# WATER QUALITY ASSESSMENT PHASE 2

## DUTCH HARBOR, ILIULIUK BAY, ILIULIUK HARBOR

Unalaska, Alaska

FINAL March 2008

Prepared for:

Alaska Department of Environmental Conservation Division of Water Non-Point Source Section Laura Eldred, Project Manager

Prepared by:





## **TABLE OF CONTENTS**

AC	RON	YMS AND ABBREVIATIONSiii			
EX	ECUT	TVE SUMMARYv			
AC	KNO	WLEDGEMENTSvii			
1.	INTRODUCTION				
	1.1.	Background1			
	1.2.	Previous Investigations1			
		1.2.1. Impairment Analysis1			
		1.2.2. April 2007 Water Quality Assessment			
	1.3.	Scope of Work3			
	1.4.	Regulatory Framework			
2.	ASSESSMENT ACTIVITIES7				
	2.1.	Water Sampling7			
	2.2.	Sediment Sampling8			
	2.3.	Field Observations 9			
	2.4.	Sample Plan Deviations9			
	2.5.	Investigation-Derived Waste			
3.	FINDINGS 1				
	3.1.	Water Samples11			
	3.2.	Sediment Samples11			
		3.2.1. Analytical Results11			
		3.2.2. TOC-Normalized Analytical Results			
	3.3.	Field Observations			
	3.4.	Comparison of Cumulative Results			
4.	QUA	LITY ASSURANCE REVIEW15			
5.	EVA	LUATION OF FINDINGS17			
	5.1.	Conclusions			
	5.2.	Recommendations 19			
6.	REF	ERENCES			
ΤA	BLES				
	1:	Sample Summary			
	2:	Water Analytical Results			
	3:	Sediment Analytical Results			
	4:	TOC-Normalized Analytical Results			
	5:	Cumulative Water Analytical Results			
	6:	Cumulative Sediment Analytical Results			

i

#### **FIGURES**

- 1: Site Location Map
- 2: Study Area
- 3: Water Sample Locations and Analytical Results
- 4: Sediment Sample Locations and Analytical Results
- 5: Sediment Sample Locations That Exceed TEL or PEL Benchmarks

#### **APPENDICES**

- A: Field Notes
- B: Photographs
- C: Water Sample Data Sheets
- D: GPS Coordinates
- E: Sediment Sample Data Sheets
- F: Laboratory Analytical Reports
- G: Quality Assurance Review

#### **ACRONYMS AND ABBREVIATIONS**

AAC..... Alaska Administrative Code

BTEX..... benzene, toluene, ethylbenzene, xylenes

CWA...... Clean Water Act

DEC..... Alaska Department of Environmental Conservation

EPA..... Environmental Protection Agency

IDW ..... investigation-derived waste

μg/kg ..... micrograms per kilogram

μg/L ..... micrograms per liter

ml ..... milliliter

OASIS ...... OASIS Environmental, Inc.

PAHs ..... polynuclear aromatic hydrocarbons

PEL ..... probable effects level

QC..... quality control

RPD..... relative percent difference

TAH ..... total aromatic hydrocarbons

TAqH..... total aqueous hydrocarbons

TBT ..... tributyltin

TEL..... threshold effects level

TMDL ..... total maximum daily load

TOC..... total organic carbon

#### **EXECUTIVE SUMMARY**

OASIS Environmental, Inc. performed a second water quality assessment focused on petroleum hydrocarbon contamination in Dutch Harbor, Iliuliuk Bay, and Iliuliuk Harbor during September 2007 for the Alaska Department of Environmental Conservation. The assessment included the collection of 36 water samples and 51 sediment samples from discrete locations. Analytical results show that numeric water quality was met for total aromatic hydrocarbons and total aqueous hydrocarbons in all water samples. Analytical results for sediment samples demonstrate that polynuclear aromatic hydrocarbons (PAHs) are present in sediments for all three water bodies, but that certain areas of the water bodies have significantly elevated concentrations of PAHs. In particular, the most impacted areas are in Iliuliuk Harbor near the Former Submarine Base/Ship Repair Facility, UniSea, and Alyeska Seafoods, as well as at the top of Dutch Harbor. Four sediment samples from Iliuliuk Harbor exceeded the Probable Effects Levels for total PAHs from the Screening Quick Reference Tables. During assessment activities, sampling personnel observed sheens at the APL Dock and personal harvest activities at Front Beach, Rocky Point, and the mouth of Margaret Bay. The main conclusion from the assessment is that water quality is not met because concentrations of PAHs in sediments may cause deleterious effects to aquatic life. Recommendations include more focused sediment sampling in the most impacted areas to determine the extent of contamination, referral of the Former Submarine Base/Ship Repair Facility to the Contaminated Sites Program for characterization, and benthic and bioassay sampling at the most impacted areas in the study area.

#### **ACKNOWLEDGEMENTS**

The Alaska Department of Environmental Conservation would like to acknowledge the following individuals and organizations that assisted in the completion of this project.

- Byron Singley for coordinating charter services and commanding the Nancy Ellen,
- Paul Wayner for serving as first mate on the *Nancy Ellen*,
- Jeff Hancock for operating the water sampling skiff,
- City of Unalaska for discussing project objectives,
- Ounalashka Corporation for discussing project objectives,
- Air Cargo Express for shipping and delivering field gear,
- Pen Air for handling shipment of samples,
- Kinnetic Laboratories, Inc., for providing technical support and the Van Veen sediment sampler, and
- The OASIS sampling team and project manager, Ben Martich.

#### 1. INTRODUCTION

Under Notice-to-Proceed No. 18-2011-26-5, the Alaska Department of Environmental Conservation (DEC) tasked OASIS Environmental, Inc. (OASIS) to conduct a second water quality assessment focused on petroleum hydrocarbon contamination in Dutch Harbor, Iliuliuk Bay, and Iliuliuk Harbor near Unalaska Island and Amaknak Island, Alaska (Figure 1). These water bodies are identified as impaired as a result of contamination from petroleum hydrocarbons. This report presents information regarding water and sediment quality conditions for the impaired water bodies.

In this report, the impaired water bodies of Iliuliuk Bay, Iliuliuk Harbor, and Dutch Harbor often are referred to as the *study area*. Figure 2 shows the study area and surrounding land features.

#### 1.1. Background

In 1990, the Alaska DEC listed Iliuliuk Bay and Iliuliuk Harbor as impaired water bodies under the Federal Clean Water Act (CWA) Section 303(d) for petroleum hydrocarbon pollution exceeding state water quality standards of 18 Alaska Administrative Code (AAC) 70. Dutch Harbor also was added to the 303(d) list in 1994 for petroleum hydrocarbon pollution. The 303(d) listings were based on frequently observed sheens and reports of numerous petroleum spills in the water bodies. The observed sheens caused violations of the water quality standard from 18 AAC 70.020(b)(17), which states in various forms that petroleum hydrocarbons "may not cause a visible sheen on the surface of the water."

Although extensive visible sheens no longer exist in the study area, the three water bodies remain on the 303(d) list as presented in the most recent Alaska DEC water quality report, *Alaska's Final 2006 Integrated Water Quality Monitoring and Assessment Report* (DEC 2006a). By mandate of the CWA, Section 303(d)(1)(C), the Environmental Protection Agency (EPA) or Alaska DEC must:

- Complete a Total Maximum Daily Load (TMDL) for an impaired water body;
- Provide evidence that a water body is not impaired; or
- Demonstrate that other controls are in place that will bring a water body back into compliance with state water quality standards.

The Alaska DEC conducted an impairment analysis of the water bodies in 2006 to initiate the process for determining which course of action to take. The findings of this report are presented in the next section.

## 1.2. Previous Investigations

#### 1.2.1. Impairment Analysis

In 2006, the Alaska DEC (2006b) produced a water quality information analysis of Dutch Harbor, Iliuliuk Bay, and Iliuliuk Harbor entitled *Dutch Harbor Water Quality and Impairment Analysis*. The objectives of the study included evaluating available

1

information for petroleum pollution in the study area, tentatively defining the current areas of impairment, identifying data gaps in the understanding of the impairment, and recommending a process for development of a TMDL or alternative approach.

The study identified six sources of existing or potential petroleum pollution: contaminated sites, spills, storm water, seafood processors, petroleum bulk storage and transfer facilities, and docks and harbors. In addition, contaminated sediments were identified as a contributing factor to potential water quality impairment. These sources were ranked based on the risk each posed to future water quality. Bulk storage and transfer facilities was the only source ranked as having a high risk, but the risk was identified only as a potential one because no documented release of petroleum to water has occurred from this group. The other sources were identified as existing causes of petroleum pollution with contaminated sites, spills, docks and harbors, and contaminated sediments equally ranked as most threatening to future water quality.

Based on this analysis of sources and their locations, the study identified three physical areas most at risk for having potential water quality impairment from dissolved phase petroleum pollutants and contaminated sediments:

- Rocky Point from the airport to the APL Dock;
- The top of Dutch Harbor between Ballyhoo Spit and the coast of Amaknak Island;
   and
- The coastline of Iliuliuk Harbor.

The study recommended the development of an alternative approach for water quality attainment instead of the development of a TMDL because the allocation of petroleum loads to contaminated sites, spills, and contaminated sediments was considered not feasible. The alternative approach outlined in the report was based on the EPA's recommended guidelines for a water body recovery plan and consisted of two main components: water quality monitoring and increased management by the Alaska DEC of petroleum sources in the study area. However, the Alaska DEC still is determining which approach is the preferred long-term plan for water quality attainment.

The subsequent April 2007 water quality assessment initiated the water quality monitoring component of an alternative approach and also determined current levels of petroleum hydrocarbons and the area/extent of impairment.

## 1.2.2. April 2007 Water Quality Assessment

In April 2007, the Alaska DEC performed a baseline water quality assessment of the study area. The assessment included the collection of 71 water samples at 39 locations, collection of discrete sediment samples at ten locations, and collection of incremental composite sediment samples within five regions. The assessment focused on the three areas identified as most at risk in the impairment analysis. The assessment also included field observations of personal harvest activities and sources of petroleum pollution within the project's study area. The significant findings from the baseline assessment included:

2

- The waters of Dutch Harbor, Iliuliuk Bay, and Iliuliuk Harbor met numeric water quality standards for total aromatic hydrocarbons (TAH) and total aqueous hydrocarbons (TAqH) in all 71 water samples collected, although concentrations of TAH and TAqH were detected in ten and three samples, respectively.
- The presence of polynuclear aromatic hydrocarbons (PAHs) in the sediments of Dutch Harbor, Iliuliuk Bay, and Iliuliuk Harbor appears to be ubiquitous. All sediment samples had detectable concentrations for a majority of PAHs, many of which were above Threshold Effects Levels (TELs) and Probable Effects Levels (PELs) from Screening Quick Reference Tables (Buchman 1999). However, the presence of PAHs in sediments does not appear to be significantly impacting water quality based on the analytical results of water samples. The most impacted sediments are located in Iliuliuk Harbor and the top of Dutch Harbor.
- Field observations of the potential sources of petroleum pollution in the study area identified three sheens: two near seafood processors and one near a dock.

The report recommended focusing on more narrowly defined at-risk areas within the three areas identified in the impairment analysis. The recommendations included the collection of water samples from seven areas (Former Submarine Base/Ship Repair Facility, Small Boat Harbor, UniSea, Front Beach, Coastal Transportation Dock, tip of Rocky Point, and top of Dutch Harbor), and the collection of multiple discrete sediment samples from Iliuliuk Harbor, the top of Dutch Harbor, and around the Delta Western Dock.

## 1.3. Scope of Work

The objectives of this water quality assessment for Dutch Harbor, Iliuliuk Bay, and Iliuliuk Harbor were to:

- Evaluate water quality data for dissolved phase petroleum pollutants in seven priority areas of Dutch Harbor, Iliuliuk Bay, and Iliuliuk Harbor during seasonally high boat traffic in September 2007.
- Evaluate sediment quality data for petroleum pollutants in three priority areas of Dutch Harbor, Iliuliuk Bay, and Iliuliuk Harbor.
- Make field observations regarding the identified sources of petroleum pollution for the purpose of developing a TMDL or alternate approach for water quality attainment.

The objectives were met by employing the rationale, methodology, and analysis described in the following sections.

## 1.4. Regulatory Framework

Alaska water quality standards and the degree of degradation that may not be exceeded are contained in 18 AAC 70, Water Quality Standards, and its supporting document Alaska Water Quality Criteria Supporting for Toxic and Other Deleterious Organic and

*Inorganic Substances*. The following table outlines water use classes, subclasses, and petroleum hydrocarbon standards for marine water bodies.

Marine Water Use Class and Subclass	Petroleum Hydrocarbon Standard
Water Supply – Aquaculture	Total aqueous hydrocarbons (TAqH) in the water column may not exceed 15 $\mu$ g/L. Total aromatic hydrocarbons (TAH) in the water column may not exceed 10 $\mu$ g/L. 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.
Water Supply – Seafood Processing	May not cause a film, sheen, or discoloration on the surface or floor of the water body or adjoining shorelines. Surface waters must be virtually free from floating oils. May not exceed concentrations that individually or in combination impart odor or taste as determined by organoleptic tests.
Water Supply – Industrial	May not make the water unfit or unsafe for the use.
Water Recreation – Contact Recreation and Secondary Recreation	May not cause a film, sheen, or discoloration on the surface or floor of the water body or adjoining shorelines. Surface waters must be virtually free from floating oils.
Growth and Propagation of Fish, Shellfish, Other Aquatic Life, and Wildlife	Same as Water Supply – Aquaculture
Harvesting for Consumption of Raw Mollusks or Other Raw Aquatic Life	May not exceed concentrations that individually or in combination impart undesirable odor or taste to organisms as determined by bioassay or organoleptic tests.

The Alaska DEC has not promulgated any sediment quality standards; however, the Contaminated Sites Remediation Program has issued the technical memorandum *Sediment Quality Guidelines* (DEC 2004), in which the use of TELs and PELs from Screening Quick Reference Tables (Buchman 1999) are recommended for evaluating sediment quality. TELs represent the concentration below which adverse effects are expected to occur only rarely. PELs represent the concentration above which adverse effects are expected to occur frequently. The following table lists the applicable TELs and PELs for this project.

Compound	TELs (μg/kg)	PELs (μg/kg)
Acenaphthene	6.71	88.9
Acenaphthylene	5.87	127.87
Anthracene	46.85	245
Benzo(a)pyrene	88.81	763.22
Benzo(a)anthracene	74.83	692.53
Chrysene	107.77	845.98
Dibenzo(a,h)anthracene	6.22	134.61
Fluoranthene	112.82	1,493.54
Fluorene	21.17	144.35
Naphthalene	34.57	390.64
Phenanthrene	86.68	543.53
Pyrene	152.66	1,397.6
Total PAHs	1,684.06	16,770.4

Source: Buchman 1999

#### 2. ASSESSMENT ACTIVITIES

This section presents a summary of the field activities that occurred to meet the objectives outlined in Section 1.3. Table 1 contains a summary of samples collected during field activities. Appendix A contains a copy of field notes, and Appendix B presents photographs depicting field activities.

#### 2.1. Water Sampling

OASIS collected water samples at 36 discrete locations in the study area. Twenty-seven (27) of the locations were at the seven priority areas identified in the *Water Quality Assessment* final report (DEC 2007a) as having potential for water quality impairment. The following list highlights the 27 sample locations by priority area:

- Former Submarine Base/Ship Repair Facility Two sample locations (SW-01 and SW-02),
- Small Boat Harbor Four sample locations (SW-03 and SW-40 through SW-42),
- UniSea Four sample locations (SW-4, SW-5, SW-43, and SW-44),
- Front Beach Five sample locations (SW-11, SW-13, and SW-48 through SW-50),
- Coastal Transportation Dock Four sample locations (SW-14 and SW-45 through SW-47),
- Tip of Rocky Point Four sample locations (SW-23 and SW-51 through SW-53), and
- Top of Dutch Harbor Four sample locations (SW-38, SW-39, SW-54, and SW-55).

In addition, nine locations previously sampled in April 2007 also were sampled. These locations were SW-8, SW-10, SW-16, SW-18, SW-26, SW-29, SW-32, SW-34, and SW-35. Figure 3 presents the water sample locations.

A single water sample was collected at each location from a depth of one meter or the bottom of the water body, whichever was less. Samples were analyzed for benzene, toluene, ethylbenzene, and xylenes (BTEX) by EPA method 602 and PAHs by EPA method 625 SIM for the determination of TAH and TAqH.

OASIS chartered a skiff to access sample locations. A GPS unit with stored location information was used to navigate to each sample location. When the sample location was reached, the outboard motor on the skiff was turned off and the sample crew anchored the skiff to maintain sample position. The following sampling methodology was used:

- Dedicated, weighted, and graduated polyethylene tubing was lowered to the sample depth and a peristaltic pump was used to draw water into a flow-through cell to measure pH, temperature, specific conductivity, dissolved oxygen, oxygen reduction potential, and salinity. Water quality parameters are included on sample data sheets in Appendix C. GPS locations of each sample are provided in Appendix D.
- After recording field parameters, samples were collected for BTEX and PAHs. BTEX samples were collected by placing three uncapped 40-millilet (ml) amber sample

vials in a Wildco® hydrocarbon sampler and lowering the sampler to sample depth. The sampler was tied off at the sample depth to allow sufficient time for the chamber of the sampler to completely fill and flush. At this point, the sampler was retrieved and the immersed sample vials were removed from inside the sampler. The vials were preserved with hydrochloric acid to a pH of less than 2 and capped so that no headspace remained in the vials.

 PAH samples were collected by using the peristaltic pump with dedicated, weighted, and graduated polyethylene tubing to collect water samples from sample depth. Two 125-ml amber bottles were filled from the end of the tubing.

#### 2.2. Sediment Sampling

OASIS collected 51 sub-tidal discrete sediment samples within the study area. The sample locations were selected to increase sample density near areas that had elevated concentrations of PAHs from the April 2007 baseline assessment. The following list highlights the locations of the 51 samples within the study area:

- Iliuliuk Harbor Eighteen samples (SD-1 through SD-4 and SD-16 through 29) were
  collected around the perimeter of the water body. Potential upland and coastal sites
  within this priority area are the Former Submarine Base/Ship Repair Facility, the
  Former Fort Mears Gasoline Station, Alyeska Seafoods, UniSea, and the Small Boat
  Harbor.
- Rocky Point Six samples (SD-6 and SD-30 through SD-34) were collected along the coastline. Potential upland and coastal sites within this priority area are the Lower Tank Farm, the Former Tank 17/18 Area, and the APL Dock.
- Delta Western Dock Six samples (SD-8, SD-9, and SD-35 through SD-38) were collected along the coastline. Potential upland and coastal sites within this priority area are the Former Upper Tank Farm, the Pre-World War II Tank Farm, and the Former Aqua Fuel System #1.
- UMC/USCG Dock Five samples (SD-39 through SD-43) were collected near the dock where the North Pacific Fuel – Ballyhoo Road facility is located.
- Light Cargo Dock Four samples (SD-44 through SD-47) were collected near this public dock.
- Top of Dutch Harbor Twelve samples (SD-10 and SD-48 through SD-58) were collected along the coastline. Potential upland and coastal sites within this priority area are the Former Mount Ballyhoo Spit Tank Farm, the North Pacific Fuel Resoff Terminal, and Icicle Seafoods.

Figure 4 shows the locations of the sediment samples. Samples were analyzed for BTEX by EPA method 8021B, PAHs by EPA method 8270C SIM, and total organic carbon (TOC) by standard method Plumb, 1981.

OASIS chartered a commercial fishing vessel, the *Nancy Ellen*, in Unalaska to access sediment sample locations. The *Nancy Ellen* has a davit and hydraulic winch for lowering and raising a Van Veen sampler to collect sub-tidal sediment samples. The

vessel's GPS unit was used to navigate to stored sample locations. The following sampling methodology was used:

- The Van Veen sampler was placed in the open position and lowered over the side of the boat. When the Van Veen sampler tripped closed on the bottom of the water body, the Van Veen sampler was retrieved using the hydraulic winch.
- On the boat, the Van Veen sampler was opened to expose the intact sediment grab. Field personnel determined whether a clean grab of sediment occurred by examining the recovery of the sampler. Grabs were considered unacceptable for a variety of reasons, but the main causes usually were that the jaws did not close completely because of an obstruction, or the sampler penetrated too shallow and did not retrieve sufficient volume for sampling. When a clean grab occurred, field personnel recorded observations and sampled the sediment material. GPS coordinates for sediment sample locations are provided in Appendix D. Field observations for sediment samples are included on sample data sheets in Appendix E.
- After observations were made, field personnel collected grab samples for BTEX, PAHs, and TOC at each location. For BTEX samples, approximately 50 grams of sample matrix was taken from the Van Veen sampler using a dedicated plastic syringe. The sample matrix was placed in a 4-ounce sample bottle and preserved with methanol following the procedures of Alaska method AK-101. For PAH and TOC samples, a dedicated stainless steel spoon was used to fill a 4-ounce sample bottle for each analytical method.

#### 2.3. Field Observations

During the course of the sampling event, OASIS field personnel observed the study area for the purpose of gathering data related to potential sources of petroleum pollution and personal harvest activities. At each water and sediment sample location, field personnel recorded observations on sample data sheets (Appendices C and E) for personal harvest activities, contaminated sites, spills, storm water, seafood processors, bulk storage/transfer facilities, and docks and harbors.

## 2.4. Sample Plan Deviations

OASIS prepared a *Water Quality Assessment Sample Plan* that outlined the strategy and methodology for the collection of water samples, sediment samples, and field observations (DEC 2007b). Some of the executed activities and details deviated from the plan. The list below identifies the deviations:

- A surface water sample was collected errantly from location SW-16, although this location was not planned.
- Sediment sample locations SD-20, SD-24, SD-27, SD-32, and SD-34 were moved further from shore in order to obtain sediment not entirely composed of rock and gravel.
- A sample spoon was used instead of a syringe to collect sediment samples for PAHs and TOC.

#### 2.5. Investigation-Derived Waste

Water quality assessment field activities generated solid and aqueous investigation-derived waste (IDW). Solid IDW included used PPE, sampling equipment, and unused sediment sample material. The used PPE and sampling equipment, which included disposable nitrile gloves, sample spoons, plastic syringes, polyethylene tubing, and used preservative vials, were contained in trash bags and disposed of at the Unalaska landfill. Unused sediment sample material was dumped overboard. Aqueous IDW included unused water matrix from sampling and decontamination rinse water for the Van Veen sampler. Unused water matrix was dumped overboard and decontamination rinse water was drained off the boat.

#### 3. FINDINGS

This section discusses the results of the assessment and includes tables and figures that show analytical results for water and sediment samples. Appendix F contains a copy of laboratory analytical data reports.

#### 3.1. Water Samples

Table 2 presents the analytical results for water samples, and Figure 3 shows quantifiable TAqH concentrations by sample location. None of the water samples have a detectable concentration of TAH. For comparison, 14 percent of the water samples had a detectable concentration of TAH from the April 2007 assessment.

Four of the 36 primary water samples have detectable concentrations of PAHs; however, all concentrations are below the water quality criteria of 15 micrograms per liter ( $\mu$ g/L) for TAqH. Location SW-02 near the Former Submarine Base/Ship Repair Facility and Harbor Crown Seafoods has an estimated concentration of fluorene at 0.124  $\mu$ g/L; location SW-43 near UniSea has an estimated concentration of naphthalene at 0.404  $\mu$ g/L; location SW-44, also near UniSea, has an estimated concentration of naphthalene at 0.283  $\mu$ g/L; and location SW-48 on Front Beach has an estimated concentration of naphthalene at 0.601  $\mu$ g/L.

#### 3.2. Sediment Samples

This subsection presents analytical results for sediment samples. Section 3.2.1 discusses results using data as provided by the analytical laboratories, while Section 3.2.2 discusses results using PAH data normalized by TOC concentrations.

#### 3.2.1. Analytical Results

Sheens were observed on the surface of many of the Van Veen grab samples. Twenty of the sediment samples had light sheening visible in the sample material. Five other locations, SD-1, SD-2, SD-10, SD-49, and SD-51, had significant sheening. A picture of the heavy sheening at SD-01 is included in Appendix B. Sample location SD-01 also had white flaking visible in the sample material. Given the location of SD-01 near the Former Submarine Base/Ship Repair Facility, there is a possibility that the white flaking may contain tributyltin (TBT), which is a common anti-fouling agent previously used in marine paints. TBT is a documented toxic compound for marine mammals and invertebrates.

Table 3 presents the analytical results for sediment samples using data as provided by the analytical laboratories. None of the sediment samples have a detectable concentration of BTEX. For comparison, 33 percent of the sediment samples had a detectable concentration of at least one BTEX compound from the April 2007 assessment.

Only one of the 51 primary samples does not have any PAH compounds detected in the analytical suite: location SD-33 at the tip of Rocky Point. For the other 50 sample

locations, 37 locations have at least one PAH compound that exceeds a TEL benchmark for sediment quality, and 14 of the samples have at least one compound that exceeds a PEL benchmark. Four of the sediment samples exceed the PEL benchmark for total PAHs: SD-01 near the Former Submarine Base/Ship Repair Facility, SD-03 and SD-22 near UniSea, and SD-26 near Alyeska Seafoods (although the concentration of total PAHs is estimated at SD-26). Seventeen other sediment samples also exceed the TEL benchmark for total PAHs. Of the 21 sediment samples that exceed TEL or PEL benchmarks for total PAHs, 20 of them are locations either in Iliuliuk Harbor or the top of Dutch Harbor. The remaining sample is location SD-37 on the north side of the Delta Western Dock. Figure 5 highlights the sediment sample locations that exceed either the TEL or PEL benchmarks.

#### 3.2.2. TOC-Normalized Analytical Results

Concentrations of PAHs in sediments often show significant variability because naturally present organic carbon acts as an attractor or accumulator of hydrophobic compounds such as petroleum hydrocarbons (Luthy 2004). As a result, concentrations of PAHs in sediments may vary between areas if one area has greater organic carbon content even though the mass of hydrocarbons released to each area may be the same. A method to address this natural variability caused by organic carbon is to normalize concentrations of PAHs by dividing analytical results by the percentage of TOC in each sample.

Table 4 shows the TOC-normalized data for PAHs. A majority of the samples (32 out of 51 primary samples) have a TOC result greater than 1.00 percent, thereby causing the resulting TOC-normalized concentrations of PAHs to decrease when the TOC result is divided into the PAH concentrations. Therefore, TOC-normalized concentrations of PAHs generally are less than the corresponding non-normalized concentrations. However, the more important issue is whether the distribution of concentrations for TOC-normalized data are significantly different than the non-normalized data. To analyze this issue, the correlation of paired data (normalized and non-normalized data at each sample location) is tested using the non-parametric Spearman's Rank Correlation Test with the following hypothesis:

- H<sub>0</sub>: There is no correlation between the concentrations of total PAHs for TOC-normalized data and non-normalized data (i.e., the ranks of concentrations by sample location are statistically different).
- H<sub>1</sub>: There is correlation between the concentrations of total PAHs for TOC-normalized data and non-normalized data (i.e., the ranks of concentrations by sample location are not statistically different).

This test is performed with a level of significance ( $\alpha$ ) equal to 0.05. The details of Spearman's Rank Correlation Test are available on the Internet and are not reproduced here. The resulting test statistic  $\rho$  = 0.798 exceeds the test's critical value of approximately 0.35; therefore, the null hypothesis is rejected in favor of the conclusion

that correlation does exist between the two data sets. This conclusion means that the ranks of total PAH concentrations between TOC-normalized data and non-normalized data are not statistically different. In summary, normalization of PAH concentrations using TOC concentrations does not change where the highest concentrations of PAHs are located in the study area. The result is that there is no difference whether the non-normalized data or normalized data is used to discuss the impact of PAHs to sediments in the study area.

#### 3.3. Field Observations

Field personnel located 26 storm water outfalls in the study area during water and sediment sampling. No sheen was identified at any of the outfalls. The locations of the outfalls are:

- Two at the Former Submarine Base/Ship Repair Facility;
- Three at the Small Boat Harbor;
- One at sample location SW-16;
- One at sample location SW-18;
- One at sample location SW-22;
- One at sample location SW-26;
- One at sample location SW-29;
- Two at sample location SW-30;
- One at sample location SW-37;
- One at sample location SW-38;
- Two at sample location SW-39
- One at sample location SD-39;
- Two at sample location SD-40;
- Two at sample location SD-41;
- One at sample location SD-43;
- One at sample location SD-53;
- One at sample location SD-55;
- One at sample location SD-56; and
- One at sample location SD-58;

OASIS sampling crews observed discharges of non-contact cooling water from seafood processing at UniSea and the Icicle Seafoods *Arctic Star* floating processor. No spills were observed during sampling, but a surface sheen was observed near the stern of a vessel that was at the APL Dock. Finally, buoys for personal harvest crab pots were documented at water sample locations SW-11, SW-13, SW-48, SW-49, and SW-50 along Front Beach in Iliuliuk Bay and at water sample locations SW-51 and SW-52 near Rocky Point.

#### 3.4. Comparison of Cumulative Results

Tables 5 and 6 show cumulative water and sediment data, respectively, from April 2007 and September 2007 for locations that were sampled during both sampling events.

For water samples, 20 locations were sampled in both April 2007 and September 2007 at a depth of one meter. Only one location, SW-02 near the Former Submarine Base/Ship Repair Facility, had detectable concentrations of TAqH during both sample events, while no location had a detectable concentration of TAH during both sample events. In April 2007, the result at SW-02 was based on concentrations of BTEX compounds that were estimated at less than laboratory reporting limits, and in September 2007, the result at SW-02 was based on a concentration of naphthalene that was estimated at less than the laboratory reporting limit. The TAqH results for both April 2007 and September 2007 were below the water quality criteria of 15  $\mu$ g/L. These cumulative results for water samples demonstrate that water quality impairment from petroleum hydrocarbons is not a current problem in the study area.

For sediment samples, eight locations were sampled in both April 2007 and September 2007. In general, the corresponding results show that total PAHs are consistently elevated in similar locations, such as SD-01, SD-02, SD-03, and SD-10, although actual concentrations of PAHs show significant variability between sampling events. The large variability is not unexpected given the unlikelihood of deploying the Van Veen sampler in the same location during different sampling events.

#### 4. QUALITY ASSURANCE REVIEW

The analytical results for all field, quality control (QC), and laboratory quality assurance samples were evaluated. The data were reviewed to determine the integrity of the reported analytical results and ensure analytical results met data quality objectives as presented in the Quality Assurance Project Plan (DEC 2007c). Appendix G presents a quality assurance review of the analytical data using the Alaska DEC's Laboratory Data Review Checklist.

The following list provides a brief review of data quality objectives. More details are presented in Appendix G.

- All work was performed by OASIS or subcontractor personnel who are qualified individuals as per 18 AAC 75.990(100).
- Completeness 100% of samples submitted were analyzed, thereby meeting the data quality objective of 90%.
- Accuracy All primary, matrix spike/matrix spike duplicate, laboratory control, and method blank samples met method criteria for surrogate recoveries. Several water samples submitted for PAH analyses had one of three surrogates outside of method acceptance limits but the method allows for one surrogate to be outside of method acceptance limits as long as its recovery was greater than 10%, therefore no data flags were assigned.
- Precision Overall there were good correlation and low relative percent differences (RPD) primary and duplicate samples. Many of the water sample results were non-detect so no valid comparison could be made. The sediment duplicates generally had good correlation on positive sample results with one noted exception: sample SD-26 had little or no correlation between the primary and duplicate samples. Failure of field duplicates to meet RPD criteria usually does not cause results to be flagged; however, in the case of SD-26 the results are so varied that they are considered as estimated concentrations because of the uncertainty. While the results qualitatively indicate a significant presence of PAHs, the concentration(s) are to be considered estimates. RPDs for matrix spike/matrix spike duplicate and laboratory control samples also met criteria.
- Comparability Samples were collected and analyzed in a manner that allowed analytical results to be compared to each other.
- Representativeness Water samples were collected in a manner that minimally disturbed the water column and retrieved the sample matrix from the desired depth. Sediment sampling procedures included the use of dedicated sampling tools and a field scale to include similar mass and volume between sample locations. Analysis of trip blank samples indicated that no cross-contamination occurred during the project.

#### 5. EVALUATION OF FINDINGS

OASIS conducted a second water quality assessment of Dutch Harbor, Iliuliuk Bay, and Iliuliuk Harbor on behalf of the Alaska DEC in September 2007. The assessment included collection of 36 water samples and 51 sediment samples at discrete locations that were mostly collected from priority areas identified during the April 2007 assessment. The assessment also included field observations of personal harvest activities and sources of petroleum pollution within the project's study area. The purpose of the assessment was to evaluate water quality during seasonally high boat activity and define impacts to sediment from petroleum hydrocarbons in identified priority areas. The following is a summary of findings from the assessment:

- None of the water samples had detectable concentrations of BTEX compounds, and therefore, no measurable concentration of TAH. Only three of the 36 water samples had detectable concentrations of PAHs. None of the concentrations for total PAHs exceeded the water quality standard of 15 µg/L for TAqH.
- None of the sediment samples had detectable concentrations of BTEX compounds. However, all but one of the 51 sediment samples had detectable concentrations for multiple PAH compounds. Thirty-seven locations have at least one compound that exceeded a TEL benchmark for sediment quality, and 14 of the samples have at least one compound that exceeded a PEL benchmark. Four of the sediment samples exceeded the PEL benchmark for total PAHs: SD-01 near the Former Submarine Base/Ship Repair Facility, SD-03 and SD-22 near UniSea, and SD-26 near Alyeska Seafoods with an estimated concentration for total PAHs. Seventeen other sediment samples also exceeded the TEL benchmark for total PAHs. Of the 21 sediment samples that exceeded TEL or PEL benchmarks, 20 of them were locations either in Iliuliuk Harbor or the top of Dutch Harbor.
- Sheening was observed on sediment sample material at approximately half of the sample locations. Location SD-01 had the most sheening; this location also had visible white flaking in the sample material. The white flaking material could be TBT given that SD-01 is adjacent to the Former Submarine Base/Ship Repair Facility.
- Statistical analysis of sediment sample analytical results for TOC-normalized PAH
  concentrations and non-normalized PAH concentrations demonstrates that the two
  data sets are statistically correlated. This means that ranking of the data sets from
  most impacted to least impacted for concentrations of total PAHs is statistically the
  same whether TOC-normalized or non-normalized data are used.
- Field personnel observed personal harvest crab pots at sample locations SW-11, SW-13, SW-48, SW-49, and SW-50 along Front Beach in Iliuliuk Bay and at sample locations SW-51 and SW-52 near Rocky Point. In addition, field personnel noted people fishing at the mouth of Margaret Bay.
- Field personnel counted 26 storm water outfalls in the study area, but none of them had a discharge with a noticeable sheen. Two seafood processors (UniSea and

Icicle Seafoods *Arctic Star* floating processor) had active discharge of non-contact cooling water. A sheen was observed off the stern of a vessel that was at the APL Dock.

#### 5.1. Conclusions

Based on the findings summarized above and data from the April 2007 sampling event, the conclusions for this assessment are:

- The waters of Dutch Harbor, Iliuliuk Bay, and Iliuliuk Harbor have met numeric water quality standards for TAH and TAqH for all 107 primary samples collected at 87 unique locations and depths during the April 2007 and September 2007 assessments. Only 16 of the 107 samples have had a detectable concentration of BTEX or PAH compounds, and seasonal variation does not appear to affect concentrations of petroleum hydrocarbons. Based on this volume of data, it appears that the impaired water bodies meet numeric water quality criteria for petroleum hydrocarbons.
- Almost half of the sediment samples from the September 2007 assessment (21 out
  of 51 samples) exceeded the TEL benchmark for total PAHs, while four exceeded
  the more important PEL benchmark. Although the impacted sediments do not
  appear to be impacting water quality, the potential deleterious effect that the
  sediments may have on aquatic life is unknown at this time.
- Data from the September 2007 assessment support the finding from the April 2007 assessment that impact to sediments from PAHs is ubiquitous in the study area. In addition, the September 2007 data for PAHs confirm that sediments in Iliuliuk Harbor and at the top of Dutch Harbor are significantly impacted. In particular, the areas around the North Pacific Fuel Resoff Terminal and the Arctic Star seafood processor, UniSea dock, and the Former Submarine Base/Ship Repair Facility have the greatest density of samples with concentrations that exceed the TEL benchmark for total PAHs. Figure 5 shows a visual distribution of the sediment samples that exceed the TEL or PEL benchmarks for total PAHs.
- In addition to the areas of concern outlined in the bullet above, samples collected near docks appear more likely to have elevated concentrations of PAHs. For instance, 18 of the 21 samples with total PAHs exceeding the TEL benchmark were collected from locations adjacent to a dock.
- While impact from PAHs may be ubiquitous, the two water quality assessments have established certain areas that appear to have PAH concentrations in sediments consistently less than the TEL benchmark for total PAHs. These areas include the portion of Dutch Harbor from approximately Magone's Marine to the eastern end of the airport runway; Iliuliuk Bay including most of Rocky Point (except the area around the Delta Western Dock; and the open water area of Iliuliuk Harbor and the southeastern portion of Iliuliuk Harbor from the mouth of Unalaska Creek to the bridge (except the area near Unisea).

- Field observations of the potential sources of petroleum pollution in the study area revealed limited evidence of continuing source contribution to water quality impairment. One sheen was observed in September 2007 at the APL Dock in addition to sheens observed at UniSea and the Light Cargo Dock during April 2007. No sheen has been documented on storm water runoff during the two assessments.
- Personal harvest activities have been documented at Front Beach in Iliuliuk Bay during both assessments. Personal harvest crab pots were noted at Rocky Point in September 2007. Lastly, field personnel observed fishing at the mouth of Margaret Bay in September 2007.

#### 5.2. Recommendations

The following recommendations are provided to further investigate and understand the impact of petroleum hydrocarbons in the study area and to provide additional information for the selection of an approach to water quality attainment. The recommendations serve as options for the Alaska DEC to consider in future project planning. The Alaska DEC is not obligated to enact or implement any or all of the recommendations.

- Construct a GIS database that shows the spatial distribution of all available sampling data for the study area.
- Water sampling across the entire study area (April 2007 assessment) and in identified priority areas (September 2007) has demonstrated that the impaired water bodies consistently meet numeric water quality criteria for TAH and TAqH. Based on this information, the need for additional water sampling does not appear necessary unless an event or new objective warrants additional water sampling.
- Analytical data from both assessments have demonstrated that BTEX compounds are rarely detectable in sediments, and the concentrations are low when present.
   The need to analyze additional sediment samples for BTEX does not appear necessary unless an event or new objective warrants additional sampling.
- Analytical data for sediments from both assessments have demonstrated that TOCnormalized concentrations of PAHs statistically do not affect where the most impacted locations are in the study area. The analysis of additional sediment samples should be limited in order to reduce costs, yet continue to verify the finding for TOC-normalized data.
- While the two assessments have identified areas in Iliuliuk Harbor, the top of Dutch Harbor, and a small area around the Delta Western Dock as being most impacted by PAHs, the sources and extent of impact are not adequately understood. Additional sample density would help delineate where PAH concentrations exceed the TEL benchmark in these priority areas. Some of these areas, such as locations close to shore at the Former Submarine Base/Ship Repair Facility, Small Boat Harbor, Margaret Bay, and the Delta Western Dock cannot be reached using the Nancy Ellen because of her draft. Therefore, a skiff should be used to access these locations and a portable Van Veen sampler should be used for sampling. The extra sample density also will help explain how upland sources are affecting sediment quality. For

example, if PAH concentrations in sediments inside the Delta Western Dock are similar or greater to concentrations at locations SD-08 and SD-37, then it can be inferred that an upland source, such as the Pre-World War II Tank Farm, is the main factor affecting sediment quality. However, if PAH concentrations in sediments are less inside the Delta Western Dock, then it can be inferred that operations on the dock or vessels moored to the dock are the main factors affecting sediment quality.

- Additional sediment sampling also should include stratified sampling to determine the
  depth of PAHs in the sediment base. For the initial two assessments, sediment
  samples have been collected from the top two inches of sediment. Future sampling
  could include deeper samples to determine how sediment thickness affects
  concentrations of PAHs.
- More focus should be placed on enacting, educating, and enforcing best management practices at docks given that docks appear to be a common location where elevated concentrations of PAHs occur in sediments. This effort likely will require interface with multiple agencies, groups, and businesses, such as the Alaska Department of Fish and Game, United States Coast Guard, Dutch Harbor Harbormaster, seafood processors, and marine transport companies, in order to initiate a successful program.
- Given the elevated concentrations of PAHs in sediments at SD-01, combined with heavy sheening and the possible presence of TBT, the Non-Point Source Water Pollution Control program should consider referring the site to the Contaminated Sites program for characterization.
- Given that BTEX is not consistently detected in water or sediment samples, the
  cumulative findings of the two water quality assessments indicate that petroleum
  hydrocarbon contamination is a result of historic spills, releases, and former
  contaminated sites rather than an intertidal plume or regular surface water discharge.
  Therefore, the use of a TMDL to address the impairment listings of Dutch Harbor,
  lliuliuk Bay, and lliuliuk Harbor is not recommended because there is no fair or
  feasible method to allocate discharge limits to intermittent and unexpected releases
  of petroleum hydrocarbons.
- Sampling of stormwater discharge in the most impacted areas, especially if it is laden with sediment, would be useful to determine potential contribution of PAHs to sediment.
- As discussed in the recommendations section of the water quality assessment report for April 2007, the "no deleterious effects to aquatic life caused by concentrations of hydrocarbons in sediments" clause of the water quality standards is the primary outstanding issue for the impairment listings of Dutch Harbor, Iliuliuk Bay, and Iliuliuk Harbor. This water quality assessment has provided additional data that better defines the most impacted sediments in the study area; however, finding a solution to this issue likely will be the most challenging part of bringing the impaired water bodies to attainment. A reasonable and economical next step for evaluating whether sediments would be to perform toxicity or bioassay tests combined with benthic

20

community surveys in the most impacted areas at the top of Dutch Harbor, UniSea, and the Former Submarine Base/Ship Repair Facility.

## 6. REFERENCES

Alaska Department of Environmental Conservation (DEC), March 2004, Sediment			
Quality Guidelines, Technical Memorandum prepared by Division of Spill			
Prevention and Response, Contaminated Sites Remediation Program.			
, December 28, 2006a, Alaska's Final 2006 Integrated Water Quality			
Monitoring and Assessment Report.			
, June 27, 2006b, Dutch Harbor Water Quality and Impairment Analysis,			
prepared for Alaska DEC by OASIS Environmental, Inc.			
, June 2007a, Water Quality Assessment, Dutch Harbor, Iliuliuk Bay, Iliuliuk			
Harbor, Final Report, prepared for Alaska DEC by OASIS Environmental, Inc.			
, September 2007b, Water Quality Assessment Sample Plan, Dutch Harbor,			
Iliuliuk Bay, Iliuliuk Harbor, prepared for Alaska DEC by OASIS Environmental,			
Inc.			
, March 2007b, Water Quality Assessment, Quality Assurance Project Plan,			
Dutch Harbor, Iliuliuk Bay, Iliuliuk Harbor, prepared for Alaska DEC by OASIS			
Environmental, Inc.			
Buchman, M.F., 1999, NOAA Screening Quick Reference Tables, NOAA HAZ			
Report 99-1, Seattle, WA, Coastal Protection and Restoration Division, National			
Oceanic and Atmospheric Administration, 12 pages.			
Luthy, Richard, 2004, Water and Sustainable Development: Opportunities for the			

Chemical Sciences – A Workshop Report to the Chemical Sciences Roundtable.

## **TABLES**

# **FIGURES**

- Page Intentionally Left Blank -

## **APPENDIX A**

**Field Notes** 



# **APPENDIX B**

Photographs



# **APPENDIX C**

**Water Sample Data Sheets** 



## **APPENDIX D**

**GPS Coordinates** 



## **APPENDIX E**

**Sediment Sample Data Sheets** 



## **APPENDIX F**

**Laboratory Analytical Reports** 



## **APPENDIX G**

**Quality Assurance Review**