WATER QUALITY ASSESSMENT
DUTCH HARBOR,
ILIULIUK BAY,
ILIULIUK HARBOR

Unalaska, Alaska

FINAL
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Prepared for:

Alaska Department of
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Division of Water
Non-Point Source Water Pollution Control
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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
MI.................. multi-incremental
µg/kg............. micrograms per kilogram
µg/L............... micrograms per liter
ml.................. milliliter
OASIS........... OASIS Environmental, Inc.
PAHs............. polynuclear aromatic hydrocarbons
PELs .... Probable Effects Level
QC .... quality control
RPD .... relative percent difference
RSD .... relative standard deviation
TAH............... total aromatic hydrocarbons
TAqH............. total aqueous hydrocarbons
TELs .... threshold effects level
TMDL .... total mass daily load
TOC .... total organic carbon

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EXECUTIVE SUMMARY

OASIS Environmental, Inc. performed a water quality assessment of Dutch Harbor, Iliuliuk Bay, and Iliuliuk Harbor for Alaska Department of Environmental Conservation. The assessment included the collection of 71 water samples from 39 locations, ten discrete sediment samples, and five multi-incremental sediment samples from five grid regions. Analytical results show that numeric water quality was met for total aromatic hydrocarbons and total aqueous hydrocarbons in all 71 water samples. Analytical results for sediment samples demonstrate that polynuclear aromatic hydrocarbons (PAHs) are present in sediments for all three water bodies. Ten of the fifteen sediment samples had at least one PAH compound that exceeds Threshold Effects Levels from the Screening Quick Reference Tables, while four of the samples had at least one PAH compound that exceeds Probable Effects Levels from the Screening Quick Reference Tables. The most impacted sediments based on both discrete and multi-incremental sample results are located in Iliuliuk Harbor and the top of Dutch Harbor. During assessment activities, sampling personnel observed sheens near UniSea, Icicle Seafoods *Bering Star* floating processor, and the Light Cargo Dock. Personal harvest activities were documented near Front Beach in Iliuliuk Bay.

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1. INTRODUCTION

Under Notice-to-Proceed No. 18-9001-14-6B, Alaska Department of Environmental Conservation (DEC) tasked OASIS Environmental, Inc. (OASIS) to conduct a water quality assessment of Dutch Harbor, Iliuliuk Bay, and Iliuliuk Harbor near Unalaska Island and Amaknak Island, Alaska (Figure 1). These water bodies are identified as impaired for contamination from petroleum hydrocarbons. This report presents baseline water and sediment quality conditions for the impaired water bodies.

During this report, the three impaired water bodies often are referred to as the study area. The term *study area* refers to the combined waters of Iliuliuk Bay, Iliuliuk Harbor, and Dutch Harbor. Figure 2 shows the study area and surrounding land features.

1.1. Background

In 1990, Alaska DEC listed Iliuliuk Bay as an impaired water body 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. Both 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 Iliuliuk Harbor is not listed on the 303(d) list, this water body has been grouped with the two listed water bodies because of its physical connection with Iliuliuk Bay and because its usage as a seaport is essentially identical to Iliuliuk Bay and Dutch Harbor.

Although continually visible sheens no longer exist in the study area, Dutch Harbor and Iliuliuk Bay 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:

1) Complete either a Total Maximum Daily Load (TMDL) for an impaired water body;

2) Provide evidence that a water body is not impaired; or

3) Demonstrate that other controls are in place that will bring a water body back into compliance with state water quality standards.

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

1.2. Impairment Analysis

In 2006, Alaska DEC (2006b) produced a water quality 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 information for petroleum pollution in the study area; 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 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, the study identified three physical areas most at risk in the study area for having potential water quality impairment from dissolved phase petroleum pollutants and contaminated sediments:

1) Rocky Point from the airport past the APL Dock;

2) Top of Dutch Harbor between Ballyhoo Spit and the coast of Amaknak Island; and

3) 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 EPA's recommended guidelines for a water body recovery plan and consisted of two main components: water quality monitoring and increased management by Alaska DEC of petroleum sources in the study area. However, Alaska DEC still is considering both approaches as the preferred long-term plan for water quality attainment. This report presents baseline findings for water quality monitoring, and these findings provide additional information that Alaska DEC will use to choose a method of water quality attainment.

1.3. Scope of Work

The objectives of this water quality assessment for Dutch Harbor, Iliuliuk Bay, and Iliuliuk Harbor, as outlined in the *Water Quality Assessment Sample Plan* (DEC 2007a), are:

- Establish a current baseline of water quality data in the study area, and in particular in the three areas of potential impairment, for dissolved phase petroleum pollutants.
- Establish a current baseline of sediment quality data in the study area for petroleum hydrocarbons.
- Observe identified sources of petroleum pollution for the purpose of verifying assumptions in *Dutch Harbor Water Quality and Impairment Analysis* and developing an approach for water quality attainment.

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 µg/L. Total aromatic hydrocarbons (TAH) in the water column may not exceed 10 µg/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.

These water standards are applied to the data that has been gathered during this assessment. Field observations are used to compare actual conditions to the narrative standard of "no sheen," and analytical data are used to compare sample concentrations to the numeric standards for total aromatic hydrocarbons (TAH) and total aqueous hydrocarbons (TAqH).

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 Threshold Effects Levels (TELs) and Probable Effects Levels (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

2. ASSESSMENT ACTIVITES

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 39 locations in the study area. Twenty-six of the locations were "near-shore" (defined as 100 feet or less from shore) from areas of potential impairment: twelve near Rocky Point, ten from Iliuliuk Harbor, and four from the top of Dutch Harbor. Seven additional samples were collected at near-shore locations near other potential sources of petroleum pollution in Dutch Harbor or Iliuliuk Bay. Lastly, six samples were collected from open water locations in the study area for comparison. Figure 3 presents the water sample locations.

For near-shore sample locations, two water samples were collected at each location: one sample at a shallow depth of one meter below water surface and the other at the bottom of the water body or five meters below water surface, whichever was less. Samples were analyzed for benzene, toluene, ethylbenzene, and xylenes (BTEX) by analytical method EPA 602 and polynuclear aromatic hydrocarbons (PAHs) by analytical method EPA 625 SIM for the determination of TAH and TAqH.

For the open water sample locations, one sample was collected at the depth of one meter. Samples were analyzed for BTEX by analytical method EPA 602 and PAHs by analytical method EPA 625 SIM for the determination of TAH and TAqH.

OASIS chartered a skiff to access sample locations. For each near-shore location (100 feet or less from shore), the following activities occurred:

- Lowered weighted and graduated polyethylene tubing to one meter below water surface and used a peristaltic pump 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 two 40-millilter (ml) amber sample vials in a Wildco® hydrocarbon sampler and lowering the sampler to a depth of one meter. The sampler was held in place until the chamber of the sampler completely filled. 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 weighted and graduated polyethylene tubing to collect water samples from a depth of one meter. Two 125-ml amber bottles were filled from the end of the tubing.

- The same sampling process was repeated for the sample collected at the bottom of the water body or five meters, whichever was less.

For each open water location, the sample process was identical to the process used to collect samples at a depth of one meter for the near-shore sample locations.

2.2. Sediment Sampling

OASIS collected 15 sub-tidal sediment samples within the study area. Five of the samples were collected from multiple locations within five grid regions using multi-incremental (MI) sampling techniques. The other ten samples were grab samples collected from ten discrete locations within areas of potential impairment.

Figure 4 shows locations of the ten discrete sediment samples collected. These locations correspond to near-shore water sample locations or potential sources of petroleum pollution. Similar to water sampling, near-shore was defined as 100 feet or less from shore, although shallow water and wind direction limited boat access for many discrete locations (SD-04, SD-05, SD-06, SD-07, SD-08, and SD-09). It should be noted that sample material from SD-05 likely had recent sediment deposition from a mud slide that occurred upland from the sample location in early 2006. Samples were analyzed for BTEX by analytical method EPA 8021B, PAHs by analytical method EPA 8270 SIM, and total organic carbon (TOC) by analytical method EPA 9060.

For the five samples using MI sampling techniques, one sample was collected from each grid region as presented in Figure 5. OASIS selected incremental locations within each grid region by randomly selecting nine grid polygons using a random number generator. For each grid polygon selected, the sample was collected from the approximate center of the polygon, thereby creating a stratified random sampling approach for each grid region. Figure 5 also shows the grid polygons that were randomly selected within each grid region. Samples were analyzed for BTEX by analytical method EPA 8021B, PAHs by analytical method EPA 8270 SIM, and TOC by analytical method EPA 9060.

OASIS chartered a commercial fishing vessel to access sediment sample locations. The vessel had a hydraulic davit and winch for the purpose of raising and lowering a Van Veen sampler to collect sub-tidal sediment samples. For discrete sediment sample locations, the following activities occurred:

- The Van Veen sampler was placed in the open position and lowered over the side of the boat using the hydraulic davit and winch. After the Van Veen sampler tripped closed on the bottom of the water body, the sampler was retrieved using the hydraulic davit and winch.

- Once the Van Veen sampler was securely on the vessel, the sampler was opened to expose the 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 jaw did not close completely because of an obstruction, or the sampler penetrated too deeply causing the top of the grab to smear and leak through the lid of the sampler. 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.

- Field personnel collected grab samples for BTEX, PAH, and TOC analysis at each location. For BTEX samples, approximately 50 grams of sample matrix was taken from the Van Veen sampler using a dedicated, transparent, plastic syringe. The sample matrix was placed in a 4-ounce sample bottle and preserved with methanol. For PAH and TOC samples, a dedicated sample spoon was used to fill two 4-ounce sample bottles.

For sediment samples collected by MI sampling techniques, sampling activities followed the first two bullets as for the discrete locations above, but the final step was:

- Field personnel collected sample increments for BTEX, PAH, and TOC analysis. For each sample container, two increments of equal volume from each side of the Van Veen sampler were collected using a dedicated, transparent, plastic syringe. For BTEX samples, 5 ml of sample material were removed using the syringe and approximately 5 grams of soil were added to the sample container. For PAH and TOC analysis, 10 ml of sample material were removed using the syringe and approximately 10 grams of sample material were added to the sample container. The increments were placed in 4-ounce sample bottles for each analysis. Samples for BTEX were preserved with methanol. The same sample bottles were used at each incremental location within each grid region so that each grid region had one sample for BTEX, PAHs, and TOC. Given that each grid region had nine sample locations, and two increments were collected at each location, there were 18 increments per sample for each grid region.

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 2007a). Some of the executed activities and details deviated from the plan. The list below identifies the deviations:

- Water samples collected on April 20 used a sample numbering scheme that included the time of sample collection instead of the date of sample collection.
- Near-shore water samples SW-07, SW-11, and SW-20 did not have a deep water sample collected because water depth was no more than 1 meter.
- Near-shore water sample SW-12 was moved out from the proposed location because of the inability of the sampling skiff to maintain position along Front Breach because of northerly winds and shallow water.
- Open water samples SW-08 and SW-28 mistakenly had a deep sample collected.
- Water samples for PAH analysis were collected with a peristaltic pump instead of a Kemmerer bottle because the sample team believed there was an option to use either device. Although the sampling occurred not as planned, the use of a peristaltic pump is a common and adequate sampling method and not expected to impact data quality.
- Discrete sediment sample SD-03, proposed to be collected near the entrance to Margaret Bay, was abandoned because water levels were too shallow in the area. The sample was relocated near the UniSea dock.
- Discrete sediment sample SD-04, proposed to be collected in Margaret Bay, was abandoned because water levels were too shallow to gain entrance to Margaret Bay. The sample was relocated to Iliuliuk Harbor in front of Margaret Bay.
- Discrete sediment sample SD-05, proposed to be collected along Rocky Point near the APL dock, was abandoned because of the inability to collect a clean grab from the rocky bottom. The sample was relocated near Magone's Marine in Dutch Harbor.
- Discrete sediment samples SD-04, SD-05, SD-06, SD-07, SD-08, and SD-09 were not collected within 100 feet of shore because these locations were limited by one or both of the following: shallow waters and wind direction that pushed the sediment sampling vessel too near to shore.

- The use of a sample spoon instead of a syringe to collect samples for PAHs and TOC at discrete sediment sample locations.

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.

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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 surface water samples, and Figure 3 shows TAH and TAqH concentrations by sample location. Of the 71 primary samples collected, ten samples had detectable concentrations of TAH; however, no TAH concentration exceeded the water quality standard of 10 micrograms per liter (µg/L). Seven of the ten samples with detectable concentrations of TAH were shallow samples collected at one meter below the water surface. For the three deep water samples that had detectable concentrations of TAH, two samples (SW-01 and SW-23) also had detectable concentrations of TAH in the corresponding shallow sample. The highest TAH concentration in any of the surface water samples was 4.92 µg/L from location SW-23 near the tip of Rocky Point. The portion of Iliuliuk Harbor near the Small Boat Harbor had the greatest density of TAH detections with four samples having detectable concentrations of TAH. Two locations (SW-11 and SW-13) at Front Beach in Iliuliuk Bay had the second and third highest concentrations of TAH. The two other locations where TAH was detected were SW-10 on the east side of Alyeska Seafoods and SW-29 near the Dutch Harbor Powerhouse.

Only three surface water samples had detectable concentrations of PAHs. The deep water sample at SW-08 in the center of Iliuliuk Harbor had a total PAH concentration of 2.18 µg/L; the shallow water sample at SW-14 near the Coastal Transportation Dock had a total PAH concentration of 3.56 µg/L; and the deep water sample at SW-35 near the Light Cargo Dock had acenaphthene detected at an estimated concentration of 0.150 µg/L. None of these three samples had a corresponding detection of TAH; therefore, the TAqH concentration is the same as the total PAH concentration. None of these three samples exceeded the TAqH water quality standard of 15 µg/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

Table 3 presents the analytical results for sediment samples using data as provided by the analytical laboratories. Five of the fifteen primary samples had at least one BTEX compound detected; however, all the detections of BTEX were at estimated concentrations less than laboratory reporting limits.

For PAHs, ten of the fifteen primary samples had at least one compound that exceeds a TEL benchmark for sediment quality, and four of the fifteen samples had at least one compound that exceeds a PEL benchmark. In addition, every sample had a detectable concentration for a majority of PAHs. Based on these results, the presence of PAHs in sediments of Dutch Harbor, Iliuliuk Bay, and Iliuliuk Harbor appears to be ubiquitous. This finding corresponds with sediment analysis performed by the EPA (2000), which found detectable concentrations of diesel range organics and residual range organics in sediments throughout Dutch Harbor and Iliuliuk Bay.

For discrete sediment sample locations, significant variation exists in the concentrations of PAHs depending on the location of each sample. The four samples from Iliuliuk Harbor were the most impacted samples when considered against the other two areas of potential impairment. The two highest concentrations of total PAHs for discrete samples were from Iliuliuk Harbor: one collected near the Former Submarine Base/Ship Repair Facility (SD-01) and the other near UniSea (SD-03). Another sample (SD-02) near the Small Boat Harbor had the fourth highest concentration of total PAHs for discrete samples, while the last location (SD-04) in Iliuliuk Harbor near Margaret Bay had the sixth highest concentration of total PAHs for discrete samples. The four samples collected around Rocky Point had the lowest average concentration of total PAHs when considered against the other two areas of potential impairment. Only sample SD-08 near the Delta Western Dock had a total PAH concentration that exceeded the TEL for total PAHs. The two discrete samples in Dutch Harbor had significantly different total PAH concentrations: sample SD-05 near Magone's Marine (the site of a landslide in spring 2006) had the second lowest total PAH concentration for the discrete samples, while sample SD-10 at the top of Dutch Harbor had the third highest concentration of total PAHs for discrete samples. Please note that sample SD-05 likely contained recently deposited sediment from an upland mud slide that occurred in early 2006. Figure 4 shows the analytical results for total PAHs in discrete sediment samples.

The analytical results for MI sediment samples show a discernible distribution of total PAH concentrations based on location. The highest concentration for a grid region was from Iliuliuk Harbor (SD-11), for which the triplicate sample averaged approximately 1,500 micrograms per kilogram (µg/kg), slightly less than the TEL benchmark. The next highest concentration was from the grid region at the top of Dutch Harbor (SD-15). The grid region around Rocky Point (SD-13) had the median concentration of total PAHs for the five grid regions, followed by the grid region in the center of Dutch Harbor (SD-14). The grid region on the east side of Iliuliuk Bay (SD-12) had the lowest concentration of total PAHs. These grid region concentrations show a similar trend as the discrete sample results: namely, that the highest concentrations of PAHs are in Iliuliuk Harbor and the top of Dutch Harbor. These two regions likely are the busiest areas in the study area for boat moorings and maintenance and have less movement of water than the Rocky Point area. In contrast, the region on the east side of Iliuliuk Bay, which has the lowest concentration of total PAHs, sees the least amount of boat traffic and has significant wave and tidal effect from the Bering Sea to the north. Figure 5 shows the analytical results for total PAHs in MI sediment samples.

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 in each sample by dividing analytical results by the percentage of TOC in each sample.

Table 4 shows the TOC-normalized data for PAHs. In thirteen of the fifteen primary sediment samples, the TOC result is 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 TOC-normalized data is significantly different than the non-normalized data. In other words, does the normalization of PAH concentrations cause a significant shift in where the highest concentrations of PAHs are located in the study area? To test this question, 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_0: 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_1: 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 (α) 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 $\rho = 0.929$ exceeds the test's critical value of 0.521; 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 other words, the 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 observed 13 storm water outfalls during water and sediment sampling. The locations of these outfalls are:

- Two at Former Submarine Base/Ship Repair Facility;
- Three at 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;
- One at sample location SW-30;
- One at sample location SW-31;
- One at sample location SW-37;

OASIS sampling crews observed discharges of non-contact cooling water from seafood processing at UniSea and Icicle Seafoods *Bering Star* floating processor. No spills were observed during sampling, but surface sheens were noticed during water sampling at SW-05 (UniSea), SW-35 (Light Cargo Dock), and SW-39 (Icicle Seafoods *Bering Star* floating processor). The sheen at SW-39 was the largest and covered most of the area in front of the *Bering Star*. It should be noted that only the deep water sample from SW-35 had a detection of TAH or TAqH. Finally, buoys for personal harvest crab pots were documented at surface water sample locations SW-12 and SW-13 along Front Beach in Iliuliuk Bay.

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 2007b). Appendix G presents a quality assurance review of the analytical data using 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 – Some sediment analytical results for PAHs were qualified as a result of surrogate recovery issues in laboratory control samples and laboratory control duplicate samples. Appendix G provides details.
- Precision – Laboratory precision associated with matrix spike and matrix spike duplicate samples and laboratory control and laboratory control duplicate samples is discussed in Appendix G. For water samples, QC sample sets met relative percent difference (RPD) goals for compounds detected above laboratory reporting limits in both primary and duplicate samples. For sediment samples, QC sample sets met RPD goals (discrete samples) and relative standard deviation (RSD) goals (MI samples) for compounds detected above the laboratory reporting limit in all QC samples.
- 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 samples were collected at planned discrete locations and from random locations for MI samples. Sample procedures included the use of dedicated syringes and a field scale to include similar mass and volume between sample locations. Based on the measured RSD and RPD values for triplicate and duplicate samples, respectively, the field team introduced an acceptable level of error during sample and field processes, thereby indicating that samples representative of actual field conditions likely were collected. An equipment rinsate blank (07-DH-0426-50-RB) was collected from the Wildco® hydrocarbon sampler to verify that cross-

contamination did not occur between surface water sample locations. No compounds were detected in the rinsate blank. Trip blanks also were submitted for analysis of volatile compounds. Samples 07-DH-0423-35-1-SW, 07-DH-0423-45-1-SW, and 07-DH-0423-34-1-SW have qualified results because of blank contamination in a trip blank. Appendix G provides details.

5. EVALUATION OF FINDINGS

OASIS conducted an assessment of Dutch Harbor, Iliuliuk Bay, and Iliuliuk Harbor on behalf of Alaska DEC. The assessment included collection of 71 water samples at 39 locations, collection of discrete sediment samples at ten locations, and collection of MI sediment samples within five regions. 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 establish baseline conditions for the water quality monitoring component of the alternative approach to water quality attainment. The following is a summary of findings from the assessment:

- Only ten of the 71 primary water samples collected had detectable concentrations of TAH. Seven of the detections were at shallow sample locations collected from one meter beneath water surface. Two of the three detections of TAH at deep sample locations also had a detection of TAH in the corresponding shallow sample. The highest concentration of TAH was 4.92 µg/L from the shallow sample at SW-23 collected near the tip of Rocky Point. No analytical result for TAH exceeded the water quality standard of 10 µg/L.

- Only three of the 71 primary water samples collected had detectable concentrations of PAHs. None of the three locations had corresponding concentrations of TAH, and none of the concentrations for total PAHs exceeded the water quality standard of 15 µg/L for TAqH.

- All detections of BTEX in sediment samples were estimated concentrations less than laboratory reporting limits. On the other hand, the presence of PAHs in the sediments of Dutch Harbor, Iliuliuk Bay, and Iliuliuk Harbor appears to be ubiquitous. All fifteen primary sediment samples had a detectable concentration for a majority of PAHs. Ten of the fifteen samples had at least one compound that exceeds a TEL benchmark for sediment quality, and four of the fifteen samples had at least one compound that exceeds a PEL benchmark. Both discrete sediment samples and MI sediment samples from grid regions show that Iliuliuk Harbor and the top of Dutch Harbor are the most impacted regions for PAHs.

- 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.

- During the April field observations, personal harvest activities were noted only at Front Beach in Iliuliuk Bay. A surface water sample collected near this area had the third highest concentration of TAH for the project.

- Two seafood processors (UniSea and Icicle Seafoods *Bering Star* floating processor) had active discharge of non-contact cooling water during the project. An extensive area in front of the *Bering Star* had a visible sheen during sampling, but water samples from this location did not have detectable concentrations of TAH or TAqH. Thirteen storm water outfalls were counted during the assessment, but none had a visible hydrocarbon sheen. Isolated sheens of hydrocarbons were observed near UniSea and the Light Cargo Dock.

5.1. Conclusions

Based on the findings summarized above, the conclusions for this assessment are:

- The waters of Dutch Harbor, Iliuliuk Bay, and Iliuliuk Harbor meet numeric water quality standards for TAH and TAqH based on the 71 primary samples collected during this assessment. In general, the shallow samples collected at one meter below water surface were more likely to have detectable concentrations of hydrocarbons than the deep samples.

- The ubiquitous presence of PAHs in sediments does not appear to be significantly impacting water quality based on the analytical results of water samples; however, the concentrations of PAHs in sediments frequently exceeded TEL benchmarks and four discrete samples had concentrations of PAH compounds that exceeded PEL benchmarks. These elevated concentrations could have a deleterious effect on aquatic life.

- The most impacted sediments appear to be located in Iliuliuk Harbor and the top of Dutch Harbor. In particular, elevated concentrations of total PAHs are located near the Former Submarine Base/Ship Repair Facility, Small Boat Harbor, UniSea, and the Trident Seafoods dock based on analytical results of discrete sediment samples. The analytical results of the MI sediment samples from grid regions also support the findings of the discrete sediment samples that Iliuliuk Harbor and the top of Dutch Harbor are the most impacted regions for PAHs.

- Of the three areas of potential impairment identified in *Dutch Harbor Water Quality and Impairment Analysis*, the coastline of Iliuliuk Harbor and the top of Dutch Harbor appear to have significant sediment quality issues that could have a deleterious effect on aquatic life. The area around Rocky Point had significantly lower concentrations of PAHs in discrete sediment samples and in the MI sediment grid sample than compared to the other two areas of potential impairment.

- Field observations of the potential sources of petroleum pollution in the study area revealed minimal evidence of contribution to water quality issues. Three sheens were observed during sample activities: two near seafood processors and one near a dock. The only sheen with significant surface area was observed at the top of

Dutch Harbor. Observed personal harvest activities during the assessment were limited to Front Beach in Iliuliuk Bay.

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 Alaska DEC to consider in future project planning. Alaska DEC is not obligated to enact or implement any or all of the recommendations.

- The need for another broad distribution of water sampling as was performed in this baseline assessment may not be necessary given the results. A possible exception to this recommendation is if there is concern regarding seasonal fluctuations of hydrocarbon concentrations. The next sampling event could focus on seven areas from this assessment that had either a high density of detections, high TAH and TAqH concentrations, or field observations that warrant further consideration. These locations are: Former Submarine Base/Ship Repair Facility, Small Boat Harbor, UniSea, Front Beach, Coastal Transportation Dock, tip of Rocky Point near sample location SW-23, and top of Dutch Harbor. The focused approach probably should include at least two additional sample locations around existing sample locations from these areas of concern. Lastly, given that most detections of TAH and TAqH occurred in the shallow sample, future sampling could eliminate the deep samples.

- Additional sediment samples should be collected to delineate the most impacted areas. The density of discrete samples should be increased in Iliuliuk Harbor, the top of Dutch Harbor, and around the Delta Western dock. The need to collect MI sediment grid samples again from the five regions does not appear necessary because the baseline data has provided a good indication of how hydrocarbon contamination is distributed in sediments within the study area. However, it would be useful to split the grid region for Iliuliuk Harbor in half (northern half and southern half) to determine if additional variation exists within Iliuliuk Harbor. All sediment samples should be analyzed for BTEX, PAHs, and TOC at least one more time. The analysis of PAHs is paramount because of the findings in this baseline assessment. Additional TOC data is necessary to verify the finding in this report that TOC-normalized data for PAHs is distributed statistically the same as non-normalized data. BTEX analysis could be eliminated from future sampling events given the absence or low concentrations detected in this assessment, but at least one more round of BTEX analysis is a prudent option to confirm that impact from BTEX is not an issue for sediment quality.

- While the results of this baseline assessment met numeric water quality for TAH and TAqH, the issue that remains is the narrative criteria of “no sheen” and “no deleterious effects to aquatic life caused by concentrations of hydrocarbons in sediments." The "no sheen" criterion can be addressed through increased management of the sources of petroleum pollution, as was discussed in *Dutch Harbor Water Quality and Impairment Analysis*. The "no deleterious effects" criterion is new to the analysis, and it is too soon in the project to select a method for addressing this issue without additional data and information. There are many potential options available. Some of the possibilities initially identified include remedial choices such as capping or dredging; a desktop option such as increased review and analysis of upland sources; an empirical option of increasing sediment sample density to delineate where releases are or have occurred; and a programmatic option of completing a risk-based analysis of sediment concentrations. Regardless of which option or combination of options is selected to address "no deleterious effects" in sediments, additional sediment quality data likely will be necessary; therefore, the collection of additional sediment samples is warranted near impacted areas identified in this baseline assessment.

- Based on elevated concentrations of PAHs in some of the discrete sediment samples, there is a need to better understand the location and extent of sources contributing to sediment quality issues. As part of this analysis, a thorough understanding of source migration and remediation should be developed. This will assist in developing a plan for water quality attainment because potential contributors of petroleum loads will be better identified and characterized.

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, 2006, *Dutch Harbor Water Quality and Impairment Analysis*, prepared for Alaska DEC by OASIS Environmental, Inc.

__________, January 2007a, *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 HAZMAT 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*.

United State Environmental Protection Agency (EPA), June 2000, *Dutch Harbor Sediment Expanded Site Inspection Report*, prepared under the Superfund Technical Assessment and Response Team contract

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TABLES

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FIGURES

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APPENDIX A

Field Notes

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APPENDIX B

Photographs

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APPENDIX C

Water Sample Data Sheets

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APPENDIX D

GPS Coordinates

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APPENDIX E

Sediment Sample Data Sheets

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APPENDIX F

Laboratory Analytical Reports

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APPENDIX G

Quality Assurance Review

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