

# Evaluation of Metals and Petroleum Derivatives in Skagway Harbor and Pullen Creek Sediments and Surface Waters

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February 6, 2009

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## **1.0 INTRODUCTION**

Skagway Harbor is listed as impaired by Alaska Department of Environmental Conservation (ADEC) due to sediment toxicity potentially due to metals and other sediment pollutants. Previous studies of the harbor have indicated relatively high concentrations of several priority pollutant metals including copper, cadmium, nickel, lead, and zinc in sediments, apparently in relation to historic metal ore transport and loading operations (Tetra Tech, 1988; SRK, 1989; Tetra Tech, 1990; Dames & Moore, 1995; PND, 2005; URS, 2006) and possibly from Pullen Creek as well (ADEC, 2004). As some of these previous studies were over 20 years old, Tetra Tech conducted sampling in 2007 to characterize current sediment quality of Skagway Harbor and Pullen Creek with respect to metal contamination. Based on the 2007 results, it was necessary to continue sediment and surface water quality characterization of Skagway Harbor and Pullen Creek in 2008, with respect to metals and petroleum derivatives contamination to potentially establish a total maximum daily load (TMDL).

The only natural drainage directly into Skagway Harbor is Pullen Creek. The entire length of Pullen Creek runs along and over the southern boundary of the City of Skagway. Approximately 2.1 miles long, its headwaters begin in the rail yard at the northeast end of town and confluence with Skagway Harbor across from the ore loading dock. Two spring fed tributaries enter Pullen Creek along its length and for much of its route it flows adjacent to the White Pass and Yukon Rail Road, which borders the City of Skagway to the southeast. Pullen Creek was further evaluated as a source of metals and petroleum derivatives to Skagway Harbor.

### ***1.1 Previous Information***

Previous sampling investigations have concentrated on White Pass Basin and the Ore Dock, as well as lead and zinc contamination (Tetra Tech, 1990; Dames and Moore, 1995; and URS, 2006). Surficial sediment concentrations have been measured in Skagway Harbor several times in the last three decades. Historical records indicate eight other sampling events focused on some aspect of Skagway Harbor sediment quality. Sediment concentrations of lead and zinc were observed to be lower with each subsequent sampling including 2007, however, sampling locations could not always be accurately confirmed in these studies.

The sampling conducted in 2007 (Figure 1) indicated that metal concentrations were at concentrations that were orders of magnitude lower than previous investigations (Tetra Tech, 2007). The results of sediment and pore water toxicity evaluations indicated that although the sediment quality may be impaired, metals were not indicated as the source of impairment. Other potential sources of toxicity cited were petroleum derivatives and a high biological oxygen demand. In addition, it was noted that Pullen Creek had elevated sediment metal concentrations at its headwaters. Metals had not apparently migrated to lower reaches and Pullen Creek was not deemed a current source of metals to Skagway Harbor. Therefore, continued monitoring was suggested to more accurately characterizes the potential of organic contaminants as sources of impairment in Skagway Harbor and the migration of metals in Pullen Creek (Tetra Tech Inc, 2008).

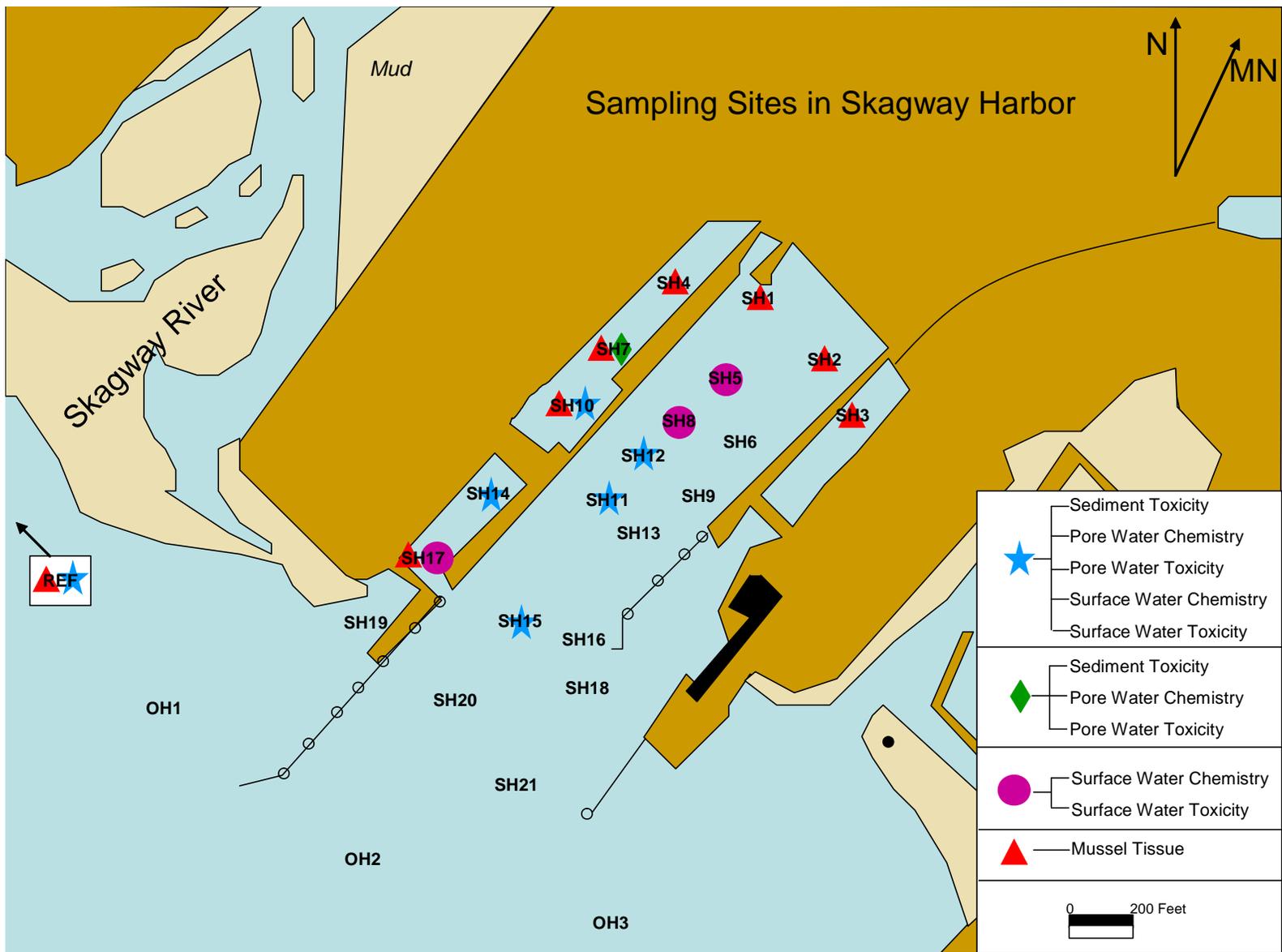
## **1.2 Project and Data Quality Objectives**

The overall objective of the 2008 monitoring was to accurately characterize current sediment and surface water quality within Skagway Harbor with an emphasis on copper in the surface waters and petroleum derivatives (i.e., VOCs, PAHs, oil and grease, TPH) in the sediments. Pullen Creek was further characterized with respect to sediment petroleum derivatives and surface water metals under both base flow and storm flow conditions.

Specific project objectives for the 2008 sampling included:

- Sampling Skagway Harbor and Pullen Creek surficial sediments to characterize the concentration of petroleum derivatives;
- Sampling of Skagway Harbor surface waters to determine the extent of copper concentrations potentially in excess of ambient water quality criteria as observed in multiple samples in August 2007;
- Sampling reference locations outside the influence of Skagway Harbor to establish potential background concentrations that will be used in the evaluation of Skagway Harbor to aid in the determination of whether pollutant concentrations are from natural or anthropogenic sources.
- Sampling of Pullen Creek surface waters under base flow and storm flow conditions to determine if Pullen Creek is a significant source of metals (i.e., Cd, Cu, Ni, Pb, and Zn) to Skagway Harbor; to determine if metals observed in the sediments of Upper Pullen Creek are mobilized under storm conditions; and to use the correct methodology when evaluating Pullen Creek in terms of a TMDL.
- Sampling a reference location in a comparable watershed in terms of size, drainage, and flow as Pullen Creek to establish potential background concentrations that will be used in the evaluation of Pullen Creek to aid in the determination of whether pollutant levels are from natural or anthropogenic sources.

The field sampling was conducted under the Quality Assurance Project Plan (QAPP) developed in August 2007, as well as a Field Sampling and Analysis Plan (FSAP) developed prior to sampling being conducted in September 2008. Measurement Quality Objectives (MQOs) including provisions for accuracy, precision, and bias are included in the ADEC and EPA-approved QAPP included in Appendix A. The ADEC and EPA approved FSAP includes detailed descriptions of sampling and chemical analysis used to evaluate sediment and surface water (see Appendix B).



**Figure 1.** Summary of 2007 sampling locations investigated in Skagway Harbor.

## **2.0 Methods**

### **2.1 Sample Design**

Sample design for the 2008 sampling was intended to build on the 2007 sampling so that a further evaluation of surface water copper contamination in Skagway Harbor could be provided, as well as a more defined investigation into the cause of sediment toxicity. Therefore, the locations selected were ones that had been sampled previously in 2007. In addition, the design was intended to provide sufficient data so that the magnitude and extent of sediment and surface water metals and petroleum derivatives could be calculated accurately.

#### **2.1.1 Skagway Harbor**

Based on the 2007 data obtained for Skagway Harbor, 6 surface water locations (SH-5, SH-9, SH-10, SH-12, SH-14, and SH-15) (Figure 2 and Table 1) were sampled for copper. Sampling sites were chosen based on sites which had 2007 copper concentrations in excess of at least the chronic water quality criteria (with the exception of SH-9, which was included due to high sediment copper concentrations). In addition, surface water samples were collected along the Railroad dock, the Ferry dock, and within the small boat harbor (Figure 3 and Table 1). These additional sites were sampled to ensure that other potential sources of copper to Skagway Harbor were characterized.

Six sediment locations (SH-4, SH-7, SH-9, SH-10, SH-14, and SH-17) were sampled for petroleum derivative characterization of surficial sediments (top 2-4 inches) within the Harbor (Figure 2 and Table 1). Sampling was particularly focused near the Ore Dock due to observations made during the chemical and toxicological evaluations in 2007.

#### **2.1.2 Pullen Creek**

The 2007 evaluation of Pullen Creek sediments indicated that metals may be impairing the upper watershed, but was unable to determine if metals are mobilized downstream. To determine if increased loads of metals are carried during periods of high flows, storm water flows needed to be characterized. Surface water at three sites, previously sampled in 2007, were sampled under base flow and storm flow conditions to evaluate the movement of metals downstream (PC-1, PC-2, and PC-5) (Figure 3 and Table 1).

In September 2008, PC-1, PC-2, PC-5, and Ref-PC were sampled for metals under base flow conditions. In October 2008 these sites were sampled again under storm flow conditions. Also, during the October 2008 storm event, sites PC-7, PC-8, PC-9, and EP-1 were sampled. Sample sites PC-7, PC-8, and PC-9 are storm water outfalls that discharge upstream, but in close proximity to sites PC-1, PC-2, and PC-5, and site EP-1 was collected from a hydroelectric plant discharge, which makes up a large portion of Pullen Creek's flow (IWC > 75%) .

The sediment at sites PC-1, PC-2, and PC-5 were also sampled for sediment petroleum derivatives. The sites were sampled to determine if the sediments of Pullen Creek are a source of petroleum derivatives to Skagway Harbor.

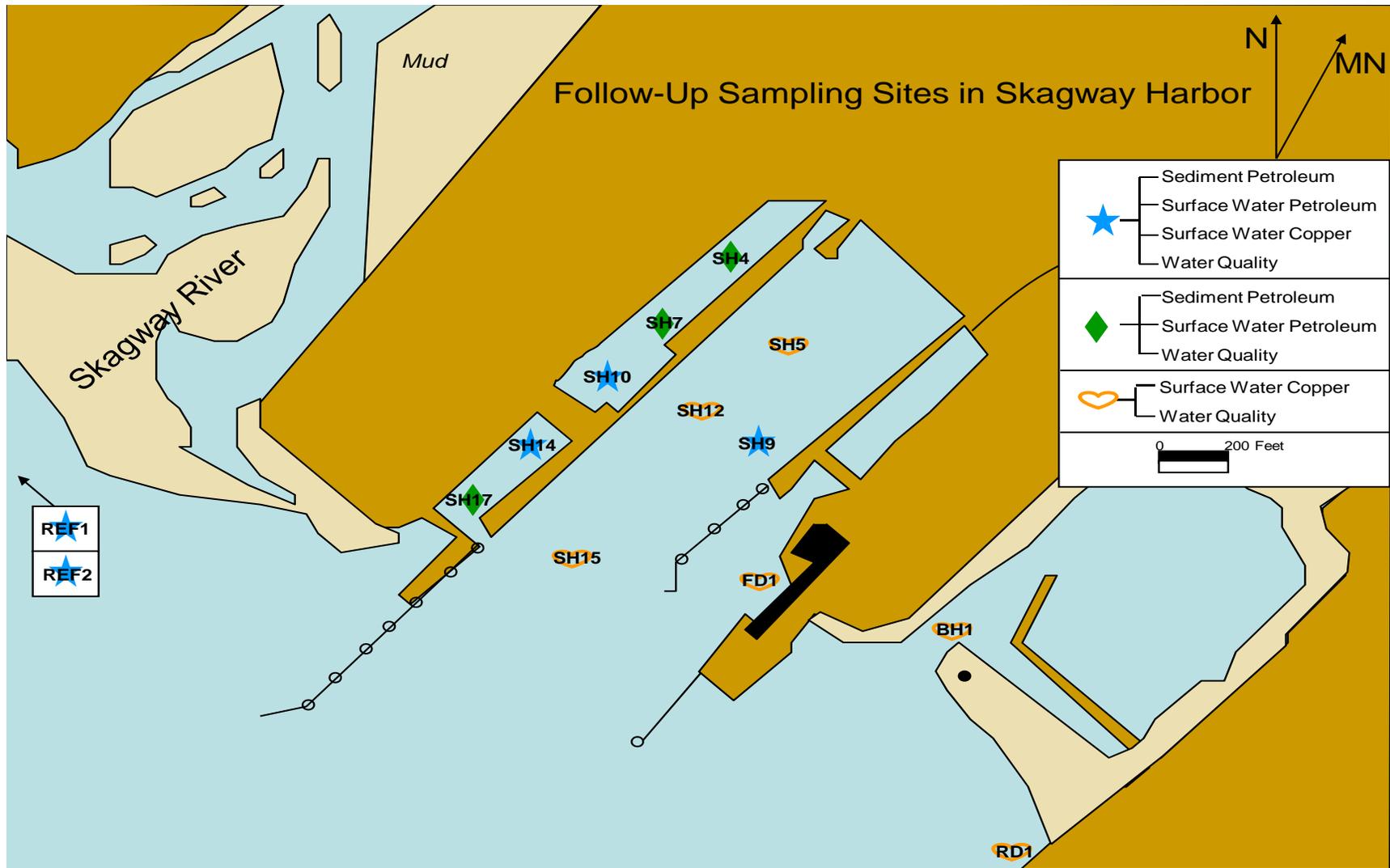


Figure 2. Sediment and surface water sampling locations for 2008 Skagway Harbor.

**Table 1.** Sampling sites and parameters completed in September/October 2008.

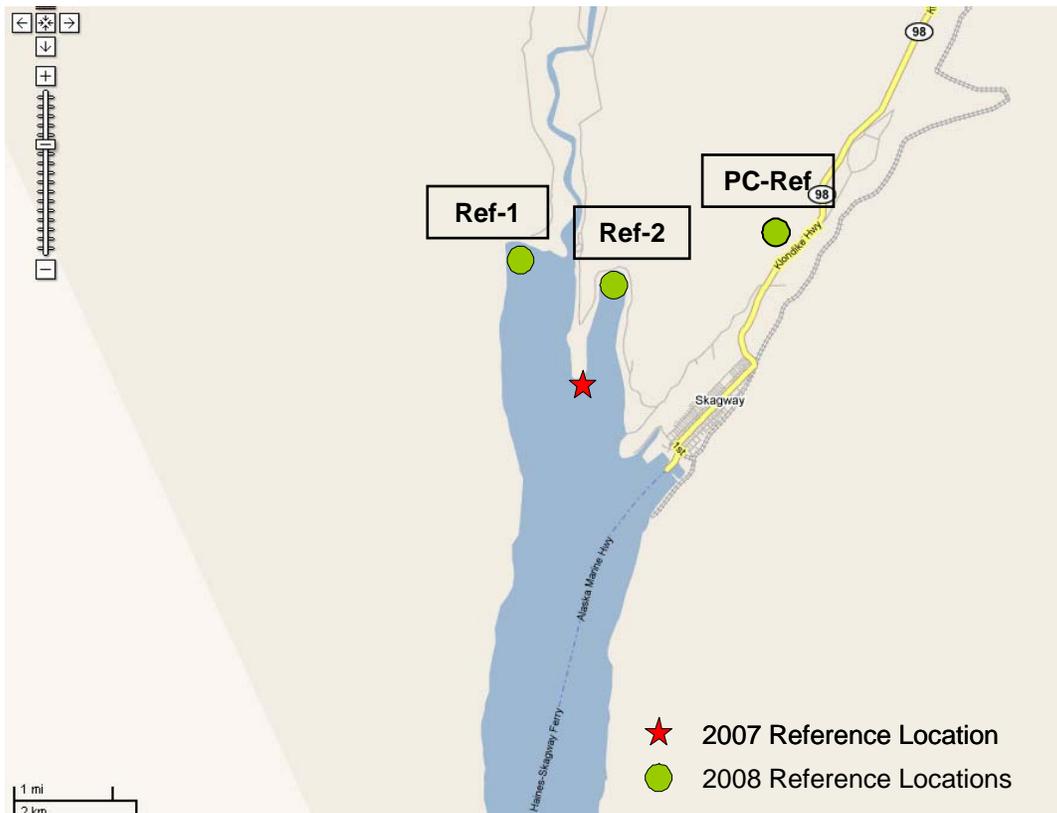
	Site	Surface Water Copper	Water Quality (i.e., pH, Conductivity, Salinity, Temperature, and DO)	Surface Water and Sediment Petroleum Derivatives and TOC	Storm Water Metals (i.e., Cd, Cu, Pb, Ni, Zn)	Base-flow Metals (i.e., Cd, Cu, Pb, Ni, Zn)	Sediment Petroleum Derivatives and TOC
Skagway Harbor	SH-1						
	SH-2						
	SH-3						
	SH-4		√	√			
	SH-5	√	√				
	SH-6						
	SH-7		√	√			
	SH-8						
	SH-9	√	√	√			
	SH-10	√	√	√			
	SH-11						
	SH-12	√	√				
	SH-13						
	SH-14	√	√	√			
	SH-15	√	√	√			
	SH-16						
	SH-17	√	√	√			
	SH-18						
	SH-19						
	SH-20						
	SH-21						
Ferry Dock	FD-1	√	√				
Railroad Dock	RD-1	√	√				
Small Boat Harbor	BH-1	√	√				
Outer Harbor	OH-1						
	OH-2						
	OH-3						
Pullen Creek	PC-1				√	√	√
	PC-2				√	√	√
	PC-3						
	PC-4						
	PC-5				√	√	√
	PC-6						
	PC-7				√		
	PC-8				√		
	PC-9				√		
REF-PC				√	√	√	
Hydro-Electric Plant	EP-1				√		
Nakhu Bay	REF1	√	√	√			
Nakhu Bay	REF2	√	√	√			



Figure 3. Sampling locations on Pullen Creek in 2008.

### 2.1.3 Reference – Nakhu Bay

There was some uncertainty, based on data collected in 2007, as to whether the reference site used may be influenced by Skagway Harbor due to tides and currents. As indicated in Figure 5, two new reference sites were established further north in Nakhu Bay. Ref-2 is used by the National Oceanic and Atmospheric Administration (NOAA) in their Mussel Watch Program. Sampling at these locations included both surficial sediment and surface water.



**Figure 4.** Current (2008) and previous (2007) reference locations.

## 2.2 Field Sampling Methods

Sampling methods followed those recommended by USEPA (2001) and ASTM (2002) and were outlined in detail in the ADEC- and USEPA-approved FSAP (Appendix B). Sampling methods for the chemical characterization of surficial sediment and surface water were based on methods previously used in and around Skagway Harbor.

### 2.2.1 Surficial Sediment

Surficial sediment samples in Skagway Harbor, the Outer Harbor and Taiya Inlet were collected using a ponar grab sampler. This sampler typically collected the top 2-4 inches of sediment, depending on the available substrate. Sediment from a minimum of three ponar grabs was collected using plastic utensils and containers at each site, composited, and homogenized to an equal color and texture before filling

sample containers. Surficial sediment was collected in Pullen Creek by hand using plastic spoons and containers. An excess of sediment was collected using plastic utensils and containers at each site, composited, and homogenized to an equal color and texture before filling sample containers.

### **2.2.2 Surface Water**

A Kemmerer sampler was used to collect surface water samples in Skagway Harbor; while surface water samples in Pullen Creek were collected by hand. Discrete water samples, at each Skagway Harbor site, were collected at three points in the water column for the metal analysis including: near the surface, mid-depth, and near the bottom. Skagway Harbor sampling for the organic analysis was done by collecting water from within the water column, just above the sediment. Care was taken not to stir up the sediment when sampling. Pullen Creek surface water was collected from mid-channel and mid-water column by hand at each location. Samples were kept on ice until transport to the analytical facility.

## **2.3 Analytical Methods**

Analytical methods used for each media sampled are summarized in Table 2 and briefly described below. Table 3 summarizes the range of reporting limits, method detection limits, and dilutions for each parameter. For a detailed summary see the QAPP in Appendix A.

### **2.3.1 Total Organic Carbon**

Total organic carbon (TOC) was determined in all sediment samples using the Walkley Black Method.

### **2.3.2 Semi-volatiles (PAHs)**

Semi-volatiles were characterized for both sediment and surface water. EPA Method 8270D was used to determine the concentration of PAHs in sediments. EPA Method 625 was used to determine the concentration of PAHs in surface water as recommended by ADEC for comparability to Alaska's water quality criteria and consistency among other state monitoring sites.

### **2.3.3 Total Petroleum Hydrocarbons (TPH)**

Total petroleum hydrocarbons were measured as the combination of the diesel and residual range organics fractions. Alaska methods 102 and 103 were used to determine TPH.

### **2.3.4 Total and Dissolved Metals**

Total and dissolved metals were measured in surface waters using inductively coupled plasma-mass spectrometry (ICP-MS) via EPA method 200.8. Samples for dissolved metals were field filtered through a 0.45 micron membrane filter to separate the dissolved fraction.

### **2.3.5 Volatile Organic Compounds (VOCs)**

Volatile organic compounds were measured in surface water using EPA Method 624 as recommended by ADEC for comparability to Alaska's water quality criteria and consistency among other state monitoring sites.

### **2.3.6 Oil and Grease**

Oil and grease was determined in surface water using EPA Method 1664.

### **2.3.7 Water Quality Parameters**

Overlying water quality parameters including dissolved oxygen, pH, salinity or conductivity, and temperature were measured at each station. Table 2 summarizes the reporting limits for each parameter.

### **2.3.8 QA/QC**

Two field quality assurance/quality control measures were used during sampling in Skagway Harbor and the surrounding area: splits and duplicates. As described in the Quality Assurance/Quality Control Methods section of the QAPP, field duplicates are used to determine the natural variability associated with the sampling area, sample handling, and laboratory operations. Blind field duplicates were collected at 10% of the surficial sediment sampling stations. Field split samples are designed to monitor overall sampling and analytical precision. Blind field splits consisted of a homogenized sample that is split into two sample aliquots and were collected at 10% of the surficial sediment stations.

Quality assurance/quality control within the analytical laboratory was accomplished by using multiple techniques including: matrix spikes, matrix spike duplicates, method blanks, laboratory control spikes, and laboratory control spike duplicates. Descriptions of the analytical quality assurance/quality control techniques are provided in the QAPP included in Appendix A.

**Table 2.** Table containing the methods, reporting limits, and method detection limits for all parameters measured in sediment and water.

Group	Analyte	Media	Method	Range of Dilutions	Range of Reporting Limits	Method Detection Limit	
TOC	Total Organic Carbon	Sediment	Walkley Black	1.202 – 1.287	0.10 – 0.13%	0.050 – 0.064%	
PAHs	1-Fluoronaphthalene	Sediment	EPA 8270	1.0 – 1.281			
	1-Methylnaphthalene	Sediment	EPA 8270	1.0 – 1.281	6.7 – 8.6 µg/kg	1.2 – 1.5 µg/kg	
	2-Methylnaphthalene	Sediment	EPA 8270	1.0 – 1.281	6.7 – 8.6 µg/kg	1.8 – 2.3 µg/kg	
	Acenaphthene	Sediment	EPA 8270	1.0 – 1.281	6.7 – 8.6 µg/kg	1.3 – 1.7 µg/kg	
	Acenaphthylene	Sediment	EPA 8270	1.0 – 1.281	6.7 – 8.6 µg/kg	0.72 – 0.92 µg/kg	
	Anthracene	Sediment	EPA 8270	1.0 – 1.281	6.7 – 8.6 µg/kg	0.95 – 1.2 µg/kg	
	Benzo[a]anthracene	Sediment	EPA 8270	1.0 – 1.281	6.7 – 8.6 µg/kg	1.0 – 1.3 µg/kg	
	Benzo[a]pyrene	Sediment	EPA 8270	1.0 – 1.281	6.7 – 8.6 µg/kg	1.1 – 1.4 µg/kg	
	Benzo[b]fluoranthene	Sediment	EPA 8270	1.0 – 1.281	6.7 – 8.6 µg/kg	1.0 – 1.3 µg/kg	
	Benzo[g,h,i]perylene	Sediment	EPA 8270	1.0 – 1.281	6.7 – 8.6 µg/kg	1.1 – 1.4 µg/kg	
	Benzo[k]fluoranthene	Sediment	EPA 8270	1.0 – 1.281	6.7 – 8.6 µg/kg	0.52 – 0.67 µg/kg	
	Chrysene	Sediment	EPA 8270	1.0 – 1.281	6.7 – 8.6 µg/kg	0.95 – 1.2 µg/kg	
	Dibenzo[a,h]anthracene	Sediment	EPA 8270	1.0 – 1.281	6.7 – 8.6 µg/kg	1.2 – 1.5 µg/kg	
	Fluoranthene	Sediment	EPA 8270	1.0 – 1.281	6.7 – 8.6 µg/kg	0.95 – 1.2 µg/kg	
	Fluorene	Sediment	EPA 8270	1.0 – 1.281	6.7 – 8.6 µg/kg	0.73 – 0.93 µg/kg	
	Indeno[1,2,3-cd]pyrene	Sediment	EPA 8270	1.0 – 1.281	6.7 – 8.6 µg/kg	1.4 – 1.8 µg/kg	
	Naphthalene	Sediment	EPA 8270	1.0 – 1.281	6.7 – 8.6 µg/kg	1.3 – 1.7 µg/kg	
	Phenanthrene	Sediment	EPA 8270	1.0 – 1.281	6.7 – 8.6 µg/kg	1.2 – 1.5 µg/kg	
	Pyrene	Sediment	EPA 8270	1.0 – 1.281	6.7 – 8.6 µg/kg	1.2 – 1.5 µg/kg	
	2,4,6-Tribromophenol	Water	EPA 625		0.943 – 1.0		
	2-Fluorobiphenyl	Water	EPA 625		0.943 – 1.0		
	2-Fluorophenol	Water	EPA 625		0.943 – 1.0		
	Acenaphthene	Water	EPA 625		0.943 – 1.0	4.7 – 5.0 µg/L	0.86 – 0.91 µg/L
	Acenaphthylene	Water	EPA 625		0.943 – 1.0	4.7 – 5.0 µg/L	0.82 – 0.87 µg/L
	Anthracene	Water	EPA 625		0.943 – 1.0	4.7 – 5.0 µg/L	0.94 – 1.0 µg/L
	Benzo[a]anthracene	Water	EPA 625		0.943 – 1.0	4.7 – 5.0 µg/L	0.94 – 1.0 µg/L
	Benzo[a]pyrene	Water	EPA 625		0.943 – 1.0	4.7 – 5.0 µg/L	0.92 – 0.98 µg/L
	Benzo[b]fluoranthene	Water	EPA 625		0.943 – 1.0	4.7 – 5.0 µg/L	0.94 – 1.0 µg/L
	Benzo[g,h,i]perylene	Water	EPA 625		0.943 – 1.0	4.7 – 5.0 µg/L	1.1 – 1.2 µg/L
	Benzo[k]fluoranthene	Water	EPA 625		0.943 – 1.0	4.7 – 5.0 µg/L	0.86 – 0.91 µg/L
	Chrysene	Water	EPA 625		0.943 – 1.0	4.7 – 5.0 µg/L	1.0 – 1.1 µg/L
	Dibenzo[a,h]anthracene	Water	EPA 625		0.943 – 1.0	4.7 – 5.0 µg/L	1.0 – 1.1 µg/L
	Fluoranthene	Water	EPA 625		0.943 – 1.0	4.7 – 5.0 µg/L	1.0 – 1.1 µg/L
Fluorene	Water	EPA 625		0.943 – 1.0	4.7 – 5.0 µg/L	0.94 – 1.0 µg/L	
Indeno[1,2,3-cd]pyrene	Water	EPA 625		0.943 – 1.0	4.7 – 5.0 µg/L	1.1 – 1.2 µg/L	
Naphthalene	Water	EPA 625		0.943 – 1.0	4.7 – 5.0 µg/L	0.78 – 0.83 µg/L	
Phenanthrene	Water	EPA 625		0.943 – 1.0	4.7 – 5.0 µg/L	0.89 – 0.94 µg/L	
Pyrene	Water	EPA 625		0.943 – 1.0	4.7 – 5.0 µg/L	0.87 – 0.92 µg/L	
TPH	Diesel Range Organics	Sediment	AK 102/103	1.0-1.253	10 – 13 mg/kg	2.0 – 2.5 mg/kg	
	Residual Range Organics	Sediment	AK 102/103	1.0-1.253	50 – 63 mg/kg	10 – 13 mg/kg	
	n-Octacosane	Sediment	AK 102/103	1.0-1.253			
	o-Terphenyl	Sediment	AK 102/103	1.0-1.253			
	Diesel Range Organics	Water	AK 102/103	1.0-4.717	0.050 – 0.24mg/L	0.023 – 0.11 mg/L	
	Residual Range Organics	Water	AK 102/103	1.0-4.717	0.20 – 0.94 mg/L	0.026 – 0.12 mg/L	
	n-Octacosane	Water	AK 102/103	1.0-4.717			
Metals	o-Terphenyl	Water	AK 102/103	1.0-4.717			
	Cadmium	Water	EPA 200.8	1.0-5.0	1.0 – 5.0 µg/L	0.094 – 0.47 µg/L	
	Copper	Water	EPA 200.8	1.0-5.0	2.0 – 10.0 µg/L	0.52 – 2.6 µg/L	
	Lead	Water	EPA 200.8	1.0-5.0	1.0 – 5.0 µg/L	0.075 – 0.38 µg/L	
	Nickel	Water	EPA 200.8	1.0-5.0	1.0 – 5.0 µg/L	0.11 – 0.55 µg/L	
VOCs	Zinc	Water	EPA 200.8	1.0-5.0	10.0 – 50.0 µg/L	1.8 – 9.0 µg/L	
	1,1,1-Trichloroethane	Water	EPA 624	1.0	3.0 µg/L	0.20 µg/L	
	1,1,2,2-Tetrachloroethane	Water	EPA 624	1.0	3.0 µg/L	0.22 µg/L	
	1,1,2-Trichloroethane	Water	EPA 624	1.0	3.0 µg/L	0.19 µg/L	

**Table 2. Continued.**

VOCs	1,1-Dichloroethane	Water	EPA 624	1.0	3.0 µg/L	0.23 µg/L
	1,1-Dichloroethene	Water	EPA 624	1.0	3.0 µg/L	0.12 µg/L
	1,2-Dichlorobenzene	Water	EPA 624	1.0	3.0 µg/L	0.25 µg/L
	1,2-Dichloroethane	Water	EPA 624	1.0	3.0 µg/L	0.074 µg/L
	1,2-Dichloropropane	Water	EPA 624	1.0	3.0 µg/L	0.16 µg/L
	1,3-Dichlorobenzene	Water	EPA 624	1.0	3.0 µg/L	0.16 µg/L
	1,4-Dichlorobenzene	Water	EPA 624	1.0	3.0 µg/L	0.20 µg/L
	2-Chloroethylvinylether	Water	EPA 624	1.0	10 µg/L	0.40 µg/L
	4-Bromofluorobenzene	Water	EPA 624	1.0		
	Benzene	Water	EPA 624	1.0	3.0 µg/L	0.12 µg/L
	Bromodichloromethane	Water	EPA 624	1.0	3.0 µg/L	0.11 µg/L
	Bromoform	Water	EPA 624	1.0	3.0 µg/L	0.23 µg/L
	Bromomethane	Water	EPA 624	1.0	3.0 µg/L	0.072 µg/L
	Carbon tetrachloride	Water	EPA 624	1.0	3.0 µg/L	0.25 µg/L
	Chlorobenzene	Water	EPA 624	1.0	3.0 µg/L	0.12 µg/L
	Chloroethane	Water	EPA 624	1.0	3.0 µg/L	0.27 µg/L
	Chloroform	Water	EPA 624	1.0	3.0 µg/L	0.15 µg/L
	Chloromethane	Water	EPA 624	1.0	3.0 µg/L	0.20 µg/L
	cis-1,2-Dichloroethene	Water	EPA 624	1.0	3.0 µg/L	0.32 µg/L
	cis-1,3-Dichloropropene	Water	EPA 624	1.0	3.0 µg/L	0.086 µg/L
	Dibromochloromethane	Water	EPA 624	1.0	3.0 µg/L	0.12 µg/L
	Dibromofluoromethane	Water	EPA 624	1.0		
	Ethylbenzene	Water	EPA 624	1.0	3.0 µg/L	0.20 µg/L
	m,p-Xylene	Water	EPA 624	1.0	6.0 µg/L	0.27 µg/L
	Methylene chloride	Water	EPA 624	1.0	3.0 µg/L	1.0 µg/L
	o-Xylene	Water	EPA 624	1.0	3.0 µg/L	0.15 µg/L
	Tetrachloroethene	Water	EPA 624	1.0	3.0 µg/L	0.10 µg/L
	Toluene	Water	EPA 624	1.0	3.0 µg/L	0.21 µg/L
	trans-1,2-Dichloroethene	Water	EPA 624	1.0	3.0 µg/L	0.22 µg/L
	trans-1,3-Dichloropropene	Water	EPA 624	1.0	3.0 µg/L	0.16 µg/L
	Trichloroethene	Water	EPA 624	1.0	3.0 µg/L	0.22 µg/L
	Trichlorofluoromethane	Water	EPA 624	1.0	3.0 µg/L	0.24 µg/L
Vinyl chloride	Water	EPA 624	1.0	3.0 µg/L	0.27 µg/L	
Xylenes, total	Water	EPA 624	1.0	3.0 µg/L	1.0 µg/L	
O&G	Oil and Grease – Total	Water	EPA 1664A	1.0-1.010	5 mg/L	1 mg/L
Water Quality	pH	Water	In situ (electronic probe)	NA	±0.01 pH units	NA
	Temperature	Water	In situ (electronic probe)		0-1: 0.001 1-10: 0.01 10-100: 0.1 (mS/cm)	
	Salinity	Water	In situ (electronic probe)		± 0.01%	
	Dissolved Oxygen	Water	In situ (electronic probe)		± 0.1 mg/L	

## **3.0 Results**

### **3.1 Skagway Harbor Surficial Sediment**

The original analytical laboratory reports for the evaluation of surficial sediment are included in Appendix C.

#### **3.1.1 Semi-volatiles (PAHs)**

The surficial sediment samples collected from the Skagway Harbor sites were analyzed for various PAHs (Table-3). Concentrations of PAHs at both reference sites, REF-1 and REF-2, were non-detected (maximum detection limit = 2.3 µg/kg). Sites SH-4 and SH-7 had detectable concentrations of all PAHs analyzed for, while chrysene, fluoranthene, and pyrene were measured in every Skagway Harbor sediment sample. Chrysene concentrations ranged from 23 (SH-17) to 1200 (SH-4) µg/kg, flouranthene concentrations ranged from 50 (SH-17) to 3300 (SH-4 and SH-7) µg/kg, and pyrene concentrations ranged from 28 (SH-17) to 2100 (SH-4 and SH-7) µg/kg. For all other parameters and measured values, see Table-3.

#### **3.1.2 Total Organic Carbon (TOC)**

Total Organic Carbon (TOC) values measured in the sediment at the reference sites, REF-1 and REF-2, were 1.9% and 0.15%, respectively (Table-3). The levels of TOC detected in the sediment at the Skagway Harbor ranged from 0.19%, at sample site SH-17, to 1.6%, at sample site SH-4. This range is similar to the range measured in 2007, which was 0.05% to 1.29% (Table-3).

#### **3.1.3 Total Petroleum Hydrocarbons (TPH)**

Diesel range organics and residual range organics were not detected in Skagway Harbor sediment or the reference sediment using a maximum detection limit of 2.5 mg/Kg and 13 mg/Kg, respectively (Table-3).

### **3.2 Skagway Harbor Surface Water**

The original analytical laboratory reports for the evaluation of surface water are included in Appendix C.

#### **3.2.1 Semi-volatiles (PAHs), Total Petroleum Hydrocarbons (TPH), and Volatile Organic Compounds (VOCs)**

Concentrations of PAHs, TPH, and VOCs in the surface water sampled from Skagway Harbor, including both reference sites, were not detected (Table-5).

**Table 3.** Results of the Skagway Harbor surficial sediment samples. U = Non-detectable. Non-detected values listed are the reporting limits.

Skagway Harbor Sediment Data																		
Group	Parameter	Units	SH-4		SH-7		SH-9		SH-10		SH-14		SH-17		REF-1		REF-2	
			Results	Q	Results	Q	Results	Q	Results	Q	Results	Q	Results	Q	Results	Q	Results	Q
PAHs	1-Methylnaphthalene	ug/kg	34		250		16		85		8.6	U	8.0	U	9.8	U	8.0	U
	2-Methylnaphthalene	ug/kg	47		390		33		140		9.6		8.0	U	9.8	U	8.0	U
	Acenaphthene	ug/kg	210		1100		97		460		41		8.0	U	9.8	U	8.0	U
	Acenaphthylene	ug/kg	82		62		27		25	U	17		8.0	U	9.8	U	8.0	U
	Anthracene	ug/kg	190		290		160		110		59		8.0	U	9.8	U	8.0	U
	Benzo(a)anthracene	ug/kg	910		670		570		390		380		17		9.8	U	8.0	U
	Benzo(a)pyrene	ug/kg	400		290		220		140		120		8.0	U	9.8	U	8.0	U
	Benzo(b)fluoranthene	ug/kg	980		520		500		240		220		18		9.8	U	8.0	U
	Benzo(g,h,i)perylene	ug/kg	77		62		38		30		22		8.0	U	9.8	U	8.0	U
	Benzo(k)fluoranthene	ug/kg	540		400		260		190		180		12		9.8	U	8.0	U
	Chrysene	ug/kg	1200		730		790		400		340		23		9.8	U	8.0	U
	Dibenzo(a,h)anthracene	ug/kg	50		31		25		25	U	14		8.0	U	9.8	U	8.0	U
	Fluoranthene	ug/kg	3300		3300		1900		1400		810		50		9.8	U	8.0	U
	Fluorene	ug/kg	230		820		190		450		42		8.0	U	9.8	U	8.0	U
	Indeno(1,2,3-cd)pyrene	ug/kg	96		74		46		37		29		8.0	U	9.8	U	8.0	U
	Naphthalene	ug/kg	42		290		9.2	U	68		8.6	U	8.0	U	9.8	U	8.0	U
Phenanthrene	ug/kg	1000		2400		730		1200		190		8.0	U	9.8	U	8.0	U	
Pyrene	ug/kg	2100		2100		1300		810		640		28		9.8	U	8.0	U	
TPH	Residual Range Organics	mg/Kg	90	U	94	U	67	U	91	U	63	U	58	U	71	U	56	U
	Diesel Range Organics	mg/Kg	18	U	20		13	U	18	U	13	U	12	U	14	U	11	U
TOC	Organic Carbon, Total (TOC)	%	1.6		1.3		0.69		0.66		0.46		0.19		1.9		0.15	
TS	Solids, Total	%	55.4		51.4		72.8		53.5		77.7		83.2		67.2		84.4	

### **3.2.2 Copper**

Concentrations of dissolved copper were below the detection limit of 2.6 µg/L in the surface, middle, and bottom of the water column for all sample locations in Skagway Harbor. Sample site REF-1 had a dissolved copper value of 5.3 µg/L, which was below the reporting limit. Concentrations of total copper detected ranged from 3.9 µg/L at site REF-1 to 24.0 µg/L at site SH-10 (Table-4). The 2008 dissolved copper concentrations are considerably lower than the dissolved copper concentrations found in 2007, which had a range of 5.0 µg/L for site REF to 11.0 µg/L at site SH-15.

### **3.3 Pullen Creek Surficial Sediment**

The original analytical laboratory reports for the evaluation of surficial sediments are included in Appendix C.

#### **3.3.1 Semi-volatiles (PAHs)**

The surficial sediment samples collected from the Pullen Creek sites were analyzed for various PAHs (Table-6). Concentrations of PAHs were not detected in the sediment at sample sites PC-2 and PC-REF, while PC-1 had detected concentrations of all PAHs (Table-6) in the sediment.

#### **3.3.2 Total Organic Carbon (TOC)**

The levels of Total Organic Carbon (TOC) found in Pullen Creek sediment samples, including the reference site, PC-REF, ranged from 0.22% at site PC-2 to 3.1% at Site PC-REF (Table-6). In comparison, the 2007 TOC values ranged from 0.19% to 12.9%.

#### **3.3.3 Total Petroleum Hydrocarbons (TPH)**

Concentrations of residual range organics were not detected in any Pullen Creek sample. Concentrations of diesel range organics were not detected at sites PC-2 and PC-REF with detection limits of 12 and 15 mg/Kg, respectively, but were detected at sites PC-1 and PC-5 with concentrations of 14 and 30 mg/Kg, respectively (Table-6).

### **3.4 Pullen Creek Surface Water**

The original analytical laboratory reports for the evaluation of surface waters are included in Appendix C.

#### **3.4.1 Zinc**

Concentrations of dissolved zinc were detected at all sample sites ranging from a minimum of 9.7 (Site PC-1 SW) to a maximum of 45.5 (Site PC-2) µg/L (Table-7), while sample sites PC-1, EP-1, and PC-8 had dissolved zinc levels of 71.4, 70.6, and 148 µg/L, respectively. Total Zinc was not detected at sites PC-5, EP-1, and PC-REF SW. Concentrations of total zinc detected ranged from 11.9 (PC-REF) to 163 (PC-8) µg/L.

**Table 4.** Skagway Harbor top, middle, and bottom surface water copper concentrations. U = non-detectable, and J = the value is below the reporting limit, but above the detection limit. Non-detected values listed are the detection limits.

Skagway Harbor Surface Water Copper Data												
Site Name	BH-1		FD-1		RD-1		REF-1		REF-2		SH-5	
	Q	Result	Q	Result	Q	Result	Q	Result	Q	Result	Q	Result
Total Copper Surface (µg/L)	U	2.6	U	2.6	J	4.4	U	2.6	U	2.6	U	2.6
Total Copper Middle (µg/L)	U	2.6	U	2.6	J	4.5	U	2.6	U	2.6	U	2.6
Total Copper Bottom (µg/L)	U	2.6	U	2.6	J	4.5	J	3.9	J	7.3		14.3
Dissolved Copper Surface (µg/L)	U	2.6	U	2.6	U	2.6	J	5.3	U	2.6	U	2.6
Dissolved Copper Middle (µg/L)	U	2.6	U	2.6	U	2.6	U	2.6	U	2.6	U	2.6
Dissolved Copper Bottom (µg/L)	U	2.6	U	2.6	U	2.6	U	2.6	U	2.6	U	2.6
Site Name	SH-9		SH-10		SH-12		SH-14		SH-15		SH-17	
	Q	Result	Q	Result	Q	Result	Q	Result	Q	Result	Q	Result
Total Copper Surface (µg/L)		11.3		24.0	J	4.5	U	2.6	J	9.1	U	2.6
Total Copper Middle (µg/L)	J	8.3	J	5.3	J	4.6		12.4	U	2.6	U	2.6
Total Copper Bottom (µg/L)	J	5.9		13.0	U	2.6	J	7.5	U	2.6	J	5.4
Dissolved Copper Surface (µg/L)	U	2.6	U	2.6	U	2.6	U	2.6	U	2.6	U	2.6
Dissolved Copper Middle (µg/L)	U	2.6	U	2.6	U	2.6	U	2.6	U	2.6	U	2.6
Dissolved Copper Bottom (µg/L)	U	2.6	U	2.6	U	2.6	U	2.6	U	2.6	U	2.6

**Table 5.** Results of Skagway Harbor surface water samples. U = Non-detectable

Skagway Harbor Surface Water PAHs, TOC, TPH, VOCs and Oil and Grease Data																		
Group	Parameter	Units	REF-1		REF-2		SH-10		SH-14		SH-17		SH-4		SH-7		SH-9	
			Results	Q	Results	Q												
VOCs	1,1,1-Trichloroethane	ug/L	3.0	U	3.0	U												
	1,1,2,2-Tetrachloroethane	ug/L	3.0	U	3.0	U												
	1,1,2-Trichloroethane	ug/L	3.0	U	3.0	U												
	1,1-Dichloroethane	ug/L	3.0	U	3.0	U												
	1,1-Dichloroethene	ug/L	3.0	U	3.0	U												
	1,2-Dichlorobenzene	ug/L	3.0	U	3.0	U												
	1,2-Dichloroethane	ug/L	3.0	U	3.0	U												
	1,2-Dichloropropane	ug/L	3.0	U	3.0	U												
	1,3-Dichlorobenzene	ug/L	3.0	U	3.0	U												
	1,4-Dichlorobenzene	ug/L	3.0	U	3.0	U												
	2-Chloroethylvinylether	ug/L	10	U	10	U												
	Benzene	ug/L	3.0	U	3.0	U												
	Bromodichloromethane	ug/L	3.0	U	3.0	U												
	Bromoform	ug/L	3.0	U	3.0	U												
	Bromomethane	ug/L	3.0	U	3.0	U												
	Carbon tetrachloride	ug/L	3.0	U	3.0	U												
	Chlorobenzene	ug/L	3.0	U	3.0	U												
	Chloroethane	ug/L	3.0	U	3.0	U												
	Chloroform	ug/L	3.0	U	3.0	U												
	Chloromethane	ug/L	3.0	U	3.0	U												
	cis-1,2-Dichloroethene	ug/L	3.0	U	3.0	U												
	cis-1,3-Dichloropropene	ug/L	3.0	U	3.0	U												
	Dibromochloromethane	ug/L	3.0	U	3.0	U												
Ethylbenzene	ug/L	3.0	U	3.0	U	3.0	U	3.0	U	3.0	U	3.0	U	3.0	U	3.0	U	
m,p-Xylene	ug/L	6.0	U	6.0	U	6.0	U	6.0	U	6.0	U	6.0	U	6.0	U	6.0	U	
Methylene chloride	ug/L	3.0	U	3.0	U	3.0	U	3.0	U	3.0	U	3.0	U	3.0	U	3.0	U	
o-Xylene	ug/L	3.0	U	3.0	U	3.0	U	3.0	U	3.0	U	3.0	U	3.0	U	3.0	U	

Table 5. Continued.

VOCs	Tetrachloroethene	ug/L	3.0	U	3.0	U										
	Toluene	ug/L	3.0	U	3.0	U										
	trans-1,2-Dichloroethene	ug/L	3.0	U	3.0	U										
	trans-1,3-Dichloropropene	ug/L	3.0	U	3.0	U										
	Trichloroethene	ug/L	3.0	U	3.0	U										
	Trichlorofluoromethane	ug/L	3.0	U	3.0	U										
	Vinyl chloride	ug/L	3.0	U	3.0	U										
	Xylenes, Total	ug/L	3.0	U	3.0	U										
PAHs	Acenaphthene	ug/L	5.6	U	4.7	U										
	Acenaphthylene	ug/L	5.6	U	4.7	U										
	Anthracene	ug/L	5.6	U	4.7	U										
	Benzo(a)anthracene	ug/L	5.6	U	4.7	U										
	Benzo(a)pyrene	ug/L	5.6	U	4.7	U										
	Benzo(b)fluoranthene	ug/L	5.6	U	4.7	U										
	Benzo(g,h,i)perylene	ug/L	5.6	U	4.7	U										
	Benzo(k)fluoranthene	ug/L	5.6	U	4.7	U										
	Chrysene	ug/L	5.6	U	4.7	U										
	Dibenzo(a,h)anthracene	ug/L	5.6	U	4.7	U										
	Fluoranthene	ug/L	5.6	U	4.7	U										
	Fluorene	ug/L	5.6	U	4.7	U										
	Indeno(1,2,3-cd)pyrene	ug/L	5.6	U	4.7	U										
	Naphthalene	ug/L	5.6	U	4.7	U										
	Phenanthrene	ug/L	5.6	U	4.7	U										
Pyrene	ug/L	5.6	U	4.7	U											
TPH	Diesel Range Organics	mg/L	0.24	U	0.25	U	0.24	U								
	Residual Range Organics	mg/L	0.94	U	1.0	U	0.94	U								
O&G	Oil & Grease, Total Recoverable	mg/L	5	U	5	U	5	U	5	U	5	U	5	U	5	U

**Table 6.** Results of the Pullen Creek surficial sediment samples. U = Non-detectable.

Pullen Creek Sediment Data										
Group	Parameter	Units	PC-1		PC-2		PC-5		PC-REF	
			Results	Q	Results	Q	Results	Q	Results	Q
PAHs	1-Methylnaphthalene	ug/kg	24		16	U	110		20	U
	2-Methylnaphthalene	ug/kg	27		16	U	150		20	U
	Acenaphthene	ug/kg	67		16	U	12	U	20	U
	Acenaphthylene	ug/kg	26		16	U	12	U	20	U
	Anthracene	ug/kg	240		16	U	12	U	20	U
	Benzo(a)anthracene	ug/kg	300		16	U	20		20	U
	Benzo(a)pyrene	ug/kg	240		16	U	12	U	20	U
	Benzo(b)fluoranthene	ug/kg	250		16	U	12	U	20	U
	Benzo(g,h,i)perylene	ug/kg	110		16	U	12	U	20	U
	Benzo(k)fluoranthene	ug/kg	180		16	U	12	U	20	U
	Chrysene	ug/kg	300		16	U	29		20	U
	Dibenzo(a,h)anthracene	ug/kg	40		16	U	12	U	20	U
	Fluoranthene	ug/kg	680		16	U	12	U	20	U
	Fluorene	ug/kg	130		16	U	18		20	U
	Indeno(1,2,3-cd)pyrene	ug/kg	91		16	U	12	U	20	U
	Naphthalene	ug/kg	21		16	U	98		20	U
Phenanthrene	ug/kg	690		16	U	94		20	U	
Pyrene	ug/kg	760		16	U	48		20	U	
TPH	Residual Range Organics	mg/Kg	63	U	60	U	86	U	74	U
	Diesel Range Organics	mg/Kg	14		12	U	30		15	U
TOC	Organic Carbon, Total (TOC)	%	0.66		0.22		2.4		3.1	
TS	Solids, Total	%	77.9		79.5		55.8		65.9	

**Table 7.** Results of the Pullen Creek Surface water metal samples. U = non-detectable, J = the value is below the reporting limit, but above the detection limit, N = spiked sample recovery not within control limits, E = the serial dilution was not within the control limits and \* = Duplicate analysis not within control limits.

<b>Pullen Creek Surface and Storm Water Metal Data</b>											
<b>Site</b>	<b>Result or Q</b>	<b>Total Zinc (µg/L)</b>	<b>Dissolved Zinc (µg/L)</b>	<b>Total Cadmium (µg/L)</b>	<b>Dissolved Cadmium (µg/L)</b>	<b>Total Copper (µg/L)</b>	<b>Dissolved Copper (µg/L)</b>	<b>Total Lead (µg/L)</b>	<b>Dissolved Lead (µg/L)</b>	<b>Total Nickel (µg/L)</b>	<b>Dissolved Nickel (µg/L)</b>
<b>PC-1</b>	Q	J		U	U	U	U	J		J	U
	Result	21.9	71.4	0.47	0.47	2.6	2.6	0.44	5.6	0.61	0.55
<b>PC-2</b>	Q		J	U	U	U	U	J		J	J
	Result	64.1	45.5	0.47	0.47	2.6	2.6	2.8	11.7	0.58	1.0
<b>PC-5</b>	Q	U	J	U	J	U	J	U		U	J
	Result	9.0	38.3	0.47	1.4	2.6	4.3	0.38	11.2	0.55	1.8
<b>PC-7</b>	Q	N	JN	J	U	E*N	JE*N		J	J	J
	Result	63.7	25.2	1.8	0.47	10.6	3.5	11.0	1.9	3.4	0.73
<b>PC-8</b>	Q	N	N	J	J	E*N	E*N		J	J	
	Result	163	148	0.50	0.53	19.5	28.1	12.8	3.9	4.7	40.2
<b>PC-9</b>	Q	JN	JN	U	U	JE*N	UE*N		J	J	J
	Result	46.0	24.5	0.47	0.47	4.8	2.6	7.0	1.9	1.9	0.69
<b>PC-1 SW</b>	Q	JN	JN	U	J	E*N	UE*N	J	J	U	J
	Result	12.3	9.7	0.47	1.9	26.8	2.6	4.8	3.0	0.55	1.7
<b>PC-2 SW</b>	Q	JN	JN	U	U	JE*N	UE*N	J	J		U
	Result	15.4	14.1	0.47	0.47	2.8	2.6	2.4	1.8	41.8	0.55
<b>PC-5 SW</b>	Q	JN	JN	U	U	UE*N	UE*N	J	J	J	J
	Result	14.4	17.8	0.47	0.47	2.6	2.6	2.4	2.9	0.63	0.64
<b>PC-REF</b>	Q	J	J	U	U	U	U	J		J	J
	Result	11.9	29.3	0.47	0.47	2.6	2.6	2.0	7.1	2.1	3.4
<b>PC-REF SW</b>	Q	UN	JN	U	U	UE*N	UE*N	J	J	J	J
	Result	9.0	13.6	0.47	0.47	2.6	2.6	1.1	2.8	0.93	1.2
<b>EP-1</b>	Q	UN	N	U	U	UE*N	UE*N	J	J	U	J
	Result	9.0	70.6	0.47	0.47	2.6	2.6	1.3	2.1	0.55	0.75

### 3.4.2 Cadmium

Concentrations of dissolved cadmium was not detected in the surface water of Pullen Creek; with the exception of sites PC-7 and PC-8, which resulted in concentrations of 1.8 and 0.50 µg/L, respectively (Table-7). Both detected values were under the reporting limit (5.0µg/L). Sites PC-7 and PC-8 were also the only sites to have detectable concentrations of total cadmium, which were 1.8 and 0.50 µg/L, respectively.

### 3.4.3 Lead

Concentrations of dissolved lead values ranged from 1.8 (site PC-2 SW) to 7.1 (site PC-REF) µg/L, while sample sites PC-2 and PC-5 had concentrations of dissolved lead of 11.7 and 11.2 µg/L, respectively (Table-7). Total lead was not detected at site PC-5. Concentrations of total lead detected ranged from 0.44 (PC-1) to 12.8 (PC-8) µg/L.

#### **3.4.4 Nickel**

Base flow sample from site PC-1 and the storm flow sample from site PC-2 resulted in no detectable levels of dissolved nickel (detection limit = 0.55 µg/L). Concentrations of dissolved nickel were measured in the base flow samples from sites EP-1, PC-2, PC-5, PC-7, PC-9, PC-REF, and in the storm flow samples from sites PC-1, PC-5, and PC-REF, with concentrations ranging from 0.64 to 3.4 µg/L. However, these detected values of dissolved nickel were below the reporting limit. Sample site PC-8 had a measured concentrations of dissolved nickel of 40.2 µg/L. Total nickel was not detected at sites PC-5, PC-1 SW, and EP-1. Concentrations of total nickel detected ranged from 0.58 (PC-2) to 41.8 (PC-2 SW) µg/L.

#### **3.4.5 Copper**

Concentrations of dissolved copper were identified in base flow samples from sites PC-5 and PC-7 (4.3 and 3.5 µg/L, respectively). However, these dissolved copper concentrations were below the reporting limit (10.0µg/L). The concentrations of dissolved copper at sample site PC-8 was 28.1 µg/L. All other Pullen Creek sample sites had no measured levels of dissolved copper (detection limit = 2.6 µg/L). Total copper was not detected at sample sites PC-1, PC-2, PC-5, PC-5 SW, PC-REF, PC-REF SW, and EP-1. Total copper concentrations detected ranged from 2.8 (PC-2 SW) to 26.8 (PC-1 SW) µg/L.

### **3.5 QA/QC**

An important point to remember while reviewing these data is that a non-detect (ND) value is not a quantified value, and should not be treated as such. The Quality Assurance/Quality Control (QA/QC) report, found in appendix D, explains in further detail the validity of the data collected, and contains the performance evaluation data for each parameter analyzed in this study.

## **6.0 Literature Cited**

Alaska Department of Environmental Conservation (ADEC). 2008. Water Quality Standards

Tetra Tech Inc. 2008. Evaluation of Skagway Harbor and Pullen Creek sediments and surface waters. Prepared for Alaska Department of Environmental Conservation (ADEC).

**Appendix A**  
**Quality Assurance Project Plan**

**Appendix B**  
**Field Sampling and Analysis Plan**

**Appendix C**  
**Analytical Laboratory Reports**  
(See the compact disc sleeve found on the back page of this report.)

**Appendix D**  
**QA/QC Report**