Surveys

Boat use surveys were conducted on each sampling date and sampling time. All boats operating, anchored, or parked within the sampling area (DR-0 to DR-1.0) were counted. The motor type, (4-cycle, 2-cycle, direct inject 2-cycle, inboard) was recorded. All boats with inboard motors and all airboats were assumed to be using 4-cycle motors. Outboard boat motor size and activity (anchored, direction of travel) were recorded. Total daily boat hours were calculated by summing the product of average boat counts between sampling times and interval between sampling times (hours), for each sampling time interval.

Stop-action cameras (Stealthcam STC SNX-1) were installed on-shore at two locations: DR-0 and near DR-0.25. The cameras were oriented and programed to photograph the river corridor area between DR-0 and DR-0.25 every hour. The camera at DR-0 disappeared 2-weeks after installation and was not replaced. Using the photos from the DR-.25 camera, additional daily boat counts were obtained by counting the number of boats that appeared within the frame of photographs.

Water Depth and Temperature

Changes in water depth were determined using water pressure and temperature loggers (Hobo U20L-04) installed at two locations: DR-0 and DR- 0.75. Loggers were installed on June 26, 2018 and removed on August 19, 2018 and recorded values every hour. An additional pressure logger was installed approximately 20 m lateral to the stream bank and used to correct for changes in air pressure. Two additional water temperature loggers (HOBO ProV2) were installed at DR-0.25 and DR-1.5 and recoded water temperature every hour.

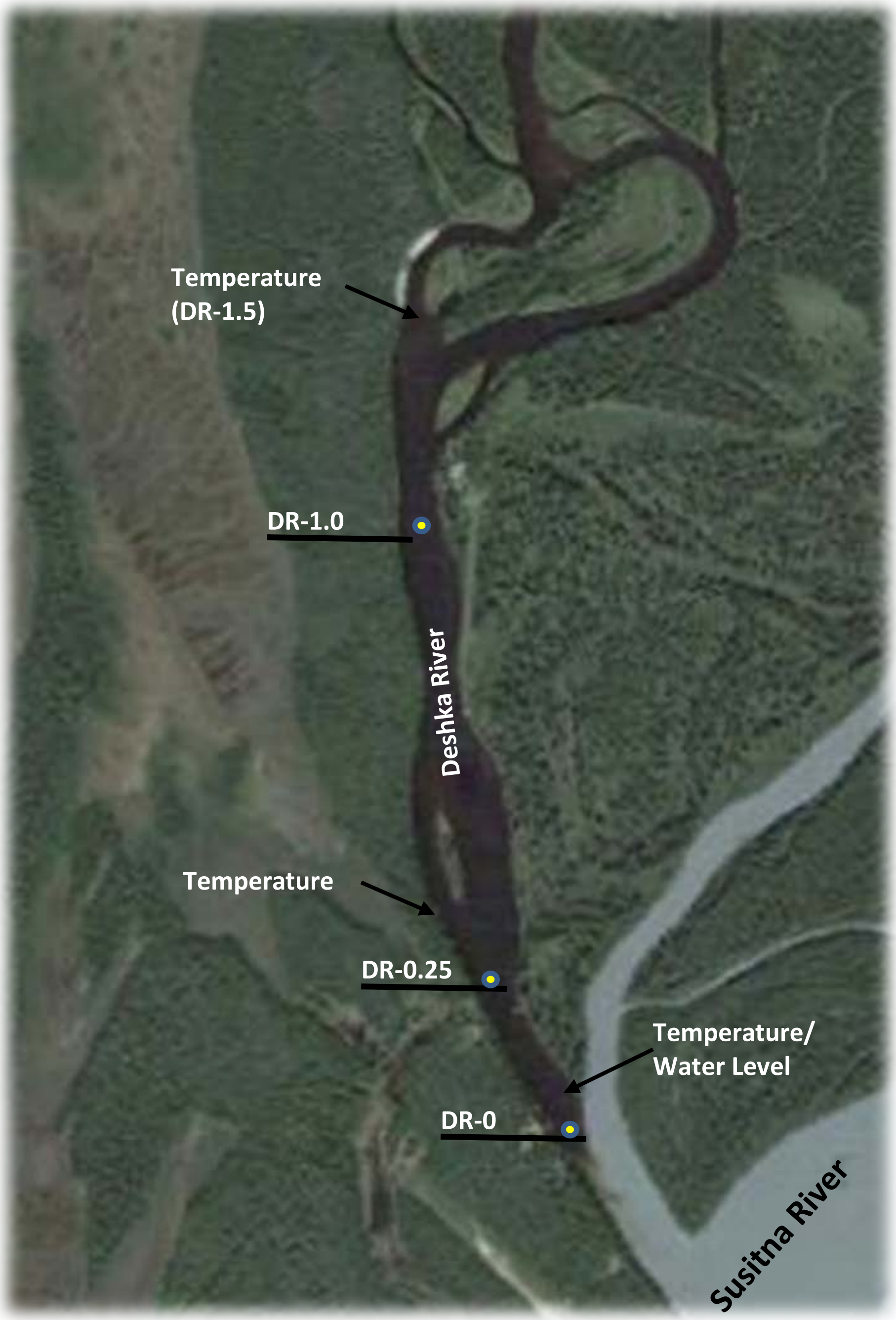


Figure 1. Lower Deshka River showing 2018 sampling sites and water temperature and water level monitoring locations.

Cross-sectional surveys were conducted at six locations August 18, 2018, in order to determine sampling reach water volume. Transects were distributed from DR-1.0 to DR-0.0. The latitude and longitude of the right and left bank points of each transect were recorded. Transect locations were plotted and distances between transects were measured using Google Earth (8/8/2007 imagery). Google Earth also was used to measure water surface area. Water depth and distance from the bank were measured in the field at 2 to 3 m intervals across the channel at each transect. Channel area at each transect was calculated from average water depth between sample points and distances between each point. The volume of the sampling reach was calculated as the sum of the product of average cross-sectional area for successive transects and distance between transects.

Sampling Results

Data Quality

Contractor analytical laboratory AM Test, Inc. in Kirkland, WA, met all project analytical quality objectives. No TAHs were present in field blanks or field equipment blanks. TAH concentrations in field replicates were all below method detection limits.

Total Aromatic Hydrocarbons (TAH)

TAH concentrations above method detection limits were found in samples collected during sampling events on August 16 and August 17, 2018. On August 16, benzene was present in a sample collected during the 08:00 sampling event. On August 17, toluene was present in a sample collected from DR-1.0 during the 14:00 sampling event, toluene from DR-0 at 17:00, and toluene and xylene at DR-0.25 during the 17:00 sampling event. Average daily TAH concentrations on August 16 and August 17 were below 1.0 µg/L (Figure 2). No hydrocarbon sheens were observed on any of the August 2018 sampling dates or monitoring locations.

Boat Use Surveys

Boat activity during the Coho Salmon fishery is shown in Figure 3 and daily boat hours in Figure 4. Counts of boats during sampling events ranged from one to a maximum of 13. Daily boat counts were highest at 08:00 on August 17, and 10:00 on the other sampling dates. Boats using 2-cycle motors were observed on August 17 (four boats) and August 19 (one boat).

Average boat-hours combines the number of boats and the average time boats are on the water and may be more closely related to TAH concentrations than daily boat counts. Average daily boat hours, including boats using all motor types, was highest on Saturday, August 18 at 93.5, approximately 2 times higher than the other sampling dates. Boat use hours for boats using 2-cycle motors was highest on Friday, August 17 (Figure 4).

Boat counts from the stop-action camera installed at DR-0.25 are shown in Figure 5. Boat counts from June 26 to August 19 where highest on weekend days, either Saturday or Sunday. Boat counts began to increase at the end of June prior to large numbers of Coho Salmon passing the weir, located 7 miles upstream and then decreased, and increased again during the sampling period.

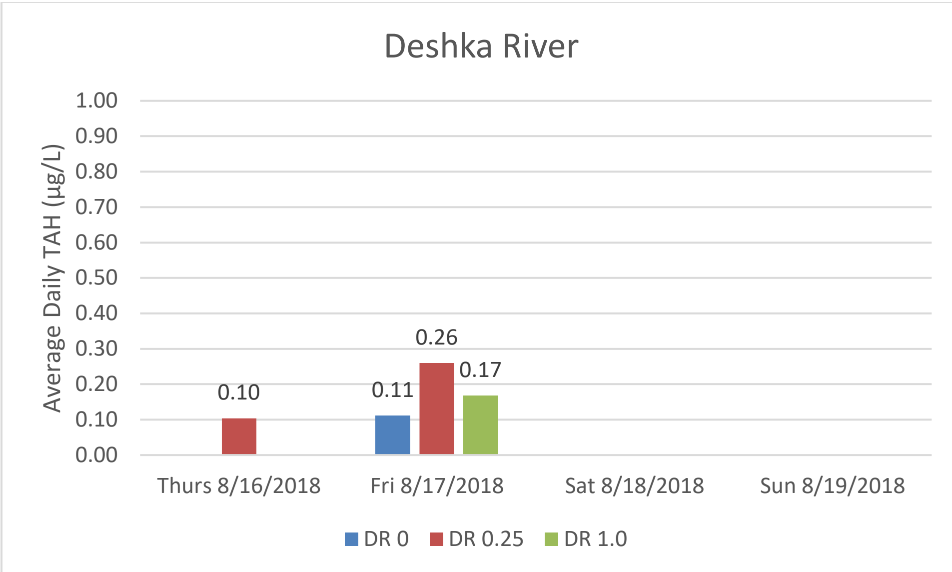
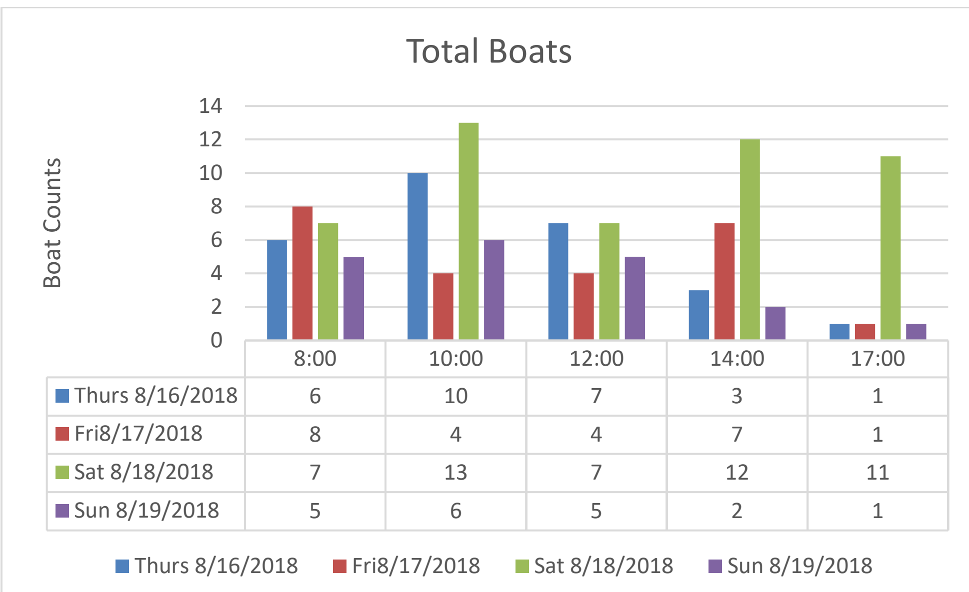


Figure 2. Daily average TAH concentrations at the three Desha River sampling sites.



	8:00	10:00	12:00	14:00	17:00
Thurs 8/16/2018	6	10	7	3	1
Fri8/17/2018	8	4	4	7	1
Sat 8/18/2018	7	13	7	12	11
Sun 8/19/2018	5	6	5	2	1

Figure 3. Counts of boats present within the sampling reach on each sampling date and sampling event.

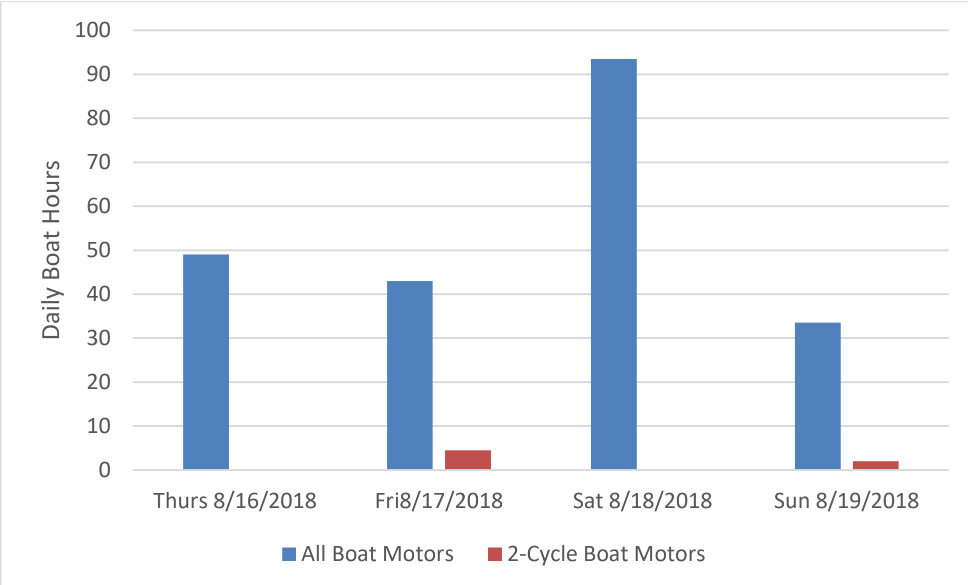


Figure 4. Total daily boat hours for all boats and those boats using 2-cycle motors.

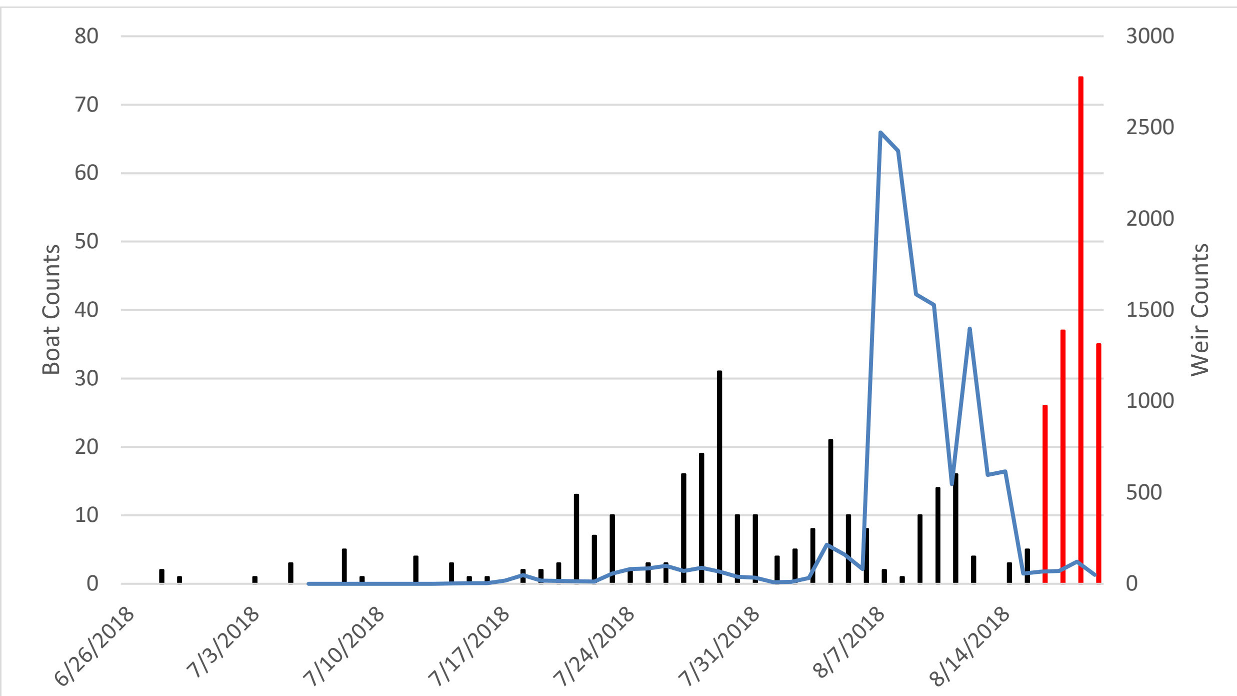


Figure 5. Number of boats counted each day from hourly photographs at DR-0.25 (columns) and counts of Coho Salmon at the Deshka River Weir (blue line). Red columns are boat counts on sampling dates.

Water Depth and Temperature

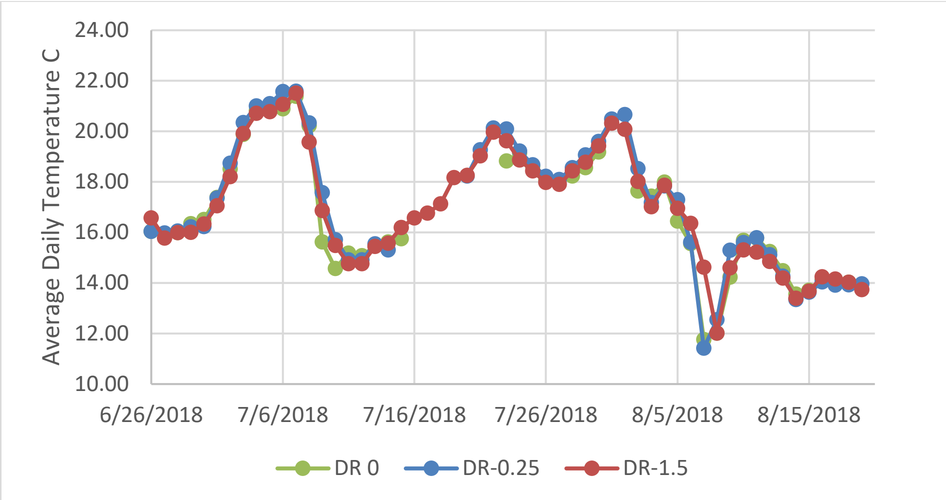
Water temperatures within the lower Deshka River are shown in Table 4 and Figure 6. Average daily water temperatures ranged from approximately 14°C to over 20°C. The difference between maximum and minimum daily temperatures average 1.6° to 2.0°. Average daily water temperatures often exceeded 15° and 20°C during this time interval. Average7-day maximum water temperatures were highest in early June and exceeded 20°C. There were little differences in average water temperatures among sampling sites from the upstream to downstream lower Deshka River basin.

Water temperatures decreased with rising water surface elevations (Figure 7). Water depths within the lower Deshka River at the DR-0 monitoring site, were variable decreasing from around 0.5 m in June to near 0 m through July, and then increased over 2 m in August. Water temperatures decreased over a two-day period in early July from over 20°C to < 15°C when water depth increased 0.5 m. A similar 5°C drop in temperature occurred in early August when water depths rapidly increased over 1 m.

Channel and basin characteristics are shown in Table 5. Channel widths ranged from 90 to 140 m. Average water depth was 2.74 m on August 18, 2018. Surface area of the sampling reach (DR-1.0 to DR-0) was measured at over 200,000 m^2, providing a mixing volume of 200,000 m^3 assuming a mixing depth of 1 m. Total volume was estimated at 565,595 m^2. Water residence time within the sampling reach is 16 days at a river discharge of 10 m^3/s.

Table 4. Water temperature characteristics for the three sampling sites on the lower Deshka River. Loggers installed on June 26 and removed on August 19. Loggers at DR-0 and DR-0.25 were exposed to air for a few days due to low water levels.

	DR-0	DR-0.25	DR-1.5
Maximum	22.62	22.85	22.18
Minimum	11.24	10.96	11.59
7-day Ave Maximum	21.16	21.77	21.16
Average Daily Range	1.60	1.63	2.00
Maximum Daily Range	5.83	4.52	4.26
Days Average > 20 °C	5	10	6
Days Average > 15 °C	35	39	42



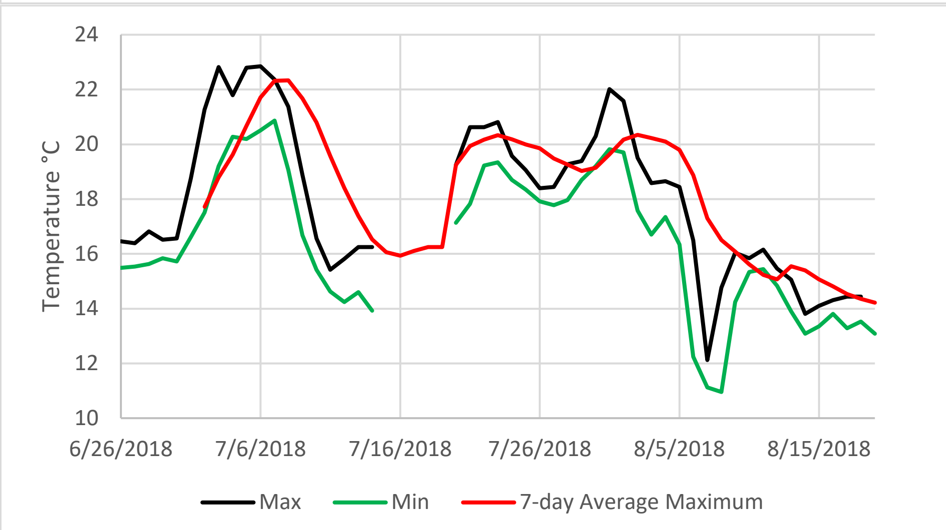


Figure 6. Average daily water temperature at three monitoring locations within the lower Deshka River (upper graph) and maximum, minimum and previous 7-day average maximum temperatures for DR-0.25 (lower graph).

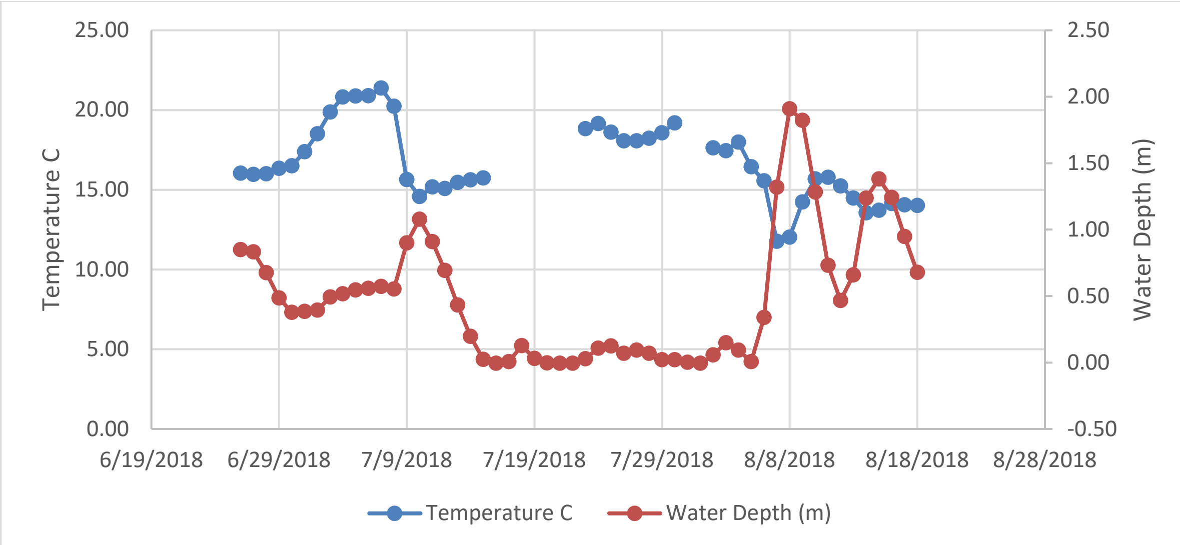


Figure 7. Inverse relationship between water temperature and water depth at DR-0 in the lower Deshka River.

Table 5. Channel width and average water depth at sampling sites, and estimates of the surface area and water volume of the sampling area.

	DR-0	DR-0.25	DR-1.0
Channel Width (m)	100	139	90
Average Depth (m)	2.57	2.43	2.74
Area (m^2)	258	338	247
Surface Area (m^2)	202,422		
Volume (m^3)	565,595		

Turbidity, Specific Conductivity, and Dissolved Oxygen

Average daily turbidity was low on all sampling dates (Figure 8). Average turbidity was below 3.0 NTU and there were no apparent trends among sampling dates or sampling times.

Specific conductivity ranged from 24 to 34 µS/cm (Figure 9). Specific conductivity increased over the 4-day sampling period concurrent with decreasing water depths.

Dissolved oxygen was > 90% saturation (average 94% 9.67 mg/L) all sampling dates and sampling times.

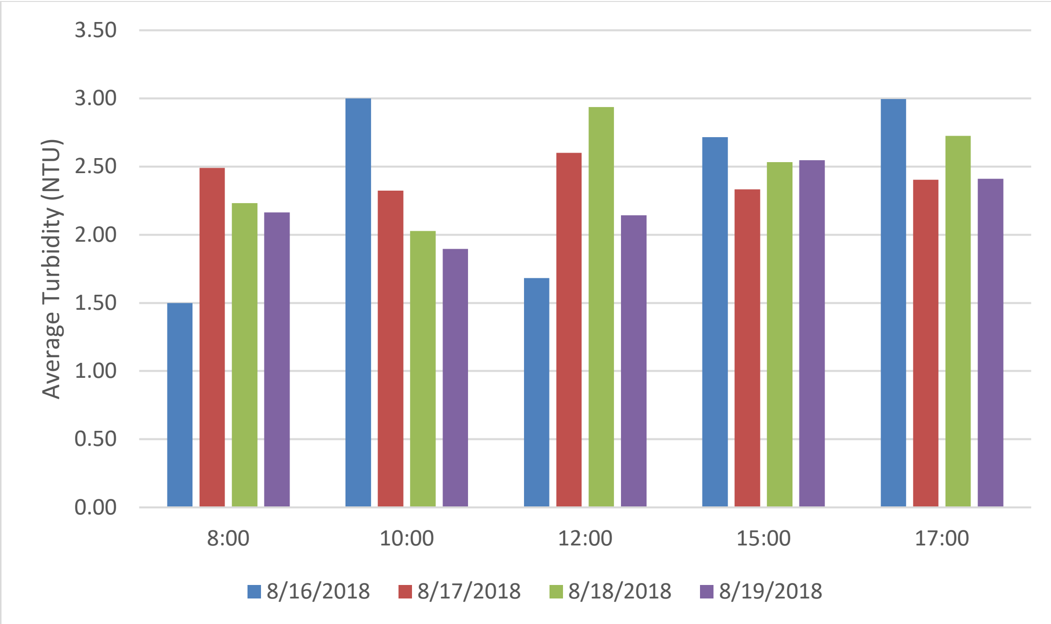


Figure 8. Average lower Deshka River turbidity on each sampling date and each sampling event.

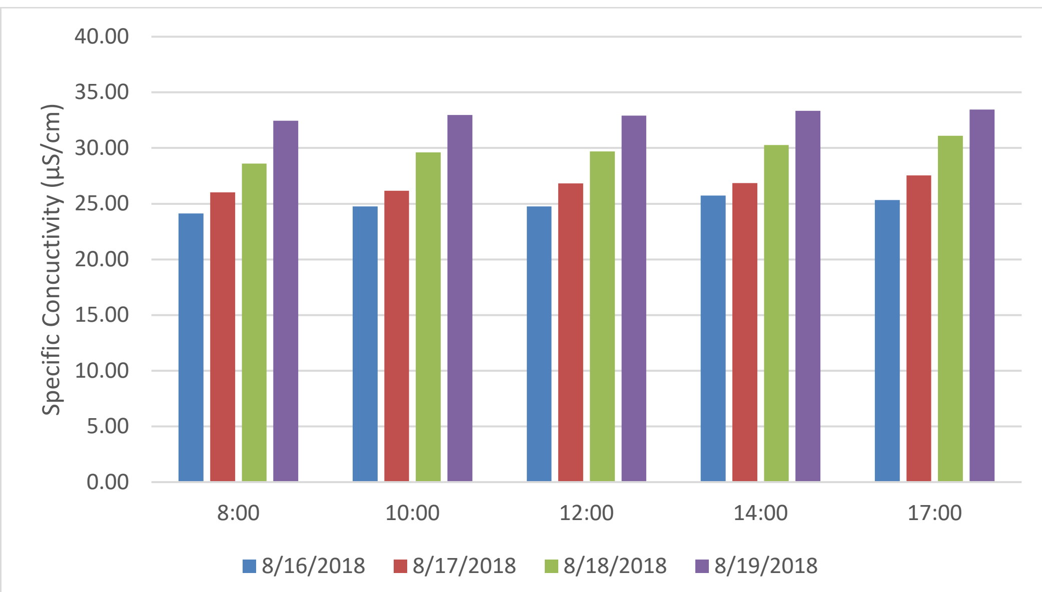


Figure 9. Average lower Deshka River specific conductivity on each sampling date and each sampling event.

Discussion

This study is important because it provides evidence that lowering the number of motorized boats using 2-cylce motors can reduce TAH concentrations in receiving waters. The number of motorized boats using 2-cycle motors had decreased since previous Deshka River water sampling due in part to national and state education programs, and state regulations on some waters. There were fewer motorized boats operating during this study, which occurred during the Coho Salmon fishery, than previous sampling which occurred during the more popular June Chinook Salmon fishery. However, the most notable difference between this study and previous studies was the reduction in the portion of motorized boats using 2-cycle motors and the associated low TAH concentrations and absence of visible sheens.

Fewer motorized boats overall, and fewer motorized boats using 2-cycle motors, were present during August 2018 sampling period compared to those surveyed in June 2011 and June 2014 (Table 6). This likely explained the relatively low TAH concentrations. A total of 98 boats were counted during a single day of sampling in June 2011 and from 58 to 150 on the four sampling dates in June 2014. On average, 26% percent of boats on the Deshka River in June 2014 were using 2-cycle motors (10 to 56 boats). In comparison, total daily boat counts in August 2018, ranged from 19 to 50 with only 5.5% of the boats counted using 2-cycle motors (5 boats). TAH concentrations over all sampling dates (2011, 2014, and 2018) were more strongly associated with the number of boats using 2-cycle motors than the total number of boats (Figure 10).

Table 6. Daily average boat counts for total boats and boats using 2-cycle motors and daily average TAH concentrations.

Date	All Boats	Boats with 2-Cycle	% 2 Cycle	Daily Ave TAH (µg/L)
8/16/2018	27	0	0	0.1
8/17/2018	24	4	16.7	0.3
8/18/2018	50	0	0	0.0
8/19/2018	19	1	5.3	0.0
6/7/2014	144	29	20.1	8.8
6/13/2014	123	26	21.1	4.2
6/15/2014	150	56	37.3	17.4
6/21/2014	58	10	17.2	5.4
6/18/2011	98	NA		24.0

TAH concentrations in receiving waters is related to the efficiency of fuel combustion and boats using 2-cycle motors have been shown to be inefficient at fuel combustion and one of the major sources of TAH to receiving waters (Jüttner et al. 1995). Low boat counts during the August 2018 4-day sampling event was likely due to Coho Salmon run timing, that peaked earlier than in previous years and extended only over a 10-day period (see Figure 5).

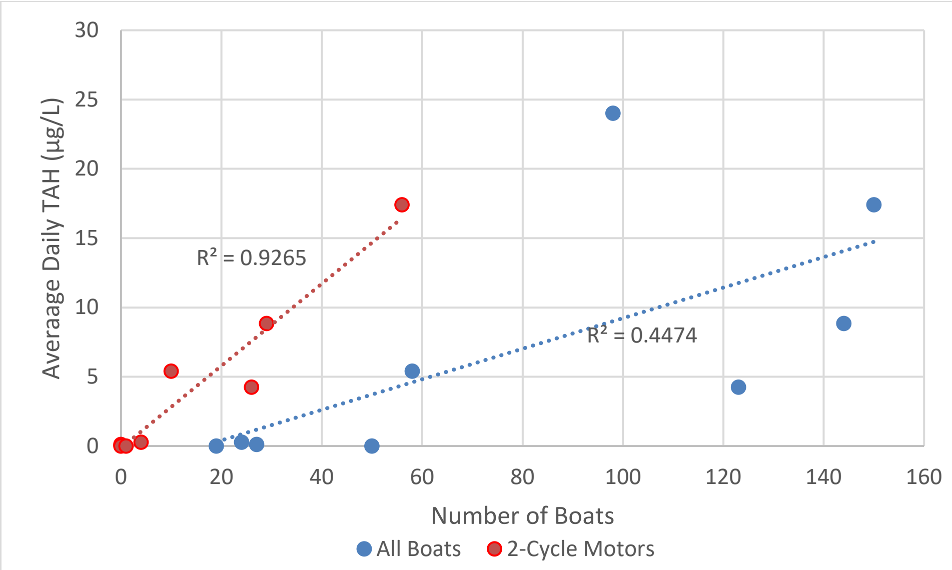


Figure 10. Relationship between average daily TAH concentration and total daily boat counts and daily counts of boats using 2-cycle motors on the Deshka River.

Water volume also can affect TAH concentrations in receiving waters. Average water depth was 2.74 m on August 18, 2018 resulting in a volume of 550,000 m3 of water. Reducing average water depth by 1 m would decrease water volume by 220,000 m3 (basin surface area), potentially doubling concentrations in response to the same TAH discharge. Water surface elevations in the lower Deshka River from June 26 through August 19, 2018 were strongly correlated with Susitna River flows (R^2 = 0.81). Susitna River water surface elevations control the outlet of the lower Deshka River and water surface elevations in the lower Deshka River drop with decreasing Susitna River flows (USGS Site 15292000) and rise with increasing Susitna River flows. Equal boat use and TAH discharge will result in higher concentrations in receiving water with a decrease in water volume, assuming complete mixing.

Water temperatures exceeded water quality numeric aquatic life criteria for water temperatures (DEC 2018). There is very little development within the Deshka River watershed, and human activities have not directly caused these exceedances. Average daily water temperatures exceeding 15° to 20 °C can reduce salmon egg viability (Richter and Kolmes 2005). Large numbers of adult Coho Salmon were not observed at the ADFG weir until August 6, and were likely present with the lower Deshka River when average water temperatures were in excess of 15°C. Water temperatures dropped below 15°C on August 8, concurrent with rising water surface elevations. Water temperatures > 16°C can block Deshka River Coho Salmon migration (Ivey 2004).

Water temperatures were very similar from the upstream to downstream end of the lower Deshka River. We anticipated that water temperatures would increase due to the long residence time and large surface area of the lower Deshka River. Water temperatures declined rapidly with increases in water depth and there was a small range in daily water temperatures at all lower Deshka River temperature monitoring sites. The low daily range may be due to the large volume of water;

however, it also may be possible that cold groundwater flows from the Susitna River are buffering water temperatures in the lower Deshka River. Increasing Susitna River flows that increase water depth within the lower Deshka River also increase groundwater discharge.

Turbidity remained low and did not appear to increase with boat activity as has been reported for the Little Susitna River (Davis and Davis 2013). Most boats navigate through the lower Deshka River at speeds that do not cause a wake reducing the size of waves reaching the banks. Water depths are greater than the Little Susitna River and the intakes of boat jets are not likely to draw water or sediment from the substrate, and the substrate within the lower Deshka River is dominated by larger cobbles at many locations. The lake-like characteristics and lack of turbulent flow also allow for sediment deposition.

References

Alaska Department of Environmental Conservation (DEC). 2010. Alaska's Final 2010 Integrated Water Quality Monitoring and Assessment Report—July 2010. Juneau, Alaska.

Alaska Department of Environmental Conservation (DEC). 2011. Alaska Water Quality Criteria Manual for Toxic and Other Deleterious Organic and Inorganic Substances, as amended through May 15, 2003. Juneau, Alaska.

Alaska Department of Environmental Conservation (DEC). 2015. Listing methodology for determining water quality impairments from petroleum hydrocarbons, oils and grease: Final Guidance (Ver. 1.0). December 14, 2015. Juneau, AK.

Alaska Department of Environmental Conservation (DEC). 2016. Deshka River Screening Level Water Quality Sampling for Petroleum Hydrocarbons; June 7, 13, 15 and 21, 2014. Anchorage, AK.

Alaska Department of Environmental Conservation (DEC). 2018. 18 AAC 70, Water Quality Standards. Juneau, Alaska.

Davis, J.C., and G.A. Davis. 2013. Water quality in the Lower Little Susitna River: Cumulative Report July 2007 through June 2012. Final Report for Alaska Department of Environmental Conservation, Alaska Clean Waters Action Program Contract No. 18-6002-12. Aquatic Restoration and Research Institute. Talkeetna, Alaska.

Davis, J.C., G.A. Davis, and A. Crabb. 2014. Big Lake water quality monitoring 2013. Final Report for Alaska Department of Environmental Conservation, Contract No. 18-6002-12. Aquatic Restoration and Research Institute. Talkeetna, Alaska.

Ivey, S.S. 2004. Deshka River Chinook and Coho Salmon escapement studies, 1995 - 2004. Alaska Department of Fish and Game, Fishery Data Series No 14-24, Anchorage.

Jüttner, F., D. Backhaus, U. Matthias, U. Essers, R. Greiner, and B. Mahr. 1995. Emissions of two-stroke and four-stroke outboard engines: quantification of gases and VOC. Water Resources. 29: 1976-1982.

Oasis Environmental. 2008. Kenai River 2007 Petroleum Assessment Report: June 30, 2008. Final Report for the Alaska Department of Environmental Conservation. Anchorage, AK.

Richard J. Yanusz, P. C., Sam Ivey, Jack W. Erickson, Dan J. Reed, Raye Ann Neustel, and Jan Bullock 2013. Distribution of Spawning Sustitna River Chinook *Oncorhynchus tshawytscha* and Pink Salmon *O. gorbuscha*, 2012. Susitna-Watana Hydroelectric Project. Anchorage, Alaska: 45.

Richter, A. and S. A. Kolmes (2005). "Maximum Temperature Limits for Chinook, Coho, and Chum Salmon, and Steelhead Trout in the Pacific Northwest." Reviews in Fisheries Science 13(1): 23-49.

Scannell, P.W., D. Dasher, L. Duffy, R. Perkins, and T. O'Hara. 2005. Acute and chronic toxicity of hydrocarbons in marine and fresh water with an emphasis on Alaska species. Alaska Department of Environmental Conservation, 610 University Avenue. Fairbanks, Alaska 99709.

Shelton, L.R. 1997. Field guide for collecting samples for analysis of volatile organic compounds in stream water for the National Water-Quality Assessment Program. U.S. Geological Survey, Open File Report 97-401.

Appendix A. Photographs

Photograph A1. Lower basin of the Deshka River.

Photograph A2. Staff gauge at DR 0.0 (6/26/18).

Photograph A3. Staff gauge at DR 0.75 (6/26/18).

Photograph A4. Staff gauge and pressure logger at DR 0.75 (7/20/18).

Photograph A5. Motorized boat use at DR 0.0 (8/19/18).

2

Appendix B. Alaska Department of Fish and Game: Emergency Fishing Orders

SPORT FISHING
Emergency Order

ALASKA DEPARTMENT OF FISH & GAME

Under Authority of AS 16.05.060

Emergency Order No. 2-KS-2-05-19

Issued at: Palmer, Monday, January 7, 2019

Effective Date: 6:00 a.m. Wednesday, May 1, 2019

Expiration Date: 11:59 p.m. Saturday, July 13, 2019, unless superseded by subsequent emergency order.

EXPLANATION:

This emergency order closes the Susitna River drainage to sport fishing for king salmon and limits sport fishing gear for other species to one unbaited, single-hook, artificial lure when fishing in Units 1 - 6 of the Susitna River drainage in those waters normally open to king salmon fishing. Single hook is defined as a hook with only one point.

Fishing for other finfish species remains open. In the waters of Unit 2 normally open to king salmon fishing, fishing for trout and other species is allowed seven days per week from 6:00 a.m. to 11:00 p.m. King salmon may not be targeted and those caught while fishing for other species may not be removed from the water and must be released immediately.

REGULATION:

The provisions of 5 AAC 61.110. (1)(A) and (B)(i), 5 AAC 61.112. (1), (4), (6)(A) and (B), 5 AAC 61.114. (1), (3) and (15), 5 AAC 61.116. (2), 5 AAC 61.118. (1), (2), (4), and (7)(A), 5 AAC 61.120. (1) and (2), and 5 AAC 61.122. (1) and (4)(A) are superseded by this emergency order. Under this emergency order, the following provisions are effective 6:00 a.m. Wednesday, May 1 through 11:59 p.m. Saturday, July 13, 2019:

5 AAC 61.110. General provisions for seasons, bag, possession, annual, and size limits, and methods and means for the Susitna River Drainage Area.

(1) king salmon

(A) sport fishing for king salmon is closed; king salmon may not be retained or possessed; king salmon that are caught must be released immediately; a person may not remove a king salmon from the water before releasing the fish;

(B) less than 20 inches in length

(i) sport fishing for king salmon is closed; king salmon may not be retained or possessed; king salmon that are caught must be released immediately; a person may not remove a king salmon from the water before releasing the fish;

5 AAC 61.112. Special provisions for the seasons, bag, possession, and size limits, and methods and means for Unit 1 of the Susitna River Drainage Area.

(1) in flowing waters only one unbaited, single-hook, artificial lure may be used;

(4) sport fishing for king salmon is closed;

(6) in the Deshka River drainage, including Trapper Lake,

(A) in flowing waters upstream of the Moose/Kroto Creeks, only one unbaited, single-hook, artificial lure may be used;

(B) from its mouth upstream to ADF&G regulatory markers located 300 feet downstream of the weir (river mile 7), and in all waters within a one-half mile radius of its confluence with the Susitna River, sport fishing for king salmon is closed; king salmon may not be retained or possessed; king salmon that are caught must be released immediately; a person may not remove a king salmon from the water before releasing the fish; from its mouth upstream to ADF&G regulatory markers near Chijuk Creek (river mile 17), and in all waters within a one-half mile radius of its confluence with the Susitna River, only one, unbaited, single-hook, artificial lure may be used; the remainder of the drainage is closed to sport fishing for king salmon;

5 AAC 61.114. Special provisions for the seasons, bag, possession, and size limits, and methods and means for Unit 2 of the Susitna River Drainage Area.
(1) from January 1 - July 13, Unit 2 is open to sport fishing for all finfish species, except king salmon; sport fishing for king salmon is closed;
(3) in flowing waters only one unbaited, single-hook, artificial lure may be used;
(15) from May 15 – July 13, sport fishing is not allowed from 11:00 p.m. to 6:00 a.m.;

5 AAC 61.116. Special provisions for the seasons, bag, possession, and size limits, and methods and means for Unit 3 of the Susitna River Drainage Area.
(2) from May 15 – July 13, fishing for king salmon is closed; sport fishing is not allowed from 11:00 p.m. to 6:00 a.m.;

5 AAC 61.118. Special provisions for the seasons, bag, possession, and size limits, and methods and means for Unit 4 of the Susitna River Drainage Area.
(1) in flowing waters only one unbaited, single-hook, artificial lure may be used;
(2) from May 15 – July 13, sport fishing is not allowed from 11:00 p.m. to 6:00 a.m.;
(4) sport fishing for king salmon is closed; king salmon may not be retained or possessed; king salmon that are caught must be released immediately; a person may not remove a king salmon from the water before releasing the fish;
(7) in the Lake Creek drainage,

(A) from an ADF&G regulatory marker located approximately 100 yards upstream of its mouth to an ADF&G regulatory marker located approximately one-quarter mile upstream of Bulchitna Lake, only one unbaited, single-hook, artificial lure may be used;

5 AAC 61.120. Special provisions for the seasons, bag, possession, and size limits, and methods and means for Unit 5 of the Susitna River Drainage Area.
(1) in flowing waters only one unbaited, single-hook, artificial lure may be used;
(2) from May 1 – July 13, sport fishing is not allowed from 11:00 p.m. to 6:00 a.m.;

5AAC 61.122. Special provisions for the seasons, bag, possession, and size limits, and methods and means for Unit 6 of the Susitna River Drainage Area.
(1) in flowing waters only one unbaited, single-hook, artificial lure may be used;
(4) in the East Fork of the Chulitna River drainage, including all waters within a one-quarter mile radius of its confluence of the East Fork and West Fork and including the Middle Fork of the Chulitna and the first quarter mile of Honolulu Creek,

(A) the waters are open to sport fishing for all finfish species, except for king salmon; sport fishing for king salmon is closed;

Doug Vincent-Lang,
Acting Commissioner

By delegation to:

Sam Ivey,
Area Management Biologist

JUSTIFICATION:

The Susitna River, Little Susitna River, and other king salmon stocks throughout Cook Inlet are experiencing a period of low productivity and, since 2007, below average run strength. The department monitors escapement on 24 streams within the Northern Cook Inlet Area, of which 17 have established escapement goals. King salmon counts have ranged from below average to poor since 2007.

The preseason forecast for the Deshka River king salmon run is 8,500 age 1.2-1.4 fish, which is below the sustainable escapement goal (SEG) of 13,000-28,000 fish. For the second consecutive year, a sibling model suggests a potential weak run of 5-year old fish. 5-year old fish typically constitute about half a given year's run. The sibling model was accurate in predicting a low return of 5-year old fish in 2018. There is also uncertainty in the forecast of 4-year old fish in 2019. The Deshka River failed to achieve its sustainable escapement goal (SEG) the past two years, despite preseason and inseason actions to restrict and eventually close the sport fishery in each year. The potential for a run size less than experienced in 2017 and 2018, warrants closure from the outset of the season.

The department monitors escapement on three streams of the Yentna River drainage (Unit 4 of the Susitna River) with established escapement goals. All escapement goals in 2017 were missed even after fisheries were closed late in the season. All SEGs were missed in 2018, despite these fisheries being restricted preseason to nonretention and eventually closed mid-season. Given that low abundance of 4-year old fish in 2017 and low abundance of 4-year old and 5-year old fish in 2018 was widespread throughout the Susitna River drainage, as evidenced by age data collected at fish wheels and reports from guides and anglers, it is assumed the low Deshka River forecast will be reflective of other areas of the Susitna River drainage during 2019. Areas within the Susitna River drainage have demonstrated an inability to achieve escapement goals when restricted to nonretention during low run years and warrant closure.

The department monitors escapement on eight streams on the Eastside Susitna River (Units 2, 3, 5, and 6) with established escapement goals. Most goals in this area were missed in 2017 despite these fisheries being restricted to nonretention from the outset of the season and eventually closed midseason. All goals were missed in 2018 even though sport fisheries in this area were closed the entire season.

Below average runs during previous years, past performance of fisheries within the Susitna River drainage under previous years' management strategies, and uncertainty over how returns may recover in the future justify starting the 2019 season with these restrictions. In addition to these management actions to the sport fishery, the Northern District commercial king salmon fishery will also be closed. Data gathered from weirs, fishwheels, and aerial surveys will be used to gauge run strength during the season.

DISTRIBUTION:

The distribution list for this emergency order is on file at the Region II Office of the Alaska Department of Fish and Game, Division of Sport Fish, 333 Raspberry Road, Anchorage, AK 99518, (907) 267-2218.

SPORT FISHING

Emergency Order

ALASKA DEPARTMENT OF FISH & GAME

Under Authority of AS 16.05.060

Emergency Order No. 2-KS-2-22-18

Issued at: Palmer, Wednesday, June 20, 2018

Effective Date: 6:00 a.m. Friday, June 22, 2018

Expiration Date: 11:59 p.m. Friday, July 13, 2018, unless superseded by subsequent emergency order.

EXPLANATION:

This emergency order supersedes Emergency Order No. 2-KS-2-10-18 issued in Palmer on March 13, 2018. This emergency order closes the Susitna River drainage to sport fishing for king salmon and limits sport fishing gear for other species to one unbaited, single-hook, artificial lure when fishing in Units 1 - 6 of the Susitna River drainage in those waters normally open to king salmon fishing. Single hook is defined as a hook with only one point.

Fishing for other finfish species remains open. In the waters of Unit 2 normally open to king salmon fishing, fishing for trout and other species is allowed seven days per week from 6:00 a.m. to 11:00 p.m. King salmon may not be targeted and those caught while fishing for other species may not be removed from the water and must be released immediately.

REGULATION:

The provisions of 5 AAC 61.110. (1)(A) and (B)(i), 5 AAC 61.112. (1), (4), (6)(A) and (B), 5 AAC 61.114. (1) and (3), 5 AAC 61.116. (2), 5 AAC 61.118. (1), (4), and (7)(A), 5 AAC 61.120. (1), and 5 AAC 61.122. (1) and (4)(A) are superseded by this emergency order. Under this emergency order, the following provisions are effective, beginning 6:00 a.m. Friday, June 22 through 11:59 p.m. Friday, July 13, 2018:

5 AAC 61.110. General provisions for seasons, bag, possession, annual, and size limits, and methods and means for the Susitna River Drainage Area.

1) king salmon

(A) sport fishing for king salmon is closed; king salmon may not be retained or possessed; king salmon that are caught must be released immediately; a person may not remove a king salmon from the water before releasing the fish;

(B) less than 20 inches in length

(i) sport fishing for king salmon is closed; king salmon may not be retained or possessed; king salmon that are caught must be released immediately; a person may not remove a king salmon from the water before releasing the fish;

5 AAC 61.112. Special provisions for the seasons, bag, possession, and size limits, and methods and means for Unit 1 of the Susitna River Drainage Area.

(1) in flowing waters only one unbaited, single-hook, artificial lure may be used;

(4) sport fishing for king salmon is closed;

(6) in the Deshka River drainage, including Trapper Lake,

(A) in flowing waters upstream of the Moose/Kroto Creeks, only one unbaited, single hook, artificial lure may be used;

(B) from its mouth upstream to ADF&G regulatory markers located 300 feet downstream of the weir (river mile 7), and in all waters within a one-half mile radius of its confluence with the Susitna River, sport fishing for king salmon is closed; king salmon may not be retained or possessed; king salmon that are caught must be released immediately; a person may not remove a king salmon from the water before releasing the fish; from its mouth upstream to ADF&G regulatory markers near Chijuk Creek (river mile 17), and in all waters within a one-half mile radius of its confluence with the Susitna River, only one, unbaited, single hook, artificial lure may be used; the remainder of the drainage is closed to sport fishing for king salmon;

5 AAC 61.114. Special provisions for the seasons, bag, possession, and size limits, and methods and means for Unit 2 of the Susitna River Drainage Area.

(1) from January 1 - July 13, Unit 2 is open to sport fishing for all finfish species, except king salmon; sport fishing for king salmon is closed;

(3) in flowing waters only one unbaited, single-hook, artificial lure may be used;

(15) from May 15 – July 13, sport fishing is not allowed from 11:00 p.m. to 6:00 a.m.;

5 AAC 61.116. Special provisions for the seasons, bag, possession, and size limits, and methods and means for Unit 3 of the Susitna River Drainage Area.

(2) from May 15 – July 13, fishing for king salmon is closed; sport fishing is not allowed from 11:00 p.m. to 6:00 a.m.;

5 AAC 61.118. Special provisions for the seasons, bag, possession, and size limits, and methods and means for Unit 4 of the Susitna River Drainage Area.

(1) in flowing waters only one unbaited, single-hook, artificial lure may be used;

(2) from May 15 – July 13, sport fishing is not allowed from 11:00 p.m. to 6:00 a.m.;

(4) sport fishing for king salmon is closed; king salmon may not be retained or possessed; king salmon that are caught must be released immediately; a person may not remove a king salmon from the water before releasing the fish;

(7) in the Lake Creek drainage,

(A) from an ADF&G regulatory marker located approximately 100 yards upstream of its mouth to an ADF&G regulatory marker located approximately one-quarter mile upstream of Bulchitna Lake, only one unbaited, single hook, artificial lure may be used;

5 AAC 61.120. Special provisions for the seasons, bag, possession, and size limits, and methods and means for Unit 5 of the Susitna River Drainage Area.

(1) in flowing waters only one unbaited, single-hook, artificial lure may be used;

(2) from May 1 – July 13, sport fishing is not allowed from 11:00 p.m. to 6:00 a.m.;

5AAC 61.122. Special provisions for the seasons, bag, possession, and size limits, and methods and means for Unit 6 of the Susitna River Drainage Area.

(1) in flowing waters only one unbaited, single-hook, artificial lure may be used;

(4) in the East Fork of the Chulitna River drainage, including all waters within a one-quarter mile radius of its confluence of the East Fork and West Fork and including the Middle Fork of the Chulitna and the first quarter mile of Honolulu Creek,

(A) the waters are open to sport fishing for all finfish species, except for king salmon; sport fishing for king salmon is closed;

Sam Cotten,
Commissioner

By delegation to:

____

Sam Ivey,
Area Management Biologist

JUSTIFICATION:

Emergency order No. 2-KS-2-10-18 issued prior to the season closed king salmon sport fisheries in Units 2, 3, 5, and 6 of the Susitna River (Parks Highway streams) and restricted the Deshka River and Unit 4 of the Susitna River (Yentna drainage) to nonretention in anticipation of run similar in size as 2017. The low forecast was driven by a predicted low return of 5-year old king salmon and uncertainty in the forecast of 4-year old fish. 5-year old fish typically constitute about half a given year’s run. To date, sizes of fish observed in department fishwheels on the lower Susitna River, the Deshka River weir, and reports from anglers suggest low abundance of age five fish. Other areas of Cook Inlet and the state are experiencing low returns of older age classes leading to widespread closures of Cook Inlet king salmon sport fisheries. In addition, all indices of abundance indicate king salmon run strength in the Susitna drainage to be lower than anticipated at the outset of the season.

The sustainable escapement goal (SEG) for king salmon in the Deshka River is 13,000 to 28,000 fish, as measured at the weir located at river mile 7. Based upon average run timing, approximately 50 percent of the escapement should have passed the weir by June 19, 2018. At this time, only 3,983 fish have passed the weir and the total escapement is projected to be approximately 7,472 fish. ADF&G monitors escapement by post season aerial count of spawners on three streams within the Yentna River drainage that have SEGs: Peters Creek, Lake Creek, and Talachulitna River. All three SEGs were missed in 2017. Any additional mortality associated with continued catch-and-release fishing cannot be justified, and all fish within the Deshka River and Yentna drainage must be conserved to provide the greatest potential for achieving escapement goals in 2018.

PREVIOUS EMERGENCY ORDERS AFFECTED:

Emergency Order No. 2-KS-2-10-18, which closed fishing for king salmon in Units 2, 3, 5, and 6 of the Susitna River, prohibited the retention of king salmon in the Deshka River and Unit 4 of the Susitna River drainage and limited sport fishing gear to one unbaited, single-hook, artificial lure only, is superseded by this emergency order.

DISTRIBUTION:

The distribution list for this emergency order is on file at the Region II Office of the Alaska Department of Fish and Game, Division of Sport Fish, 333 Raspberry Road, Anchorage, AK 99518, (907) 267-2218.

Appendix C. Quality Assurance Project Plan

Deshka River Total Aromatic Hydrocarbon (TAH) Sampling

Quality Assurance Project Plan: Version 2.1

Prepared on June xx, 2018 for the:

Alaska Department of Environmental Conservation

By:

Deshka River Total Aromatic Hydrocarbon Sampling
June 2018
Revision 2.1

Cover Photograph. Boat activity at the mouth of the Deshka River in June 2011 during the Chinook Fishery, with inset showing the removal of sample bottles from the VOC sampler.

A1. Deshka River Total Aromatic Hydrocarbon (TAH) Sampling

Aquatic Restoration and Research Institute

Project Manager: ______________________ Jeffrey C. Davis **Date:** 7/9/2018

Quality Assurance Officer: ______________________ Gay A. Davis **Date:** July 9, 2018

Alaska Department of Environmental Conservation

Project Manager: ______________________ Laura Eldred **Date:** ______________

Quality Assurance Officer (acting): ______________________ Chandra McGee **Date:** ______________

Effective Date: ______________________

A2. Table of Contents

A3. Distribution List

Laura Eldred, DEC Project Manager
Alaska Department of Environmental
Conservation
1700 E. Bogard Rd., Bldg B, Ste 103
Wasilla, Alaska 99654
Phone: 907-376-1855
laura.eldred@alaska.gov

Chandra McGee, DEC Quality Assurance Officer
(acting)
Alaska Department of Environmental
Conservation
610 University Ave.
Fairbanks, AK 99709
Phone: (907) 451-2140
Email: chandra.mcgee@alaska.gov

Jeffrey C. Davis, ARRI Project Manager
P.O. Box 923
Talkeetna, AK 99676
Phone: (907)733-5432
Email: arri@arrialaska.org

Gay A. Davis, ARRI Quality Assurance Officer
P.O. Box 923
Talkeetna, AK 99676
Phone: (907) 733-5432
Email: arri@arrialaska.org

Kathy Fugiel, Analytical Laboratory Manager
Am Test, Inc.
13600 NE 126th Pl, Suite C
Kirkland, WA 98034
Phone: 425-885-1664
Email: kathyf@amtestlab.com

A4. Project/Task Organization

The project organization chart (Figure 1) shows the relationship between DEC, ARRI team members, and the contract laboratory.

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

Chandra McGee, DEC Division of Water QA Officer (acting). Ms. McGee will be responsible for the review/approval of the QAPP. She 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 will be responsible for project components including data collection, entry, analyses, and reports. 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 all field data collection and sample handling until samples are returned to the ARRI Laboratory.

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. Ms. Davis also will assist in field data collection.

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.

A5. Problem Definition/Background

Concentrated boat use can result in the direct discharge of hydrocarbons or indirect discharge due to incomplete gasoline ignition. Water quality sampling conducted by the Department of Environmental Conservation (DEC) has documented concentrations of total aromatic hydrocarbons (TAH) concentrations above the water quality numeric criteria in rivers and lakes of Southcentral Alaska including the Little Susitna River, Kenai River, and Big Lake. TAH concentrations are due to the discharge of fuel from boat motors, primarily, inefficient carbureted 2-cycle motors, at locations and during times of concentrated boat use. Concentrated boat use is often associated with boat-accessed fishing.

The Deshka River is the largest Chinook and coho salmon producing Susitna River tributary. Over 40% of Chinook salmon tagged in the Susitna River at Susitna Station (downstream from the Yentna River) migrate to the Deshka River. The Deshka River can only be accessed by boat or by plane. The major route of access is by motor boat from Deshka Landing which is located on the Susitna River approximately 3 miles upstream of the mouth of the Deshka River. The abundant salmon returns to a river largely accessed by boat results in a high probability that concentrations of hydrocarbons will exceed water quality standards. Other influencing factors include the larger motor sizes that are used to navigate the Susitna River, concentrated fishing within the mouth of the Deshka River, the lake-like aspect of the lower Deshka River basin, the no-wake-zone within this basin, the high dissolved organic carbon concentrations, and high water temperatures.

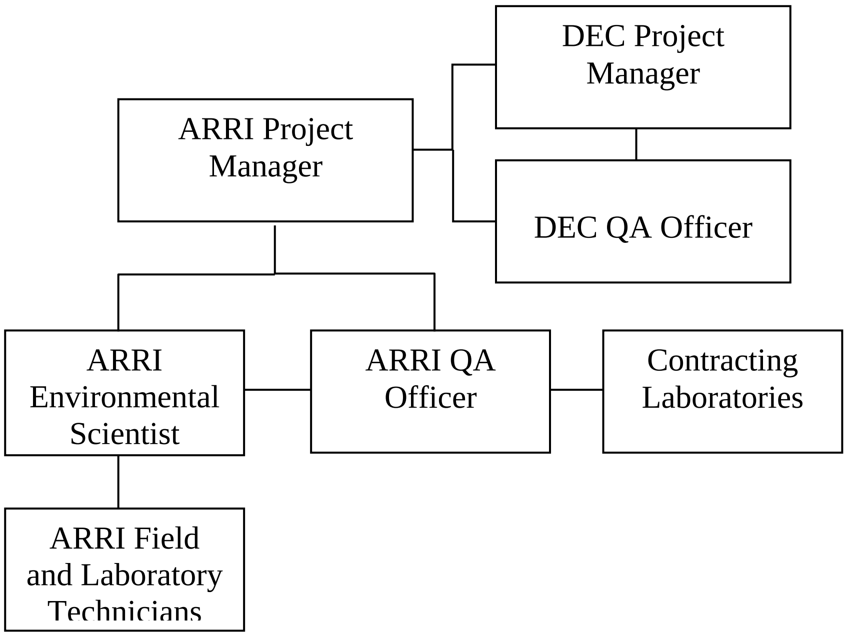


Figure 1. Relationship and lines of communication among personnel and organizations.

Historic DEC Sampling

Methods and results of previous water quality sampling in the Deshka River are described in a 2016 DEC summary report (DEC 2016, Appendix A). Water sampling was conducted at four lower Deshka River sampling locations on June 18, 2011, and on four dates in June of 2014 (June 7, 13, 15 and 21) during the Chinook Salmon fishery. In 2011, and in 2014 three sampling sites were located between the confluence of the Susitna River and 1 mile upstream where most of the boat use during the Chinook and Coho Salmon fishery is concentrated (Figure 2).

In 2011 samples were collected in the morning and evening, and in 2014 samples at two sampling sites (DR – 0.0 and DR – 1.0) were collected at 08:00, 10:00, 12:00, 14:00, and 17:00 in order to obtain average daily values. Water samples were collected 20 cm below the water surface using a USGS volatile organic carbon sampler. Water samples were submitted to an analytical laboratory and analyzed for benzene, toluene, ethyl-benzene, and xylene, which were summed to obtain a measure of total aromatic hydrocarbons (TAH). In 2014, samples also were collected at a subset of sites and analyzed for polycyclic aromatic hydrocarbons to obtain a measure of total aqueous hydrocarbons (TAqH). The water surface was observed for any hydrocarbon sheens.

Boat use surveys were conducted concurrent with water sample collection. Surveys counted all boats and boat motor type (2-cycle, direct injection 2-cycle, 4-cycle outboard, and 4-cycle inboard).

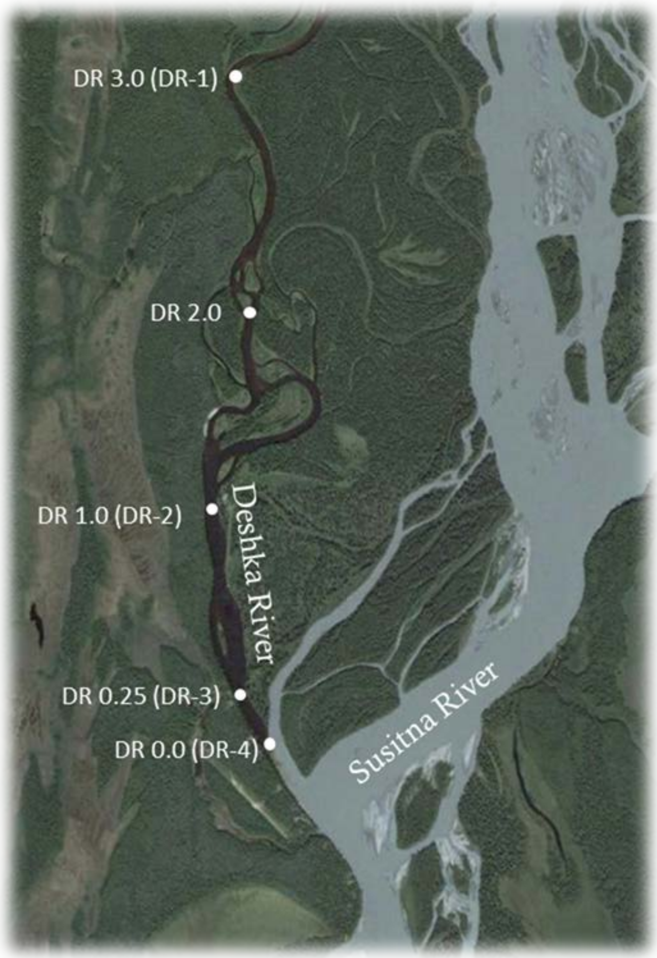


Figure 2. Deshka River 2014 sampling sites with 2011 site names in parentheses. Sample site names correspond to river miles upstream from the Susitna River confluence.

Additional water quality and physical parameters were collected concurrent with water sampling. These included pH (YSI 63), specific conductivity (YSI 63), temperature, turbidity (LaMotte 3000), and channel width and water depth. Discharge was measured at the upstream sampling location (Swoffer 3000). Samples were analyzed for benzene, toluene, ethyl-benzene, and xylene (BTEX). BTEX results were summed to provide total aromatic hydrocarbon concentrations. TAH concentrations were evaluated relative to State water quality standards (18 AAC 70).

Historic DEC Sample Results

In 2011, TAH concentrations were above state water quality standards (10 µg/L) at three of the 4 locations (Figure 3). Maximum TAH concentrations were over 24 µg/L. A total of 98 boats were counted during sampling. TAH flux or flow-corrected TAH values ranged from 46 to 207 mg/s.

Surface oil sheens were observed during sampling at DR03. In 2014, average daily TAH concentrations in the Deshka River exceeded 10 µg/L at sites from the confluence with the Susitna River to 1 mile upstream (Figure 4). Maximum average daily TAH concentration was 17.5 µg/L.

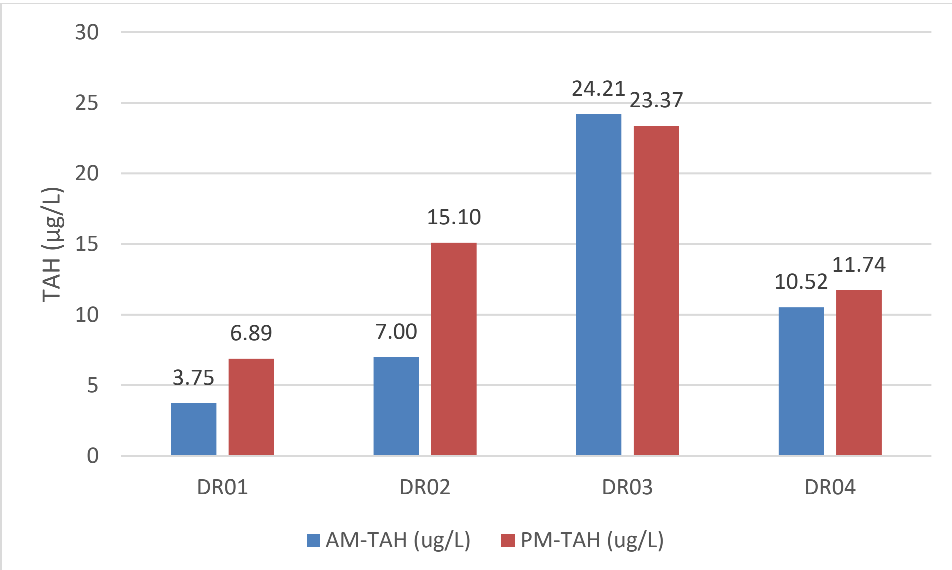


Figure 3. Deshka River TAH concentrations on June 18, 2011. DR04 is downstream and DR01 is upstream.

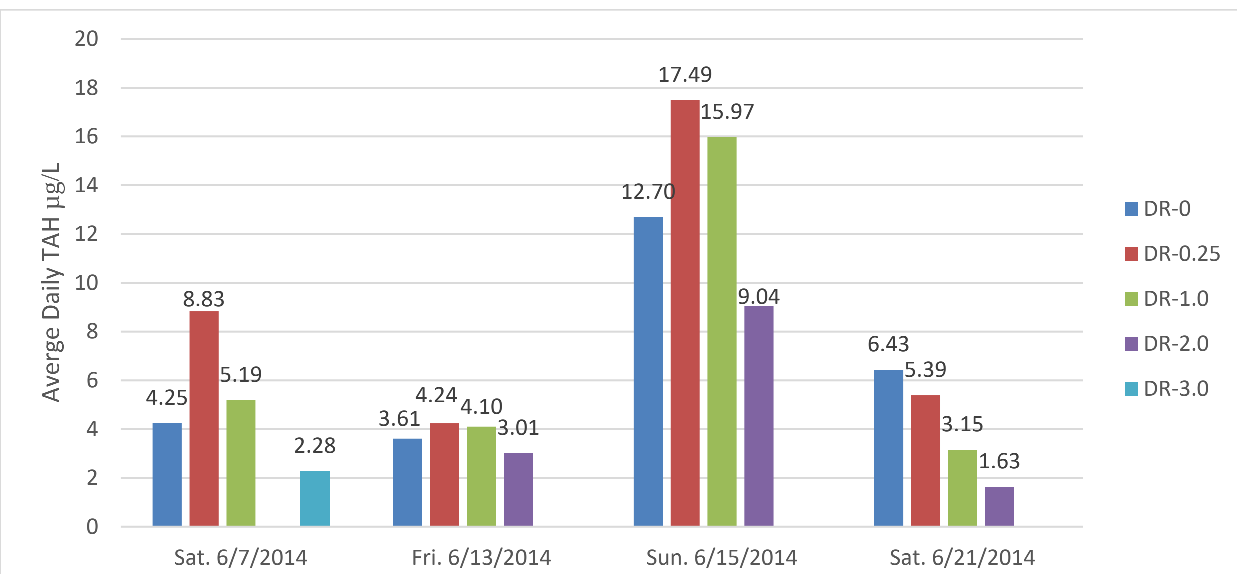


Figure 4. Deshka River average daily TAH concentration in June of 2014. DR-0 is Deshka River Mile 0 at the confluence with the Susitna River.

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 1). Exceedances of water quality standards for hydrocarbons are based upon chronic effects, or 96-hour averages that exceed numeric criteria.

The purpose of this project is to obtain measures of hydrocarbon concentrations for DEC to compare to water quality standards following the "Listing Methodology for determining Water Quality Impairments from Petroleum Hydrocarbons, Oils, and Grease" (DEC 2015). Additional field data will be collected and used to determine possible hydrocarbon sources, loading, and dilution of any discharge. These measures include surveys of boat use by motor type and receiving basin water volume and residence time.

Table 1. Alaska Water Quality Standards (18 AAC 70) for Petroleum Hydrocarbons for Fresh Water Uses.

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).

FY18 and FY19 sampling locations

ARRI will conduct sampling at the lower 3 monitoring locations sampled in 2014 (Table 2 and Figure 2). These monitoring locations bracket the area of most boat activity. The DR-1.0 mile site is upstream of most active fishing but within the transportation corridor. This site should provide an upstream boundary to any potential water quality exceedances. DR-0.0 will provide a downstream boundary to potential exceedances prior to the Deshka joining with the Susitna River

Table 2. Deshka River TAH sampling locations.

Site Name	Description	Latitude	Longitude
DR – 0	Site located at the mouth of the Deshka River downstream from most boat activity.	61.69845	-150.31871
DR – 0.25	Site 0.25 miles upstream of the mouth of the Deshka River and just upstream from the concentrated fishing area.	61.70162	-150.32215
DR – 1.0	Site 1 mile upstream of the mouth and at the upper end of backwater water reach. Site upstream of the floatplane runway and adjacent to the Deshka River lodge.	61.71241	-150.32532

Sampling Events

ARRI will conduct three 96-hour sampling events. Sampling events will occur during the peak Chinook salmon fishery in June and/or the peak coho salmon fishery in August. ARRI will track the Alaska Department of Fish and Game (ADFG) in-season real-time weir counts, emergency regulations, and consult with the DEC project manager to determine exact June and August sampling dates as the time nears. Preference is for sampling to occur during both fisheries; however, sampling events will be coordinated with the DEC project manager and will depend on salmon run size, run timing, and potential fishing restrictions (which impacts boat numbers).

Historically the peak Chinook salmon fishery has occurred through the 2nd and 3rd weeks of June. Preliminary proposed sampling dates are June 14 – June 17, 2018 and from June 21 – June 24, 2018. If June 2018 sampling does not occur due to ADFG emergency closure orders, ARRI will be prepared to sample in June 2019 instead.

The coho salmon return is highly variable year to year. Preliminary proposed sampling dates are August 16 – August 19, 2018.

FY18 and FY19 Sampling Dates and Time

Proposed sampling dates and times are provided in Table 3. Sampling will occur during periods when boat activity is at its highest as recommended by DEC. Sampling will occur Thursday through Sunday from 08:00 to 17:00. Sampling days may vary based on the management of the sport fishery.

Table 3. Potential Deshka River TAH sampling dates and times.

Salmon Fishery	Sampling Start Date	Sampling End Date	TAH sample Times
Chinook	June 14, 2018 or 2019	June 17, 2018 or 2019	08:00, 10:00, 12:00, 14:00, 17:00
Chinook	June 21, 2018 or 2019	June 24, 2018 or 2019	08:00, 10:00, 12:00, 14:00, 17:00
Coho	August 16, 2018	August 19, 2018	08:00, 10:00, 12:00, 14:00, 17:00

Water Sample Collection for TAH Analyses

ARRI will coordinate with AM Test, Inc. the project analytical laboratory, to obtain sample bottles and hydrochloric acid (HCl) preservative prior to the first sampling date.

Field sampling will be conducted by a minimum of two ARRI staff during each sampling event: the project manager and a field technician. ARRI staff will travel to and from the Deshka River on each sampling date.

Field sampling will begin at 06:00 to prepare for the 08:00 sample. Sites will be accessed by boat from Deshka Landing using a 4-stroke motor. Sampling will begin at the downstream sampling station and work in an upstream direction. Upon reaching a sampling site, the boat will be anchored and the motor turned off. The sample will be collected off of the bow after the motor has been off for 5 minutes. During this interval, water depth, channel width, and water temperature will be measured at 10 cm intervals from the surface. The water surface will be inspected for oil sheens, site photographs taken, and the latitude and longitude recorded. ARRI will use the clean-hands method, and submersible VOC sampler for sample collection (See Appendix A for VOC sampling methods). The clean-hands method means the person operating the boat and handling the anchor will not touch the sample bottles, preservative, labels, or VOC sampler.

Samples will be collected near the main channel adjacent to the thalweg in order to obtain a well-mixed sample, while not disrupting navigation. Clean sample bottles and preservative will be obtained from the analytical laboratory. Sample bottles will be placed within the VOC sampler using clean exam gloves and avoiding touching the inside of the cap or bottle. Samples are carefully removed from the VOC sampler, preserved with HCl, capped, checked to ensure that there are no air bubbles in the sample bottle, and placed within a cooler on ice. Preserved water samples will be kept in a cooler on ice and shipped directly to the analytical laboratory. Trip blanks, field blanks, and replicates will be used for field quality assurance. One field blank will be collected on each sampling date using TAH-free water. The analytical laboratory (AM Test, Inc.) will use surrogates, matrix spikes, and duplicates for quality assurance.

Additional Data Collection

Changes in water volume can alter concentrations under conditions of similar discharge. The amount of water within the basin at the mouth of the Deshka River changes with Deshka River discharge, but can also increase due to backwater from the Susitna River. Water volume will be estimated from measures of basin area and water depth. Water depth will be measured using water level loggers installed at two locations DR-0.25 and DR – 1.0.

Water temperature can influence hydrocarbon uptake and toxicity. Water temperature in the large basin at the mouth of the Deshka River can vary with depth (stratification and Susitna River backwater), and laterally. Stream water temperature will be measured concurrent with water sample collection. Water temperature will be measured with a temperature specific thermistor and meter at 0.1 m depth intervals at DR-0 and DR-0.25, and DR-1.0. Stream water temperature will also be measured at two locations (approximately DR 0.5 and DR 1.5) using temperature loggers, providing a total of four temperature monitoring locations. Channel width and water depth will be measured at all sampling locations. Stream water pH, specific conductivity, dissolved oxygen, and turbidity will be measured at each location using calibrated hand-held meters.

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 numbers by motor type. Boat use data will be obtained by counting the number of boats operating in the lower basin (between DR-0.0 and DR-1.0) by conducting transect surveys after each sampling collection (5 times/day). Data collected will include total boat counts, counts of inboard motors, outboard motor size, and outboard motor type including 4-stroke, 2-stroke, and 2-stroke direct inject. For each boat counted ARRI will document whether the boat is anchored or operating and whether the boat is headed to the upper river or fishing in the lower basin. Additional boat use data will be obtained using stop-action photography. Stop action cameras will be setup at two locations (DR 0.0 and DR 0.25) and set to take a photograph every hour.

Project Reporting

Periodic project reporting to the DEC project manager is outlined in Table 4.

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 exceed state water quality standards (18 AAC 70). Temperature, pH, conductivity, dissolved oxygen, and basin volume are secondary measures. Water temperature will be measured to evaluate effects to TAH evaporative losses. Boat counts are used to interpret the differences in TAH concentrations.

Table 4. List of project progress and completion reports and due dates.

Report	Due Date
Field reports including photos (Email)	within 48 hours following each sampling event
Laboratory reports (PDF and Excel)	Upon receipt from laboratory and completion of QA evaluation.
Draft AWQMS data template (Excel workbook)	December 31, 2018
Final AWQMS data template (Excel workbook)	March 31, 2019 or July 31, 2019
Copies of the Chain-of-Custody forms field data sheets/notes in PDF format	March 31, 2019 or July 31, 2019
Data analysis/evaluation Excel spreadsheet(s)	February 28, 2019 or June 30, 2019
Draft data assessment project report	January 14, 2019 or June 30, 2019
Final data assessment project report	March 31, 2019 or July 31, 2019

Table 5. 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%
Specific Conductivity (µS/cm)	EPA 120.1 Meter	0.1	150 to 300	85 to 115	10%	90%
pH	EPA 150.2 Meter	0.1	7.0 to 8.5	85 to 115	10%	90%
Dissolved Oxygen (mg/L)	EPA 360.1 Meter	1.0	8 to 14	85 to 115	10%	90%
Temperature Loggers (°C)	EPA 170.1 Field Measure	0.01	4.00 to 20.00	95 to 105	10%	90%
Water level (pressure loggers) (kPa)	ASTM D5413-93	0.014	90 to 120	95 to 105	10%	90%
Temperature (°C) Thermometric	SM 2550 B	0.1	4 to 25	85 to 115	10%	90%
Turbidity (NTU)	EPA 180.1 Field Measure	0.1	0.0 to 20.0	85 to 115	10%	90%
Boat Counts	Boat Survey: with photos	1	0 to 100	N/A	5%	90%

Criteria for Measurement of Data

Measurement Quality Objectives (MQOs) are a subset of Data Quality Objectives (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 5 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.

Quality Assurance Definitions

<u>Detectability</u>

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

<u>Accuracy</u>

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.

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

<u>Precision</u>

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).

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

<u>Representativeness</u>

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.

<u>Comparability</u>

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.

<u>Completeness</u>

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

Quality Assurance for Measurement Parameters

<u>Detectability</u>

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 5.

<u>Accuracy</u>

The percent accuracy for the acceptance of data is shown for each parameter in Table 5. 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.

<u>Precision</u>

Table 5 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.

<u>Representativeness</u>

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 operate the Omega meter, pH, specific conductivity, turbidity, and dissolved oxygen meters. Any new 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 25 years of experience in stream research. Mr. Davis has managed 12 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 nearly 30 years of experience in stream evaluation and restoration. Ms. Davis has over 20 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 by the State of Washington, Department of Ecology and is subjected to annual proficiency certification.

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. Copies of field data books will be provided to the DEC project manager. Laboratory reporting and requested laboratory turnaround 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:

<u>Field sampling reports</u>: Field sampling reports will be prepared and submitted to the DEC project manager following each 4-day sampling event as email summaries. Reports to the DEC project manager will occur daily if problems occur in implementing the approved sampling plan. Field reports will review all activities, any problems with data collection, and comments on observations.

<u>Laboratory Reports</u>: Analytical laboratory reports as signed pdf documents and Excel spreadsheets that comply with the electronic reporting rule 2 or 3 will be submitted to the DEC project manager upon receipt and approval from the ARRI QA officer. Laboratory analytical reports will contain copies of chain-of-custody forms and lab processing time.

<u>Field Data Sheets</u>: Field data sheets and data books will be scanned and submitted to the DEC project manager as Adobe pdf documents.

<u>Raw Data Files: Raw data files downloaded from equipment will be submitted to the DEC project manager.</u>

<u>Data Analyses Spreadsheets:</u> Data analyses spreadsheets will contain all of field and laboratory data and any equations used to calculate daily average TAH values, TAH loading, and other calculated data. The spreadsheets will contain all of the tables and figures used in the draft and final project reports.

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

<u>Photographs</u>: Electronic copies of all project photographs will be submitted to the project manager using the naming protocols established by DEC.

<u>Draft Project Report</u>: The draft project report will present all of the field and laboratory data in a narrative format. Sampling methods will be outlined. Evaluation of compliance with quality assurance measures will be described. The report will describe any exceedances of water quality standards and any analyses that may affect the potential for standards to be exceed (basin area and boat use by motor type). The narrative will be supported by tables and figures as necessary.

Final Project Report: The final project report will incorporate any comments received from the DEC project manager on the draft project report.

B1. Sampling Process Design

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

External Data
External data will include USGS gauge data for the Susitna River at Gold Creek (USGS Gauge 15292000).

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 VOC 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 for TAH analyses 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 analytical laboratory. One sample to be analyzed for TAH will be collected (2- 40 ml 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. 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 12 cm below the water surface. The attached rope and weighted sampler will be used to keep the sampler upright. HCl acid, provided by the analytical 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 hydrocarbon-free water.

Materials Required:

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

Specific Conductivity, pH, Dissolved Oxygen, and Turbidity

Stream water specific conductivity, pH, and temperature will be measured using a YSI Pro 1030 meter and probe. Stream water pH is a measure of hydrogen ion activity and will be measured concurrently with specific conductivity. All meters will be tested for accuracy and calibrated prior to field sampling. Specific conductivity will be calibrated at 1 mS/cm and pH meters at 4.0, 7.0, and 10.0. Probes will be submerged to approximately 0.5 times water depth within the flowing channel avoiding areas of stagnant water. Probes will be allowed to equilibrate for 2 minutes prior to recording results. Dissolved oxygen will be measured using a YSI Pro ODO meter and probe. Turbidity will be measured *in situ* using appropriate meters and manuals (LaMotte TC-3000we.) Support equipment will include extra batteries and sample bottles. Clean sample bottles will be used. All meters will be tested and calibrated prior to use.

Materials Required.

- YSI Pro 1030 pH and Specific conductivity meter,
- YSI Pro ODO Meter and Probe,
- LaMotte TC turbidimeter (0, 10, and 100 NTU standards).

Water Temperature

Point measures of water temperature will be taken concurrent with hydrocarbon sampling with an Omega HH801A temperature logger with thermistor or the YSI Pro1030 meter.

Materials Required:

- Omega meter and thermistor.

Water Level (Pressure)

Water pressure and temperature loggers will be used to calculate changes in water depth. Water pressure loggers will be installed at two underwater locations (DR 0.25 and DR 1.0) and a third logger will be deployed above the water surface to correct for changes in air pressure. Pressure loggers will be placed within perforated pvc pipe (2.54 cm inside diameter) attached to rebar. The rebar will be driven into the stream bed until secure. A staff gauge will be secured to the rebar in order to measure water depth. Changes in underwater pressure loggers, corrected for differences in air pressure, will be used to calculate changes in water depth. Changes in water depth will be used to calculate changes in basin area or the volume of water available for mixing with discharged hydrocarbons.

Materials Required:
- Pressure loggers (Hobo U20L-04) (3),
- temperature loggers (Hobo Pro V2) (2),
- rebar (2),
- staff gauges (2),
- sledge hammer, and
- perforated pvc pipe.

Time Lapse Photography

Time lapse cameras will be deployed at two locations (DR 0.0 and DR 0.25) to track boat use throughout the summer. The cameras will be set to take an exposure every hour. Cameras will be checked and downloaded during each sampling event.

Materials Required:
- Cameras (Stealthcam STC SNX-1) (2),
- camera tree brackets (2),
- batteries,
- sd cards,
- ladder.

Boat use Surveys

The number of boats operating by motor type will be determined through boat surveys during each sampling event. Five times each day we will slowly navigate from the mouth of the Deshka River upstream. We will count each boat on the river and note whether the motor is running or not, motor type (inboard, outboard 4 stroke, outboard 2 stroke, or outboard 2 stroke direct inject).

Materials Required:
- Binoculars,
- camera,
- data book,
- pencils.

Weather Observations

The weather on each sampling date will be noted as either, sunny, partly cloudy, intermittent showers, or rain. Air temperature will be measured and recorded. Weather observations will also include, as much as possible, weather conditions (rain, dry, intermittent showers) 24 hours prior to sampling.

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 (see Appendix C for AM Test Chain of Custody form). Sample preservation and holding times are shown in Table 6. Samples will be placed within a cooler with frozen gel packs, 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.

B4. Analytical Methods Requirements

Sample analytical methods are shown in Table 7 and 8. Field samples will be collected by ARRI staff and delivered to the commercial laboratory for subsequent analyses by the identified standard method.

Table 6. Preservation and Holding Times for Sample Analysis. No preservation or holding times for *in situ* measures of pH, temperature, dissolved oxygen, turbidity, specific conductivity, or pressure.

Analyte/Method	Method	Matrix	Container	Necessary Volume	Preservative	Holding Time
TAH	EP 624	Surface Water	G, FP lined septum	40 ml each (2 bottles)	HCl to pH <2, Cool≤6°C, do not freeze,	14 days

G = glass, FP = flouropolymer

B4. Analytical Methods Requirements

Sample analytical methods are shown in Tables 7 and 8. Field samples will be collected by ARRI staff and delivered to the commercial laboratory for subsequent analyses by the identified standard method.

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.

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

Table 7. List of Analytical methods and detection limits for study parameters.

Measurement	Collection/ Analyses	Method	Equipment	Method Detection Limits	Turnaround Time (days)
Temperature	ARRI	EPA 170.1	Omega Thermister Or YSI 63 meter	0.1°C	Direct Measure (*in situ*)
Temperature (Data Logger)	ARRI	EPA 170.1	Hobo Pro V2	0.2°C	Direct Measure (*in situ*, Hourly)
Water Level (Pressure)	ARRI	Not Available	Hobo U20L-04	0.014 kPa	Direct Measure (*in situ*, Hourly)
Total Aromatic Hydrocarbons	ARRI/ AM Test Inc	EPA 624	USGS VOC Sampler	0.0015 mg/L	14 days (Laboratory)
Turbidity (NTU)	ARRI	EPA 180.1 Meter	LaMotte 220we	0.1 NTU	Direct Measure (*in situ*)
pH	ARRI	EPA 150.1	YSI Pro 1030	0.1 pH Units	Direct Measure (*in situ*)
Specific Conductivity (µS/cm)	ARRI	EPA 120.1	YSI Pro 1030	1.0 µS/cm	Direct Measure (*in situ*)
Dissolved Oxygen	ARRI	EPA 360.1	YSI ODO Meter	0.1 mg/L	Direct Measure (*in situ*)

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,
- Chemical reagents and standard reference materials are used prior to expiration dates;
- Proper field sample collection and analysis techniques;

- Correct sample labeling (location, site, date, time, samplers, analyses, preservation) 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).
- Field blank every sampling date.

Table 8 below defines the field QC types, frequency and acceptance criteria limits.
Maintaining Cooler Temperatures. Water samples for TAH will be held in coolers for 8 to 10 hours prior to returning to the ARRI laboratory and for up to 24 hours when shipped from the ARRI laboratory to AM Test, Inc. Sample temperature needs to be reduced and held between 1°C and 6°C. A total of 15 samples will be collected on each sampling date and will include a trip blank and a field blank for a total of 34 40-ml sample bottles (2 bottles/sample) each day. To ensure these temperatures are maintained, ARRI will conduct a laboratory test to determine the number of frozen gel-paks necessary to meet these requirements. Surrogate sample bottles (>28) and a temperature blank will be filled with 20C° tap water. The water temperature in the blank will be measured. The sample bottles will be placed in a cooler with frozen gel-packs (approximately 1, 16 oz. pack for every 6 bottles). The cooler will be placed within a room held at an air temperature of 20°C for 24 hours and then the temperature of the blank re-measured. This process will be repeated, adjusting cooler size and the number of gel-paks until a final temperature of <6°C can be confidently achieved.

B.5.2 Laboratory Quality Control (QC) Measures

Quality Control in laboratories includes the following (see Table 9):

- 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/DEC.

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 samples analyzed will be 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 actions.

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 recording the dates calibration is conducted. All calibrating, testing and storage will follow the manufacturer's recommendations. The QA officer will inspect the calibration records.

Table 8. 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	4/sampling event, 12 total	≤ BETX MDL
Trip Blank	TAH (BETX)	1/cooler	1/sampling event, 3 total	≤ BETX MDL
Temperature Blank	Temperature	1/cooler	1/sampling event, 3 total	≤6°C < 10°C Flagged
Field Replicate (Blind to Lab)	TAH (BETX)	14% and at least 1/sampling day event	4/sampling event, 12 total	See BETX and precision criteria listed in section A7 Table 5
Equipment Blank	TAH (BETX)	1/sampling day event	4/sampling event, 12 total	≤ BETX MDL
Field Replicate Measurement	Boat Count	N/A	N/A	N/A
Field Replicate Measurement	pH/Specific Conductivity/DO/Turbidity	1/every 10^{th} Sample	1	See precision criteria listed in section A7 Table 5

Table 9. Laboratory Quality Control Samples

Laboratory Quality Control Sample	Measurement Parameter	Frequency of Occurrence	QC Acceptance Criteria Limits
Lab Blank	All method 624 and 625 analytes	1 per batch	< detection limit (1)
Lab Fortified Blank	All method 624 and 625 analytes	1 per curve	
Calibration Verification Check Standard	All method 624 and 625 analytes and surrogates	1 per calibration curve	%RSD ≤ 30%
Continuing Calibration Verification Check Standard	All method 624 and 625 analytes and surrogates	1 every 12 hrs	%RSD ≤ 20%
Matrix Spike/Matrix Spike Duplicate	All method 624 and 625 analytes	1 per 12 hr shift	See below
Lab Duplicate Sample	All method 624 and 625 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

B7. Instrument Calibration and Frequency

The pH, specific conductivity, DO, and turbidimeters will be checked for accuracy against commercial standards prior to each sampling event. If meters are not within acceptable limits (pH 0.1, 5 µS/cm, 1% Saturation, 0.5 NTU), meters will be calibrated. The accuracy of the temperature meter and data loggers will be checked against a NIST certified thermometer at three temperatures (~0, 10, and 20°C) prior to deployment.

All instrument accuracy checks will be recorded in the laboratory data book and include the following information:

- Date/Time
- Name
- Instrument
- Calibration standard (including expiration date and lot#)
- Instrument reading (and pass/fail against acceptable limits described above)
- Re-calibration (if necessary)

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

Flow data obtained online from the U.S. Geological Survey gauge stations will be assumed accurate.

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 5) depicts how data will be collected, processed, QA/QC, and distributed.

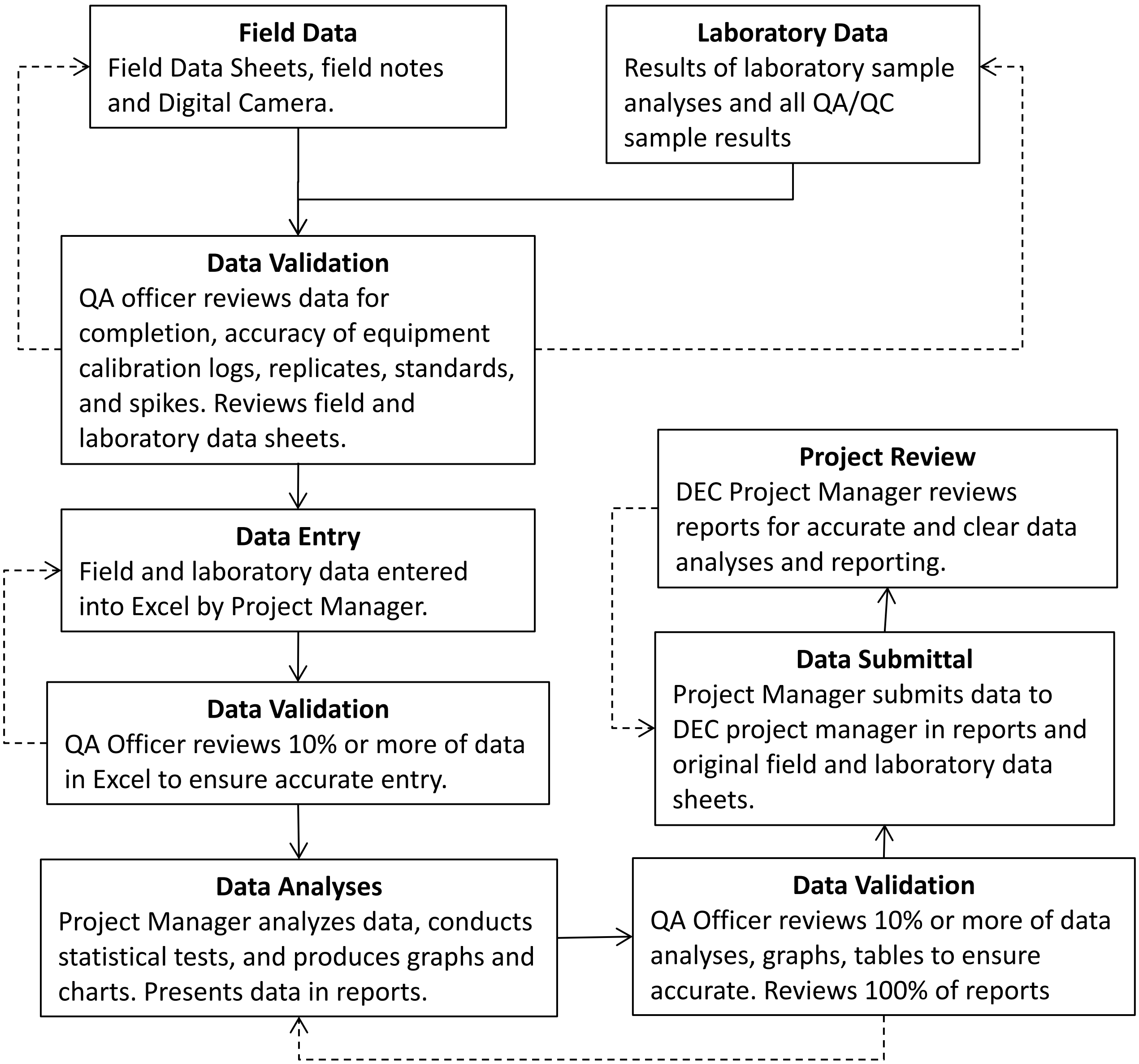


Figure 5. Data management flowchart.

Field data will be entered into rite-in-the-rain books. The quality assurance officer will scan 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 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.

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) using the data template provided by DEC.

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 as soon as possible. The project manager will prepare all of the reports. Reports will be reviewed by the quality assurance officer for errors. The reports 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.

A list of all project reports in provided in section A9.

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 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 draft and final reports. The quality assurance officer will check the data result calculations for accuracy. The project manager will correct any errors found.

D3. Reconciliation with User Requirements

ARRI's Project Manager and QA Officer will review and validate the data prior to the final reporting stages. If there are any problems with quality sampling and analyses, these issues will be addressed immediately and methods will be modified to ensure that data quality objectives are being met. Modifications to monitoring will require notification to DEC and subsequent edits to the approved QAPP.

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 when submitted to DEC. 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 to DEC.

References

Alaska Department of Environmental Conservation. 2011. Alaska Water Quality Criteria Manual for Toxic and Other Deleterious Organic and Inorganic Substances, as amended through May 15, 2003. Juneau, Alaska.

Alaska Department of Environmental Conservation. 2011. 18 AAC 70, Water Quality Standards. Juneau, Alaska.

Alaska Department of Environmental Conservation. 2016. Deshka River Screening Level Water Quality Sampling for Petroleum Hydrocarbons; June 7, 13, 15 and 21, 2014. Anchorage, AK.

Alaska Department of Environmental Conservation. 2010. Alaska's Final 2010 Integrated Water Quality Monitoring and Assessment Report—July 2010. Juneau, Alaska.

ASTM D5413-93(2013), Standard Test Methods for Measurement of Water Levels in Open-Water Bodies, ASTM International, West Conshohocken, PA, 2013, www.astm.org.

Davis, J.C., and G.A. Davis. 2013. Water quality in the Lower Little Susitna River: Cumulative Report July 2007 through June 2012. Final Report for Alaska Department of Environmental Conservation, Alaska Clean Waters Action Program Contract No. 18-6002-12. Aquatic Restoration and Research Institute. Talkeetna, Alaska.

Davis, J.C. and G.A. Davis. 2007. The Little Susitna River—An ecological assessment. Final Report for the Alaska Department of Environmental Conservation. ACWA 07-11. Aquatic Restoration and Research Institute. Talkeetna, Alaska.

Davis, J.C. G.A. Davis, and N.R. Ettema. 2009. Water Quality Evaluation of the Lower Little Susitna River: July 2008 through June 2009. Final Report for the Alaska Department of Environmental Conservation. ACWA 09-02. Talkeetna, AK..

Davis, J.C., and G.A. Davis. 2008. Water quality evaluation of the lower Little Susitna River. Final Report fo the Alaska Department of Environmental Conservation. ACWA 08-02. Aquatic Restoration and Research Institute. Talkeetna, Alaska.

Davis, J.C., G.A. Davis, and A. Crabb. 2014. Big Lake water quality monitoring 2013. Final Report for Alaska Department of Environmental Conservation, Contract No. 18-6002-12. Aquatic Restoration and Research Institute. Talkeetna, Alaska.

Davis, J.C., G.A. Davis, and L. Eldred. 2006. Little Susitna Water Quality Monitoring Report (March 2005-April 2006). Aquatic Restoration and Research Institute. Final Report for the Alaska Department of Environmental Conservation. Talkeetna, Alaska.

Hauer R. F., and V. H. Resh. 2007. Macroinvertebrates. Pages 435-454 *In* Methods in Stream Ecology 2nd Edition (eds R. Hauer & G. A. Lamberti), Academic Press, 896 pgs.

Moulton, S.R. II, J.G. Kennen, R.M. Goldstein, and J.A. Hambrook, 2002. Revised protocols for sampling algal, invertebrate, and fish communities as part of the national water-quality assessment program. U.S. Geological Survey, Open-File Report 02-150.

Scannell, P.W., D. Dasher, L. Duffy, R. Perkins, and T. O'Hara. 2005. Acute and chronic toxicity of hydrocarbons in marine and fresh water with an emphasis on Alaska species. Alaska Department of Environmental Conservation, 610 University Avenue. Fairbanks, Alaska 99709.

Shelton, L.R. 1997. Field guide for collecting samples for analysis of volatile organic compounds in stream water for the National Water-Quality Assessment Program. U.S. Geological Survey, Open File Report 97-401.

Appendix A. Deshka River Screening Level Water Quality Sampling for Petroleum Hydrocarbons; June 7, 13, 15 and 21, 2014

ALASKA DEPARTMENT OF ENVIRONMENTAL CONSERVATION

Deshka River Screening Level Water Quality Sampling for Petroleum Hydrocarbons; June 7, 13, 15 and 21, 2014

Findings Report

dated January 2016

This project was conducted under contract #18-6002-12-08 with the Aquatic Restoration and Research Institute (ARRI) of Talkeetna, AK.

SUMMARY

Petroleum hydrocarbon sampling was conducted for the Department of Environmental Conservation (DEC) at five sampling sites on the Deshka River on four separate sampling days during June 2014. This sampling was conducted subsequent to initial findings from 2011 of petroleum hydrocarbons in the river in excess of State Water Quality Standards (WQS).

The samples were laboratory analyzed for total aromatic hydrocarbons (TAH). Additionally, a subset of samples were analyzed for polycyclic aromatic hydrocarbons (PAH) to measure total aqueous hydrocarbons (TAqH). Results were compared against WQS in 18 AAC 70.

Of the 46 TAH samples taken, 10 (or 22%) exceeded the state water quality criterion of 10 micrograms per liter (μg/L). TAH concentrations ranged from 1.63 μg/L to over 17 μg/L. June 15 had the highest TAH results with 8 of 12 samples exceeding 10 μg/L. No samples in the study exceeded the TAqH criterion. Surface water sheening was observed at two sampling sites on multiple sampling dates and times.

INTRODUCTION

The Deshka River is located in south-central Alaska and is the largest king salmon and silver salmon producing tributary of the Susitna River. The Deshka River can only be accessed by boat or plane. The major route of access is by motor boat from Deshka Landing which is located on the Susitna River approximately three miles upstream of the mouth of the Deshka River (aerial photo in Appendix A).

Looking upstream from the mouth of Deshka River at boats fishing for king

The Deshka River is a popular fishery due to abundant salmon returns. The king salmon fishery is busiest during the month of June (Appendix B) and the silver salmon fishery in the month of August. Fishing activity is largely conducted using motorized boats.

King salmon that migrate up the Susitna River from Cook Inlet leave the turbid mainstem Susitna River and enter the clear-water mouth of the Deshka River. King salmon mill in this area at the mouth of the Deshka River prior to continuing their migration to spawning locations in the upper drainage. Fishing is concentrated in this milling fish area with only a portion of boats traveling farther upstream to fish. Also located in the lower Deshka River are a float plane air strip and a Matanuska-Susitna Borough campground with a dock and fish cleaning stations. There are also several cabins, residences and a lodge. The Alaska Department of Fish and Game (ADF&G) maintains a fish counting weir site on the Deshka River approximately six miles upstream of the mouth.

PROJECT BACKGROUND

The heavy boat use traffic on the lower Deshka River raised concerns about water quality and petroleum hydrocarbon pollution coming from the motorized boats. DEC has investigated petroleum pollution from motorized boats in other south-central Alaska waters including the Kenai River, Little Susitna River and Big Lake. The physical characteristics of the lower Deshka River with a wide, deep and slow moving channel along with the no-wake-zone in the area of concentrated motorized boat use (boat motors are less efficient when idling or operating at slower speeds and petroleum discharge can increase) led DEC to begin investigating the level of petroleum pollution. Through a contract with the Aquatic Restoration and Research Institute (ARRI), DEC conducted screening level petroleum hydrocarbon sampling in the Deshka River on one day in June 2011 and on four non-consecutive sampling days in June 2014.

2011 TAH SAMPLING

2011 Methods

Water sampling was conducted at four lower Deshka River sampling locations on June 18, 2011 during the king salmon fishery. Sampling had initially been planned to be conducted on the nearby Little Susitna River (under a DEC approved Quality Assurance Project Plan (QAPP)) but when the fishery closed, the sampling was shifted to the Deshka River. Sampling followed similar procedures as had been approved for the Little Susitna River. Deshka River sampling locations were distributed from near the confluence with the Susitna River (site “Deshka 4”) to 3.7 miles upstream (site “Deshka 1”). See Table 1.

2011 Sample Results

Deshka River water physical properties and TAH concentrations from the one day of sampling in June 2011 are shown in Table 1. Stream water discharge was 308 cubic feet per second (cfs). Stream water turbidity and specific conductivity were highest at site “Deshka 4”, which likely reflected partial mixing with the Susitna River. TAH concentrations were above state water quality criterion (10 µg/L) at three of the four sampling sites. Five of the eight samples taken exceeded state criteria with a maximum TAH concentration of over 24 µg/L. A total of 98 boats were counted during sampling. Surface oil sheens were observed during sampling at site “Deshka 3”.

Table 10. Summary of June 18, 2011 TAH sampling results. Sites “Deshka 3” and “Deshka 4” were within the concentrated fishing area.

Site	Latitude	Longitude	Channel Width (ft)	Water Temp. (C)	Turbidity (NTU)	Specific Cond. (µS/cm)	Morning -TAH (µg/L)	Afternoon -TAH (µg/L)
Deshka 1	61.73986	-150.32202	233	17.0	4.66	74.5	3.75	6.89
Deshka 2	61.71056	-150.32594	415	16.2	4.21	74.4	7.00	15.10
Deshka 3	61.70040	-150.32158	277	16.2	4.33	74.4	24.21	23.37
Deshka 4	61.69706	-150.31766	394	16.3	7.11	84.9	10.52	11.74

The results of this initial sampling led to further TAH sampling conducted in June 2014 under a DEC approved QAPP. The remainder of this report focuses on the 2014 study and results.

2014 SAMPLING METHODS

2014 Sampling Locations

The sampling locations used in 2014 are distributed from the mouth of Deshka River (DR- 0) to three miles upstream (DR-3.0). A majority of the sampling sites are within the lower one mile of the river since this is the area with the concentrated boat use. Sample site distribution also serves to determine the longitudinal extent of TAH in the river. Figure 1 shows the sampling locations and Table 2 provides a description. Note that the 2014 sample site names refer to the river mile where the sample site is located. This is a different naming convention than that used in 2011 and more sites were sampled in 2014.

Sampling at site DR-3.0 was only conducted on June 7. For safety reasons in motoring to this site, it was removed from the project after June 7.

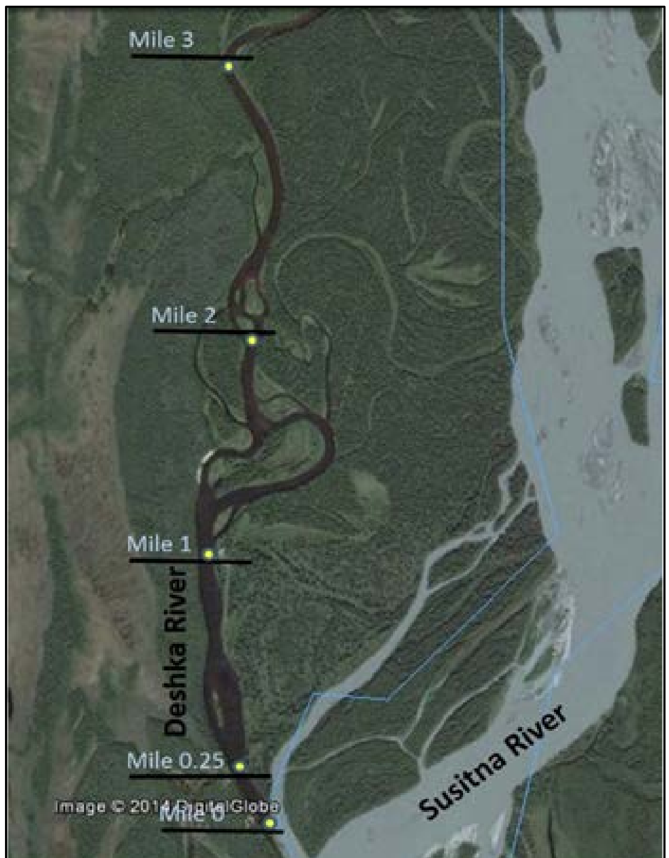


Figure 1. Deshka River sampling locations from the confluence with the Susitna River to 3 miles upstream on the Deshka River.

2014 Sampling Frequency

Water samples were collected for TAH analyses at 08:00, 10:00, 12:00, 14:00, and 17:00 at the intensive sampling locations DR-0 and DR-0.25 on each sampling date.

Water samples were collected for TAH analyses at sites DR-1.0, DR-2.0, and DR-3.0 once between 15:00 and 17:00 on each sampling date.

Water samples were collected for TAqH at site DR-0 and DR-0.25 at 14:00 on each sampling date. See Table 3.

Site Name	Description	Latitude	Longitude

DR – 0	Site located at the mouth of the Deshka River. Site has some mixing with Susitna River waters. Lentic area.	61.69845	-150.31871
DR – 0.25	Site 0.25 miles upstream of the mouth of the Deshka River and part of the concentrated fishing area. Lentic area.	61.70162	-150.32215
DR – 1.0	Site 1 mile upstream of the mouth and at the upper end of lentic water reach. Site upstream of the floatplane runway and adjacent to the Deshka River lodge.	61.71241	-150.32532
DR – 2.0	Site located 2 miles upstream from the mouth and within the lotic reach.	61.72662	-150.32160
DR – 3.0	Site located 3 miles upstream from the mouth and the most upstream sampling site. Lotic reach. Site only sampled June 7.	61.73868	-150.32278

Table 2. June 2014 Deshka River sampling sites.

Table 3. Sampling schedule for Deshka River TAH and TAqH monitoring.

Sampling Date	TAH Sample Time DR-0 and DR-0.25	TAqH Sample Time DR-0 and DR-0.25	TAH Sample Time DR-1.0, DR-2.0, and DR-3.0
Saturday, June 7, 2014	08:00, 10:00, 12:00, 14:00, 17:00	14:00	Between 14:00 and 17:00
Friday, June 13, 2014	08:00, 10:00, 12:00, 14:00, 17:00	14:00	Between 14:00 and 17:00
Sunday, June 15, 2014	08:00, 10:00, 12:00, 14:00, 17:00	14:00	Between 14:00 and 17:00
Saturday, June 21, 2014	08:00, 10:00, 12:00, 14:00, 17:00	14:00	Between 14:00 and 17:00

2014 Field Collection Techniques

TAH water samples were collected 20 cm below the water surface using a U.S. Geological Survey (USGS) volatile organic carbon sampler. The samples were packed in coolers with gel packs and shipped to a laboratory for analysis. Samples were analyzed for benzene, toluene, ethyl-benzene, and xylene (BTEX). BTEX results were summed to provide TAH concentrations. TAH concentrations were evaluated relative to state water quality criteria.

Water samples for TAqH were collected in the river channel at 0.5 times the water depth. Samples were collected in 1 liter amber glass bottles, packed in coolers with gel packs and shipped to the laboratory for analysis. TAqH concentrations were evaluated relative to state water quality criteria.

Observations for water surface sheening were made at each sample site and time. If a sheen was observed, basic testing methods were used to differentiate an oil sheen from a biogenic sheen by using a stick to break up the sheen ("stick test"). If the sheen swirled and quickly re-coalesced it was documented in the field notes as a petroleum sheen.

Stream discharge was measured using a Swoffer 3000 Velocity meter on each sampling day at the farthest upstream site. On June 7 this was at the site located 3 miles upstream from the mouth (DR-3.0) and for the remaining sampling dates discharge was collected 2 miles upstream from the mouth (DR-2.0). Stream discharge information allows for evaluation of dilution due to changes in water volume.

Stream water temperature was measured concurrent with water sample collection. Water temperature was measured using a temperature specific thermistor and meter at 0.1 meter depth intervals at DR-0 and DR-0.25 due to deeper water depth. All other sites measured water temperature at 0.5 times the water depth.

Channel width and water depth were measured at all sampling locations. Stream water pH, specific conductivity, dissolved oxygen, and turbidity were measured at each location.

Weather conditions were recorded during each sample event and photographs were taken at each sample site (Appendix A).

2014 Boat Use Surveys

Boat use data is necessary to calculate TAH loading to the river and to investigate relationships between TAH discharge and boat motor type. Boat use data was obtained by using a transect survey to count the number of boats operating in the lower river (between DR-0 and DR-1.0) during each sampling event. Transect surveys were conducted by counting each boat or other watercraft passed while driving upstream from DR-0 to DR-1.0. Boat count transect surveys were conducted approximately every two hours on each sampling date for a total of five counts each date.

Data collected included total boat counts distinguished between inboard and outboard motors (4-stroke, 2-stroke, or 2-stroke direct fuel injected (DFI)). If discernable, outboard motor size was documented. Photographs were taken at each sampling site and sampling time to assist in documenting boat density on each sampling date (Appendix A).

2014 RESULTS and DISCUSSION

Total Aromatic Hydrocarbons

Of the 46 TAH samples taken, 10 (or 22%) exceeded water quality criteria of 10 μg/L. TAH concentrations ranged from 1.63 μg/L to over 17 μg/L (Figure 2). If concentrations were below Practical Quantitation Limits, a value of 0.5 times the detection limit was used to calculate TAH concentration. The highest TAH concentrations were on Sunday, June 15 with 8 of 12 samples exceeding 10 μg/L. The lowest TAH concentrations were on Friday, June 13.

Combining all of the TAH samples from each site taken per day, a daily average TAH concentration was calculated (Figure 3). Daily average TAH concentrations exceeded criteria on Sunday, June 15 with the daily average of 13.80 μg/L.

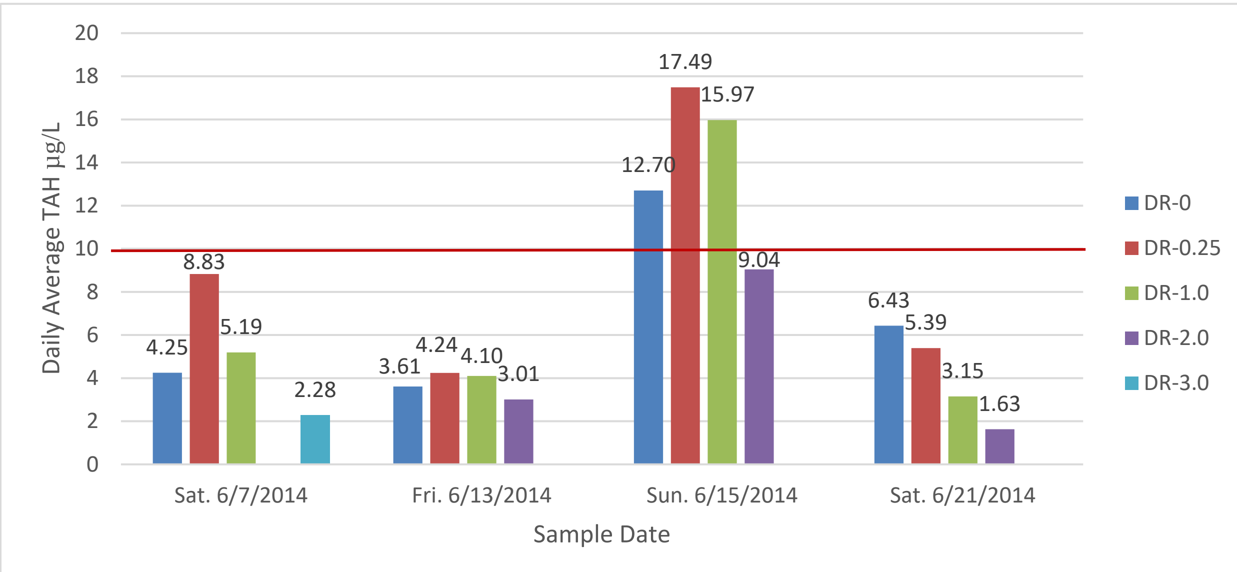


Figure 2. Deshka River TAH concentrations averaged for each sampling date and site. The red line notes the state water quality criterion of 10 μg/L.

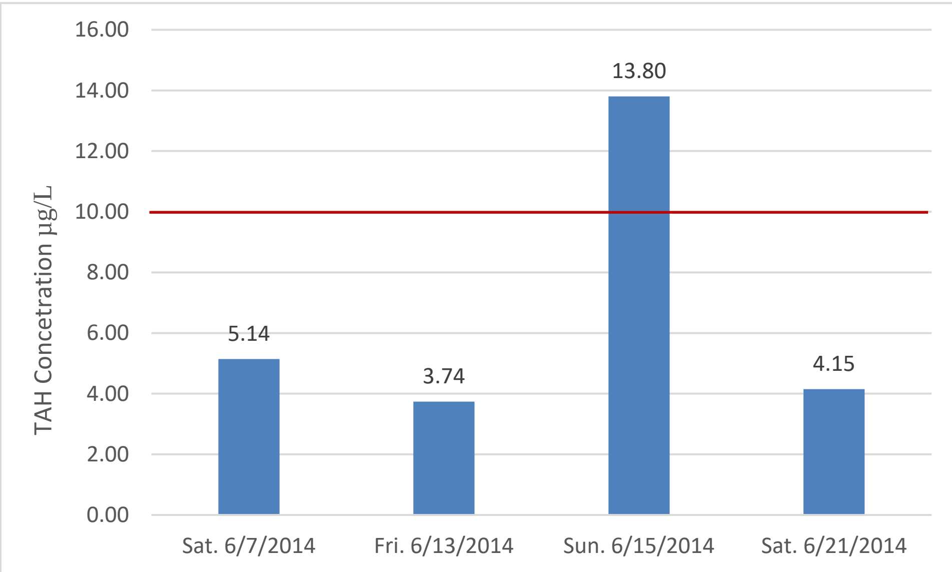


Figure 3. Deshka River daily average TAH concentration for each sampling date. The red line notes the state water quality criterion of 10 µg/L.

Total Aqueous Hydrocarbons

TAqH concentrations were all below the water quality criterion of 15 µg/L on all sampling dates, times and locations. PAH constituents of TAqH were all non-detected.

Surface Sheening

Surface sheening was observed at the two lower most sampling sites (DR-0 and DR-0.25). No sheens were observed at the upper sampling sites (DR-1.0, DR-2.0 or DR-3.0). Sheens were observed at site DR-0 on two sampling days; sheens were observed at site DR – 0.25 on three sampling days (Table 4). Site DR-0 had observed sheening at all sample times on June 15. Site DR-0.25 had sheening on four out of five sampling times on this same date. Site DR-0.25 had the most recorded sheens of the sites sampled in the project.

Table 4. Petroleum hydrocarbon sheening was observed on the surface of the water at two Deshka River sampling sites on 3 sampling dates.

Sampling Date	# Times Sheen Observed During Sampling DR-0	# Times Sheen Observed During Sampling DR-0.25
6/7/2014	0	3
6/13/2014	1	1
6/15/2014	5	4
6/21/2014	0	0

Boat Use Surveys

Table 5 shows the boats counted between river mile zero (DR-0) and river mile 1 (DR-1.0) for each sampling date. Counting boats operating and anchored up in this mile captured a majority of boats operating on the river since this is the area of most concentrated use. The results are broken down by inboard, outboard 4-stroke, 2-stroke, or 2-stroke DFI. Engine horsepower proved difficult to

gather depending on the orientation of boats anchored while fishing. The field notes record horsepower information as much as possible (available from DEC).
A majority of the boats counted were 4-stroke or inboard motors. Carbureted 2-stroke motors accounted for 26 percent of the total boats counted.

Table 5. Deshka River boat counts by motor type for each sampling date.

Date	2-Stroke	2-Stroke DFI	4-Stroke	Inboard	Total Boat Count
6/7/2014	29	8	56	51	144
6/13/2014	26	7	49	39	123
6/15/2014	56	6	39	49	150
6/21/2014	10	1	18	29	58

Other Field Parameters

Discharge

River discharge measures the volume rate of water flow. Discharge (cfs) was measured once during each sampling event at the upper most sample site. On June 7 this was at site DR-3.0 and for the remainder of sample dates discharge was measured at DR-2.0 (Table 6). Water levels were lower on the last day of sampling June 21.

Table 6. Deshka River measured discharge during each sampling event.

Date	Sample Site	River Discharge (cfs)
6/7/2014	DR-3.0	519
6/13/2014	DR-2.0	579
6/15/2014	DR-2.0	571
6/21/2014	DR-2.0	399

Water Depth and Channel Width

The depth of the water column down to the surface of the river bottom was measured at each sampling site during each sampling time. The lower one mile of the Deshka River is wide and deep and more lake like in nature. Average bottom depths at each sampling site are shown in Table 7. The width of the channel was measured at each sampling site and sampling time. Channel width was not measured at site DR-3.0. The channel is widest in lower one mile and in general becomes narrower as you travel upstream. Averaged channel widths are shown in Table 7.

Table 7. Average depth to bottom and average channel width measured at each sampling site on the Deshka River.

Sample Site	Average Depth to Bottom (feet)	Average Channel Width (feet)
DR-0	8.5	428
DR-0.25	10.2	289
DR-1.0	6.2	338

DR-2.0	2.8	278
DR-3.0	3.3	not measured

Weather
Weather conditions during sampling varied between mostly sunny with high temperatures in the 60's to raining with cooler temperatures (Table 8).

Table 8. Weather conditions for each sampling date.

Date	Weather Conditions	Daily High Air Temperature
6/7/2014	Partly sunny	68 °F
6/13/2014	Overcast with a trace of rain	60 °F
6/15/2014	Partly sunny	66 °F
6/21/2014	Overcast with rain, heavy at times	55 °F

Turbidity
Turbidity was measured at each sampling site during each sampling time through grab samples. Daily average turbidity values for each sample site are shown in Figure 4.
Turbidity WQS are determined by comparing the natural condition value to an impacted area's value. The most stringent water quality criteria requires that the two values be within 5 NTU of each other. Because all of the samples measured were less than 5 NTU, this means WQS have been met.

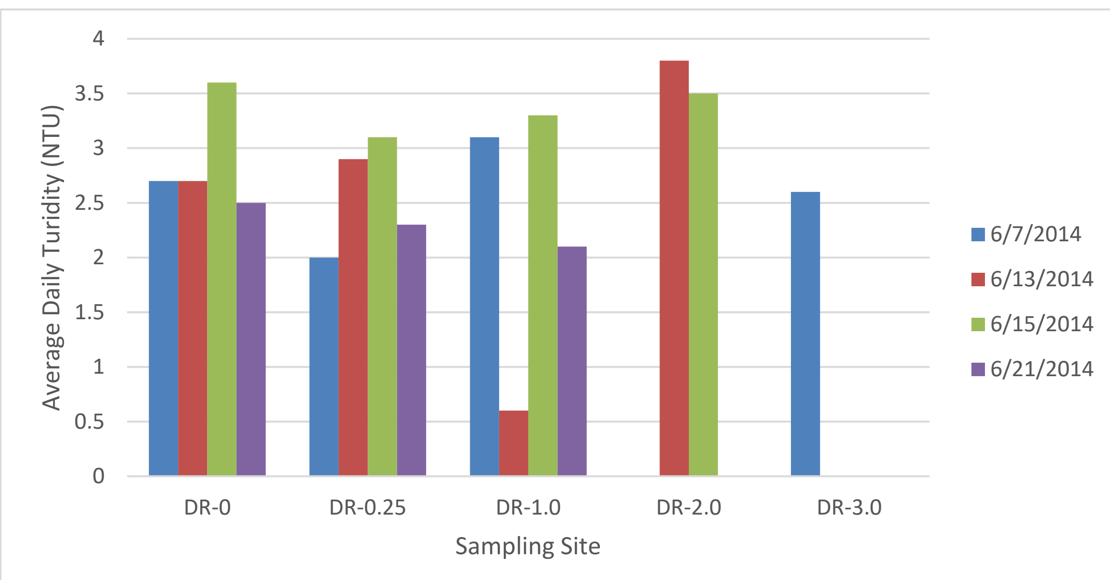


Figure 4. Daily average turbidity for each sampling site and date. Turbidity was only measured during one sampling event at site DR-3.0 and two sampling events at DR-2.0.
Water Temperature
Water temperature was measured at each site during each sampling time. Coolest temperatures were on June 13 at each site. Warmest water temperatures varied by sample date and site. Daily average water temperatures are shown in Figure 5. Daily average water temperatures were above water

quality criteria for fish spawning and egg and fry incubation (13 C°); fish migration and rearing (15 C°) at certain sites and dates.

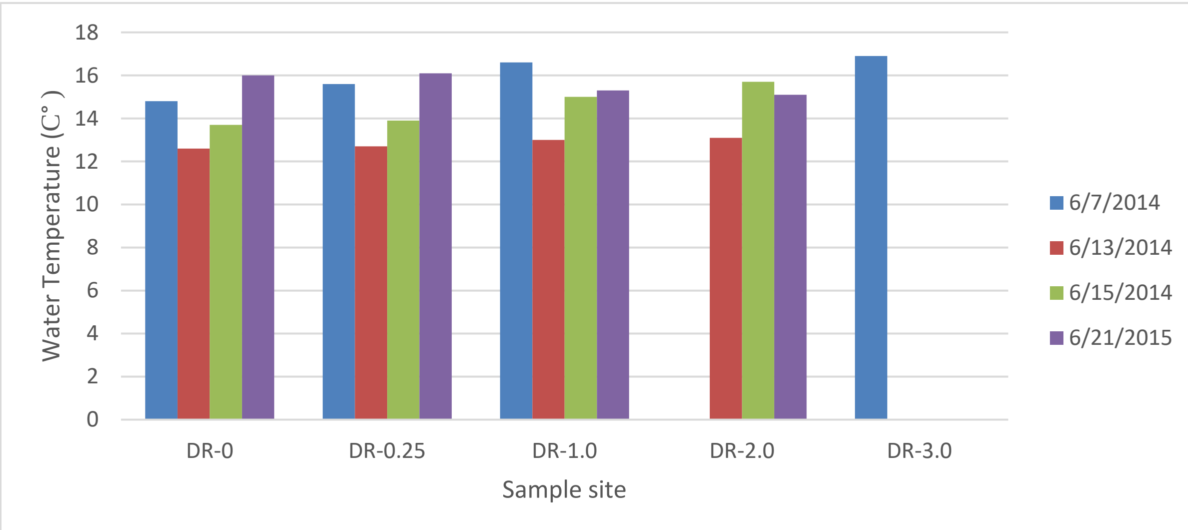


Figure 5. Daily average water temperature for each sampling site and date. Temperature was only measured during one sampling event at site DR-3.0.

<u>Other Field Parameters</u>
Specific conductivity, pH and dissolved oxygen were collected at each sampling site during each sampling time using a calibrated meter. All results met WQS.

CONCLUSIONS
Screening level water quality sampling was conducted for TAH and TAqH in the lower 3 miles of the Deshka River during the king salmon fishery in June 2014. TAH concentrations exceeded the water quality criteria with observed surface sheening and measured TAH concentrations above the aquatic life criterion of 10 µg/L. June 15 had the highest TAH concentrations and also the highest boat counts. TAqH levels were non-detected.

Boat count surveys show that carbureted 2-stroke motors make up approximately 26% of the boats operating on the lower Deshka River. Inboard motors and 4-stroke outboard motors made up the majority of boats counted. Of the dates sampling was conducted, June 15 had the highest number of boats counted.

River discharge was high at the beginning of June but started to drop off by the end of the month. Discharge and water volume generally impact TAH concentrations by dilution in higher flows. The highest recorded TAH concentrations were on June 15 when water volume was also high. This may indicate that the TAH loading for that day was particularly high.

Turbidity grab sampling results were all less than 5 NTU. Even though a natural condition was not established, no WQS exceedances occurred. The grab sampling focused more within the lower one mile reach of the river which is hydrologically different than the upper reaches of the river where the river channel becomes narrower and shallower. Boat traffic may have a greater impact on water quality by increasing turbidity levels in the upper reaches of the river.

Water temperature results exceeded state water quality standards on certain dates and locations. This result is in agreement with other recent temperature studies conducted on the Deshka River. As part of the National Water Quality Assessment Program, the USGS identified the Deshka River as being likely to experience more extreme temperature increases as climate changes (Kyle and Brabets, 2001).

RECOMMENDED NEXT STEPS

More intensive TAH sampling during the king salmon fishery in early summer (primarily the month of June) is needed to determine whether the Deshka River is water quality impaired. While no TAH sampling has occurred during the silver salmon fishery, based on the results from the king fishery and the popularity of fishing during the silver salmon fishery, collecting TAH data during the silver salmon fishery in late July – August is warranted. Sampling should follow the DEC's *Listing Methodology for Determining Water Quality Impairments from Petroleum Hydrocarbons, Oils and Grease. Final Guidance* (2015). TAqH sampling is not recommended. Concurrent with water sampling, conducting observations for surface sheening is recommended.

Boat count data should be collected either through transect surveys or some other approved method to determine the number of boats operating in the sample reach. Motor type (2-stroke, 2-stroke DFI, 4-stroke or inboard), engine horsepower (if discernable) and whether the boat is anchored with engine off, trolling or traveling on the river should all be collected.

Recommended water temperature sampling should use continuous reading data loggers and at a minimum follow protocols outlined in *"Stream Temperature Data Collection Standards and Protocols for Alaska: Minimum Standards to Generate Data Useful for Regional-scale Analyses, 2014"*.

Other basic field measurements (temperature, pH, dissolved oxygen, and specific conductivity) should also be collected and compared against WQS. Discharge measurements should also be collected during each sampling event and should be used to calculate TAH loading to the river.

Turbidity sampling should be conducted using continuous reading data loggers at a reference site and downstream site(s) impacted by motorized boat use. Recommended river miles are between river mile 1 and river mile 6. Turbidity sampling should follow the DEC's latest turbidity listing methodology policy for project design and data analysis guidance.

All water quality sampling must be conducted under a DEC approved QAPP.

REFERENCES

Alaska Department of Environmental Conservation (ADEC). 2003. *18 AAC 70 Water Quality Standards*. As amended through June 26, 2003. Juneau, Alaska.

ADEC. 2008. *Alaska Water Quality Criteria Manual for Toxic and Other Deleterious Organic and Inorganic Substances*, as amended through December 12, 2008. Juneau, Alaska.

ADEC. 2015. *Listing Methodology for Determining Water Quality Impairments from Petroleum Hydrocarbons, Oils and Grease. Final Guidance.* December 14, 2015. Juneau, Alaska.

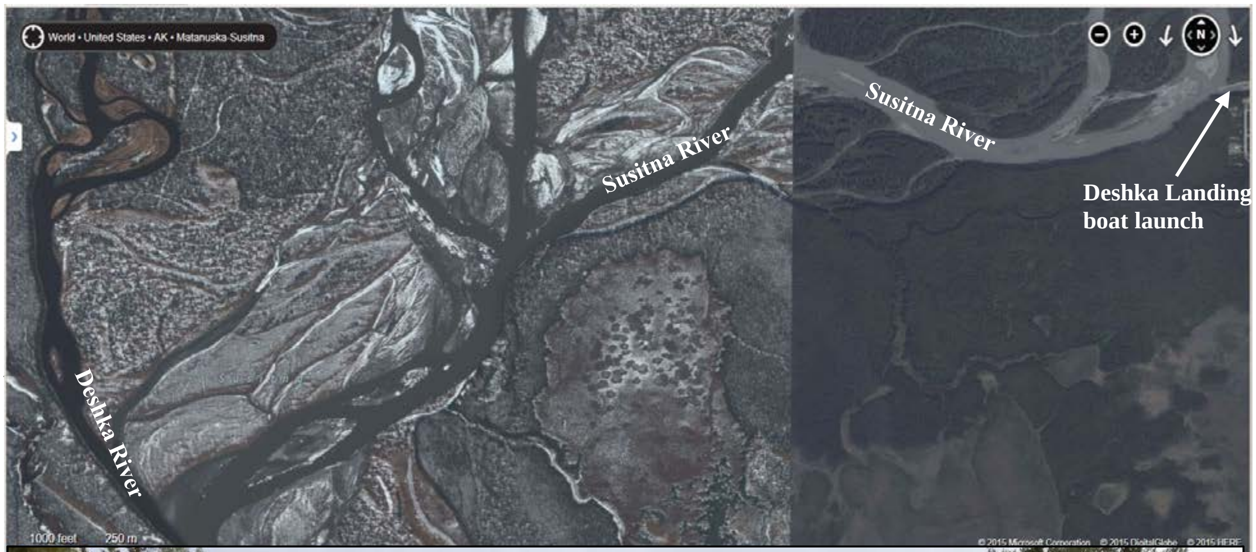
Alaska Department of Fish and Game. 2015. Fish Count Data Search Web Site. http://www.adfg.alaska.gov/sf/FishCounts/index.cfm?ADFG=main.home

Davis, J.C., and G.A. Davis. 2014. *Deshka River Water Quality Sampling as Related to Petroleum Hydrocarbon Pollution; Quality Assurance Project Plan: Version 1.1 Final.* Aquatic Restoration and Research Institute for ADEC under Contract #18-6002-12. Talkeetna, AK.

Kyle, R.E. and T.B. Brabets, 2001. Water temperature of streams in the Cook Inlet basin, Alaska, and implications of climate change. U.S. Geological Survey Water-Resources Investigation Report 01-4109.

Mauger, S., R. Shaftel, E.J. Trammell, M. Geist, and D. Bogan. 2014. Stream temperature data collection standards and protocol for Alaska: minimum standards to generate data useful for regional-scale analyses. Cook Inletkeeper, Homer, AK and Alaska Natural Heritage Program, UAA, Anchorage, AK. 53 pp.

APPENDIX B: Project Photographs



Sampling site DR-0 on June 7, 2014 looking upstream. This is where the Deshka River empties into the Susitna River. There is a side branch of the Susitna River at the very right side of photo.

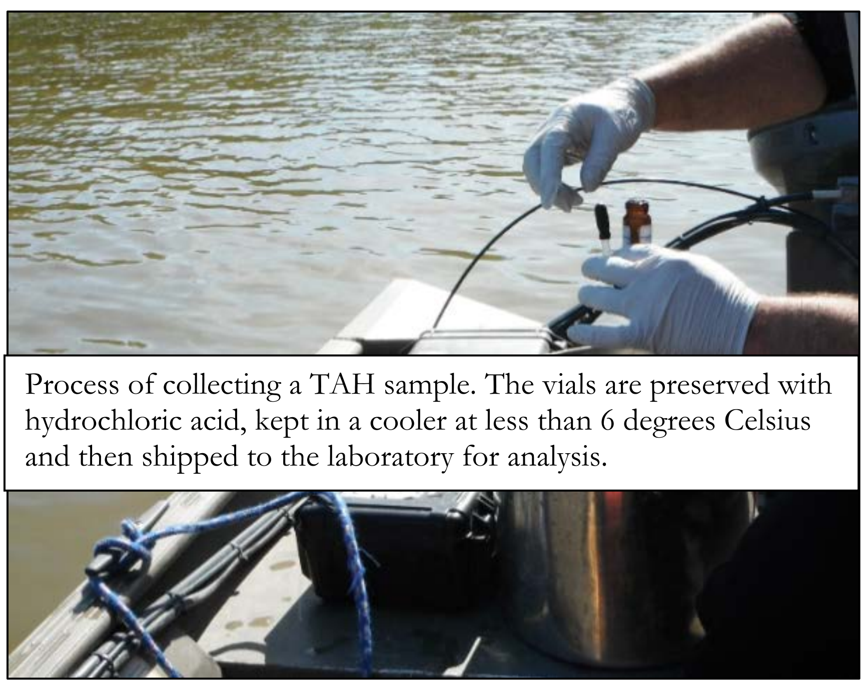
Sampling site DR-0.25 on June 15, 2014 looking downstream. Most boats are anchored up to fish in this area as the salmon mill before moving further upstream. This site had the highest TAH concentration measured.

Sampling site DR-1.0 looking upstream on June 15, 2014.

Sampling site DR-2.0 looking upstream on June 13, 2014. The river has a tight bend and hidden gravel bars that boats navigate through to get further upstream.

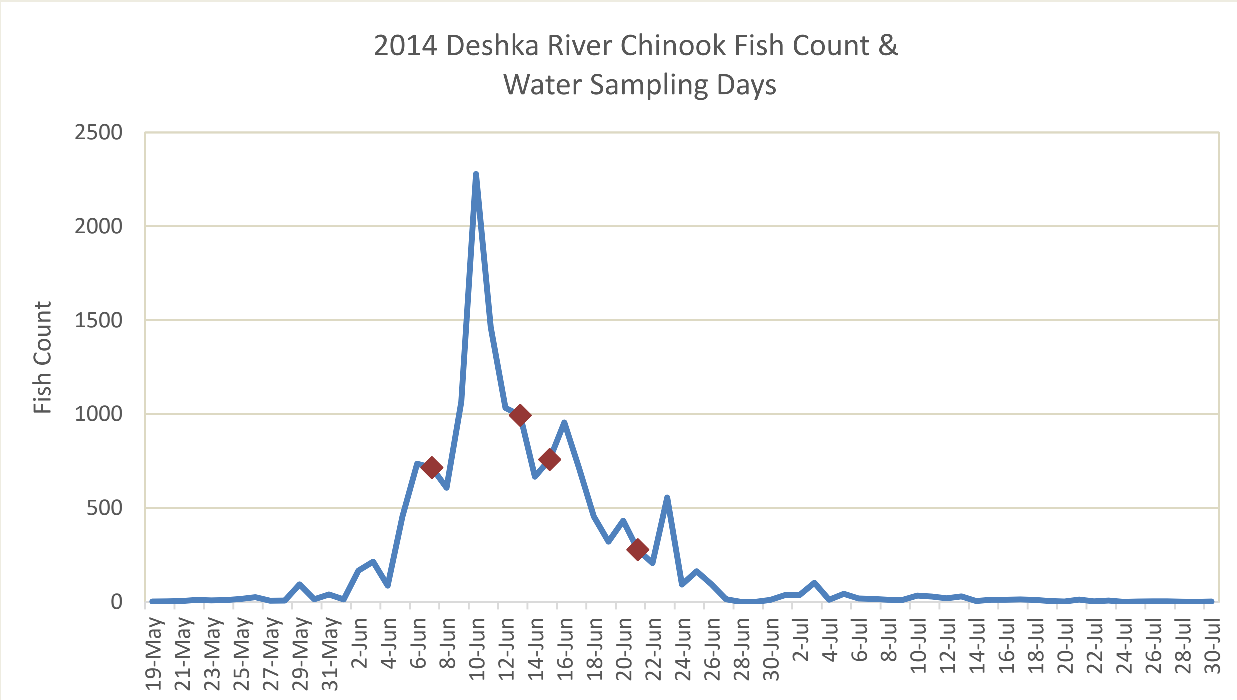
Sampling site DR-3.0. Furthest upstream sample site and only measured on June 7, 2014. The ADF&G weir site and fish counting station is located 3 river miles further upstream from this sampling site.

Example of a petroleum surface sheen observed on June 15, 2014 at site DR-0.

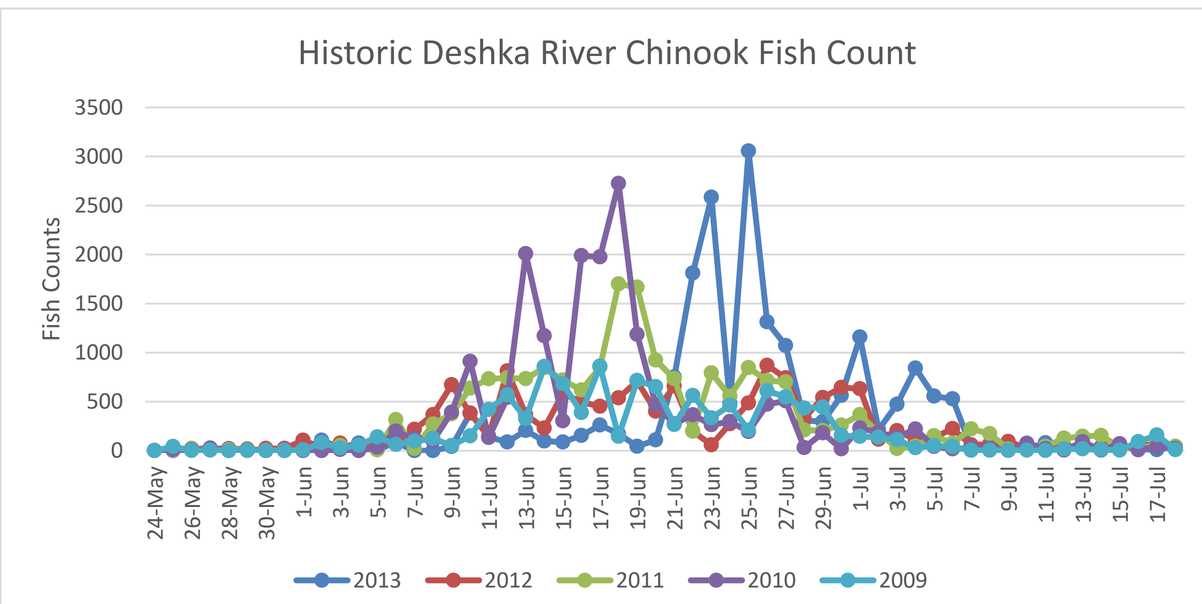


Process of collecting a TAH sample. The vials are preserved with hydrochloric acid, kept in a cooler at less than 6 degrees Celsius and then shipped to the laboratory for analysis.

APPENDIX B: Deshka River Fish Count Information



2014 king salmon fish counts at the Deshka River weir. Orange diamonds represent water quality sampling dates. (Fish count data downloaded from ADF&G/Sport fishing website and graphed by DEC with water sampling dates.)



Historic king salmon fish counts at the Deshka River weir 2009 through 2013. (Information downloaded from ADF&G/Sport fishing website with no changes.)

Appendix A. DEC Deshka River TAH Summary Report

Appendix B. USGS Open File Report 97- 401

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
Gorden P. Eaton, Director

For printed copies of the published report contact:

U.S. Geological Survey
Field Technical Support, NAWQA
Placer Hall, 6000 J St.
Sacramento, Ca. 95819

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).

REFERENCES CITED

Brown, Eugene, Skougstad, M.W., and Fishman, M.J., 1970, Methods for collection and analyses of water samples for dissolved minerals and gases: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 160 p.

Gilliom, R.J., Alley, W.M., and Gurtz, M.E., 1995, Design of the National Water-Quality Assessment Program: Occurrence and distribution of water-quality conditions: U.S. Geological Survey Circular 1112, 33 p.

Hirsch, R.M., Alley, W.M., and Wilber, W.G., 1988, Concepts for a National Water-Quality Assessment Program: U.S. Geological Survey Circular 1021, 42\x11p.

Kilpatrick, F.A., Rathbun, R.E., Yotsukura, N., Parker, G.W., and DeLong, L.L., 1989, Determination of stream reaeration coefficients by use of tracers: U.S. Geological Survey Techniques of Water-Resources Investigations, book 3, chap. A18, 52 p.

Koterba, M.T., Wilde, F.D., and Lapham, W.M., 1996, Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program: Collection and documentation of water-quality samples and related data: U.S. Geological Survey Open-File Report 95-399, 113 p.

Lopes, T.J., and Price, C.V., 1997, Study plan for urban stream indicator sites for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 97-25, 15 p.

Majewski, M.S. and Capel, P.D., 1995, Pesticides in the atmosphere: Distribution, trends, and governing factors: Chelsea, Mich., Ann Arbor Press, Pesticides in the Hydrologic System series, v. 1, 214 p.

Mueller, D.K., Martin, J.D., and Lopes, T.J., 1997, Quality-control design for surface-water sampling in the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 97-223, 17 p.

Shelton, L.R., 1994, Field guide for collecting and processing stream-water samples for the National Water-Quality Assessment Program: U.S. Geological Survey Open-File Report 94-455, 42 p.

Shampine, W.J., Pope, L.M., and Koterba, M.T., 1992, Integrating quality assurance in project work plans of the U.S. Geological Survey: U.S. Geological Survey Open-File Report 92-162, 12 p.

Squillace, P.J. and Price, C.V., 1996, Urban land-use study plan for the National Water-Quality Assessment Program: U.S. Geological Survey Open File Report 96-217, 19 p.

Wilde, F.D., and Radtke, D.B., eds, in press, National field manual for collection of water-quality data, U.S. Geological Survey: Field measurements: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A6, variously paged.

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

---

Back to:
PNSP Publications
USGS Water Resources of California
NAWQA Program

For questions concerning this document, contact: Larry Shelton <lshelton@usgs.gov>
The URL for this page is <http://ca.water.usgs.gov/pnsp/pest.rep/voc.html">