# CPVEC Ambient Water Quality Monitoring: Juneau and Skagway Harbors September 2015 through October 2017



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Alaska Department of Environmental Conservation
Division of Water
Commercial Passenger Vessel Environmental
Compliance Program

By:



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## Introduction

The Alaska Department of Environmental Conservation (DEC), Commercial Passenger Vessel Environmental Compliance (CPVEC) program is responsible for authorizing proposed discharges from cruise ships to marine waters. The DEC has issued a general permit (GP) for these discharges that requires compliance with water quality standard criteria at the point of discharge or submitting a request for a mixing zone. In order to authorize a mixing zone and determine the mixing zone size, the concentration of elements and physical properties of the receiving water, or ambient water quality, must be known. The current general permit is based on the best available ambient water quality data; however, these data are limited.

The objective of this project is to provide more complete ambient water quality data for the Juneau and Skagway Harbors. More specifically those water quality constituents that have the most likely potential to result in water quality exceedances due to cruise ship discharge: ammonia-N, copper, nickel, zinc, and fecal coliform bacteria.

This report summarizes ambient water quality data from samples collected in the Skagway and Juneau Harbors from September 2015 through October 2017, prior to and following the Commercial Passenger Vessel (CPV) season, and water quality data from the Skagway Harbor in June of 2017 during the cruise ship season.

# Methods

Field and sampling and laboratory methods were implemented as described within the approved Quality Assurance Project Plan (QAPP) with minor modifications.

## Sampling Locations

A total 24 to 25 possible sampling locations distributed systematically within each harbor were identified as potential sampling sites (Figures 1 and 2). One of six subsets that included 12 of these sites was selected randomly on each sampling date.

# Sampling Dates and Times

The dates and times water samples were collected is shown in Table 1. Sampling was conducted in the spring prior to and in the autumn following the CPV season. One sampling date was during the CPV season in the Skagway Harbor.



Figure 1. Locations of the possible sampling locations in Gastineau Channel; Juneau Harbor. Twelve of these locations were sampled on each sampling date.



Figure 2. Locations of the possible sampling locations in the Skagway Harbor. Twelve of these locations were sampled on each sampling date.

Table 1. Dates and times sampling was conducted in the Juneau and Skagway Harbors and times of high and low tides. C is clear, PC is partly cloudy, LR is light rain, HR is heavy rain.

Juneau Harbor					
Sample Date	Sample Time	Weather	Low Tide	High Tide	
9/28/2015	09:00 to 14:00	HR	07:41	13:57	
4/18/2016	09:20 to 12:40	PC	05:54	12:00	
10/3/2016	09:42 to 11:56	PC	09:01	15:05	
4/17/2017	09:58 to 11:57	C/PC	11:40	05:07	
10/10/2017	13:00 to 15:00	С	10:48	16:54	
Skagway Harbor					
Skagway Harb	or				
Sample Date	or Sample Time	Weather	Low Tide	High Tide	
		Weather PC/LR	Low Tide 05:20	High Tide 11:45	
Sample Date	Sample Time				
Sample Date 9/25/2015	Sample Time 08:00 to 09:30	PC/LR	05:20	11:45	
Sample Date 9/25/2015 4/20/2016	Sample Time 08:00 to 09:30 09:30 to 13:00	PC/LR C	05:20 07:09	11:45 13:18	
Sample Date 9/25/2015 4/20/2016 9/28/2016	Sample Time 08:00 to 09:30 09:30 to 13:00 09:10 to 11:45	PC/LR C PC	05:20 07:09 06:14	11:45 13:18 12:37	

## Sample Collection Methods

Water samples were collected from ~1 meter depth. Harbor water was pumped water through Teflon tubing into laboratory-provided sample bottles using a peristaltic pump (Solonist 410). Tubing and bottles were flushed for approximately 3 minutes prior to sample collection at each sampling location. In September 2015, water samples to be analyzed for dissolved metals were field filtered; however, beginning in April of 2016, all samples were filtered in the analytical laboratory to minimize the potential for sample contamination in the field.

Water temperature, pH, salinity, and dissolved oxygen were measured at 1, 2, 3, and 4 meter depths at each sampling location. Water pH and salinity was measured with a YSI 1030 meter and dissolved oxygen and temperature with a YSI Pro ODO meter and probe.

Water samples were collected for measures of total fecal coliforms and *E. coli* from 3 sampling locations in each harbor.

Three combined field/equipment blanks were collected from each harbor on each sampling date through September 2016, and one field and two field/equipment blanks thereafter. Field blanks were collected in each harbor by pouring laboratory-provided deionized water directly into the sample bottles. Field/equipment blanks were collected using the same field methods as those for sample collection; however, water was pumped from laboratory-provided deionized water bottles. Replicate samples were collected at one of the twelve sampling locations within each harbor.

#### **Analytical Methods**

Water samples collected in September, 2015, were shipped to Brooks Applied Labs and AM Test lab for analyses. Dissolved copper was analyzed by Brooks Applied Labs by EPA method 1640, and total copper,

total and dissolved nickel, and zinc by EPA method 200.8 at AM Test. Ammonia-N was analyzed using EPA method 350.1.

In April of 2016 and September of 2016, water samples were analyzed by Brooks Applied Labs (Bothell, WA) for total and dissolved copper, nickel, and zinc by EPA method 1640 and ammonia-N by EPA method 350.1. In April, June, and September of 2017 samples were analyzed by ALS Environmental by EPA method 200.8 following reductive precipitation reaction.

Water samples were analyzed for total fecal coliforms by Admiralty Environmental (Juneau, AK) using EPA method 9222D and *E. coli* by the most probable number method.

# Results

Water temperature, dissolved oxygen, pH, and salinity

#### Water temperature

Average harbor water temperatures for the Skagway Harbor is shown in Figure 3 and for the Juneau Harbor in Figure 4. There were large differences in water temperatures between sampling dates but little differences with water depth or among sampling locations within either harbor. Water temperatures in both harbors tended to be cooler in April compared to September. In the Skagway Harbor, water temperatures tended to be coldest near the water surface in June and September and slightly cooler with depth in April. There was very little difference in water temperatures with depth in the Juneau Harbor, with temperatures tending to be higher near the water surface.

#### Salinity

Salinity was variable among sampling dates in both harbors and occasionally with water depth; however, there was little variability in salinity within either harbor. Salinity at 1 m depth ranged from a low of 8.4 ppt to 32 ppt in the Skagway Harbor (Figure 5). Salinity was highest in April of 2016 and 2017 and lowest in June of 2017. Seasonal and depth differences in salinity likely are due to runoff from the Dyea and Skagway Rivers and Pullen Creek.

Salinity in the Juneau Harbor was less variable ranging from 18 ppt to 30 ppt among sampling dates (Figure 6). Average salinity at 1 m depth ranged from 18.4 to 29.7 ppt in the Juneau Harbor. Salinity was higher in April compared to the September sampling dates. Lowest average Juneau Harbor salinity occurred in September of 2015 during heavy rain.

#### Dissolved oxygen

The average percent saturation of dissolved oxygen in the Skagway and Juneau Harbors on each sampling date is shown in Figures 7 and 8. Dissolved oxygen in both harbors ranged from just below to above 100% saturation. There were no seasonal trends in dissolved oxygen and little variability within either harbor. There were no sites or locations within either harbor that would suggest a higher oxygen demand. Dissolved oxygen tended to decrease with depth in both harbors.

#### рΗ

The average pH of water within the Skagway harbor ranged from 7.2 to 8.3 (Figure 9) and from 7.2 to 8.1 in the Juneau Harbor (Figure 10). Harbor water pH tended to be lower in in April and June than in September. Harbor water pH did not vary within either harbor or with water depth.

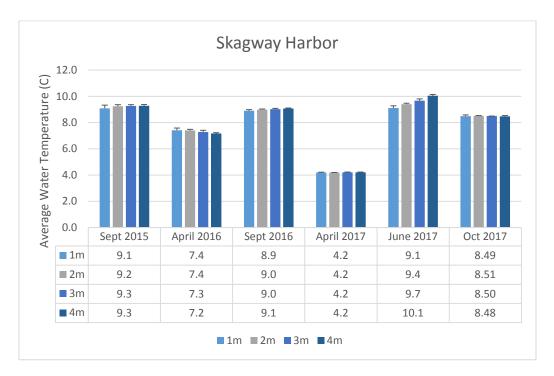


Figure 3. Average Skagway Harbor water temperature at 1 m depth intervals for each sampling date. Error bars are one standard deviation.

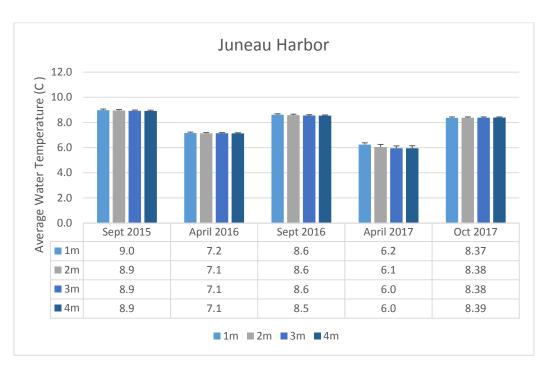


Figure 4. Average Juneau Harbor water temperature at 1 m depth intervals for each sampling date. Error bars are one standard deviation.

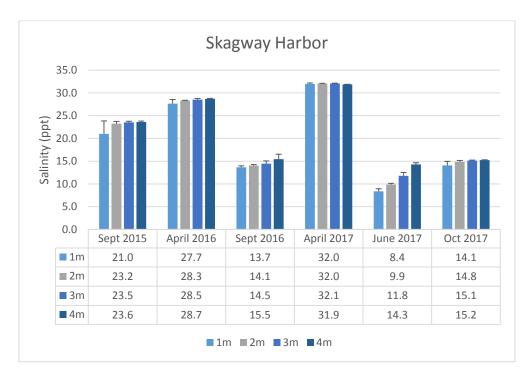


Figure 5. Average salinity at 1 m depth intervals in the Skagway Harbor for each sampling date. Error bars are one standard deviation.

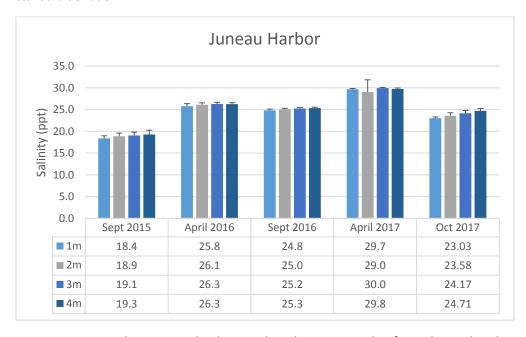


Figure 6. Average salinity at 1 m depth intervals in the Juneau Harbor for each sampling date. Error bars are one standard deviation.

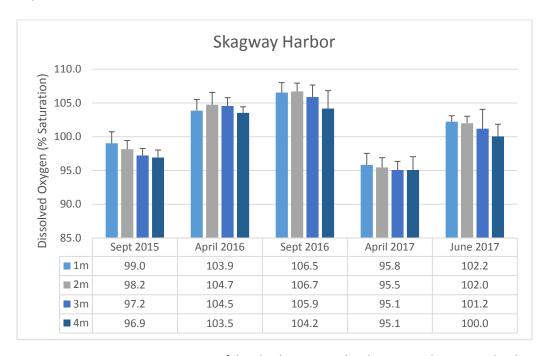


Figure 7. Average percent saturation of dissolved oxygen in the Skagway Harbor at 1 m depth intervals on each sampling date. Error bars are one standard deviation.

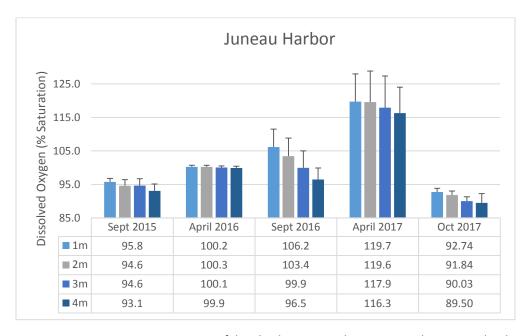


Figure 8. Average percent saturation of dissolved oxygen in the Juneau Harbor at 1 m depth intervals on each sampling date. Error bars are one standard deviation.



Figure 9. Average pH of marine waters in the Skagway harbor on each sampling date and at 1 m depth intervals. Error bars are one standard deviation. pH was not measured in October 2017 due to equipment problems.

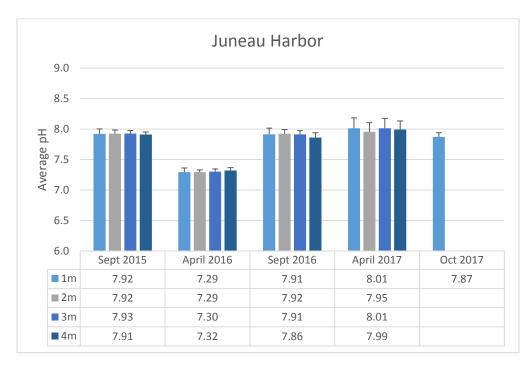


Figure 10. Average pH of marine waters in the Juneau harbor on each sampling date and at 1 m depth intervals. Error bars are one standard deviation. pH was measured at the water surface in October 2017.

#### Ammonia and Metals

#### Ammonia-N

Quality Assurance. Ammonia-N concentrations from samples collected in April of 2016 are not reported due to high laboratory method detection limits (MDL). The MDL for ammonia-N in September of 2015 and April 2016 was 0.04 mg/L. This is below the project quality assurance MDL within the QAPP (0.112 mg/L), but above average ammonia-N concentrations in either harbor. Laboratory and field blanks on these dates that resulted in values below the laboratory MDL could have exceeded the average harbor values, resulting in erroneously high harbor concentrations. In September of 2016, all of the samples collected in both harbors were below the MDL of 0.04 mg/L and average harbor concentrations were calculated using a value of 0.02 mg/L or 0.5 x the MDL.

Harbor Values. Average concentrations of ammonia-N for the Skagway and Juneau Harbors are shown in Figure 11. Average concentrations in the Skagway harbor ranged from 0.012 to 0.045 mg/L, and from 0.007 to 0.030 mg/L in the Juneau Harbor. Average harbor concentrations using all values were 0.025 and 0.022 mg/L for the Skagway and Juneau Harbors, respectively (Table 3) and concentrations were not significantly different between the harbors (t-test, p > 0.05). Concentrations of ammonia-N were similar among sampling locations within each harbor, and there was no indication that ammonia concentrations were higher in one or more location.

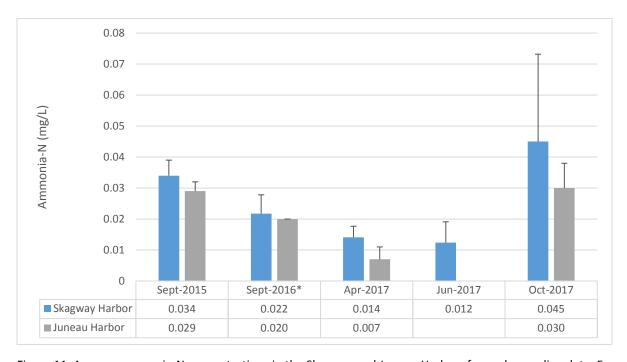


Figure 11. Average ammonia-N concentrations in the Skagway and Juneau Harbors for each sampling date. Error bars are one standard deviation. Average Harbor concentrations for September 2016 were calculated using  $0.5 \times 10^{-5} \times 10^{-5$ 

#### Total and Dissolved Copper (Cu)

Quality Assurance. Results from samples collected in September of 2015 are not reported due to high copper concentrations in laboratory and field blanks. Dissolved Cu concentrations in June of 2017 exceeded total concentrations due to laboratory sample contamination and are not reported. Residual dissolved copper was present in field and field/equipment blanks above MDLs in samples collected in April and September of 2017 at an average concentration of 0.13  $\mu$ g/L in the Skagway harbor and 0.06  $\mu$ g/L in the Juneau Harbor. Residual total copper was present in field and equipment blanks at an average concentration of 0.09 and 0.06  $\mu$ g/L in the Skagway and Juneau Harbors, respectively. Reported copper concentrations in both harbors may exceed true values.

Harbor Values. Acute WQC for total Cu in marine waters is 4.8 μg/L and the chronic criteria is 3.1 μg/L (DEC 2012). Average total and dissolved Cu concentrations in the Skagway and Juneau Harbors is shown in Figures 12 and 13. Average Skagway harbor total copper concentrations ranged from 0.25 to 0.45 μg/L and average dissolved concentrations from 0.16 to 0.38 μg/L. In the Juneau Harbor average total copper concentrations ranged from 0.45 to 0.64 μg/L, and average dissolved concentrations from 0.40 to 0.48 μg/L. Average harbor concentrations of total and dissolved copper including all samples are shown in Table 3. Average concentrations of total and dissolved Cu were significantly higher in the Juneau Harbor than the Skagway Harbor (t-test, p « 0.001).

#### Total and Dissolved Zinc (Zn)

Quality Assurance. Results from samples collected in September of 2015 and April of 2016 are not reported due to high MDLs. Laboratory MDLs for these two dates were 10 and 12.6  $\mu$ g/L, respectively, well above the MDL of 0.08  $\mu$ g/L specified within the QAPP. Most harbor values collected on these dates were below the MDL and calculation of average harbor values using 0.5 x MDL would have resulted in erroneously high concentrations. Dissolved Zn concentrations in April of 2017 exceeded total concentrations due to contamination within the laboratory and also are not reported. Residual total Zn was present in field and equipment blanks at an average concentration of 0.28  $\mu$ g/L. Residual dissolved Zn was present in field and equipment blanks at an average concentration of 0.36 and 0.43  $\mu$ g/L in the Skagway and Juneau Harbors, respectively.

Harbor Values. Average Concentrations of total and dissolved Zn for the Skagway and Juneau Harbors on each sampling date are shown in Figures 14 and 15. The average concentration of total Zn in the Skagway harbor ranged from 0.89 to 1.80 μg/L, and average concentration of dissolved Zn ranged from 0.77 to 1.6 μg/L. Concentrations on all sampling dates were well below acute and chronic WQC of 90.0 and 81.0 μg/L. Average harbor total zinc concentrations were 1.42 and 1.16, and average harbor dissolved zinc concentration were 1.15 and 0.98 μg/L for the Skagway and Juneau Harbors (Table 3). Average concentrations of total Zn were significantly higher in the Skagway Harbor (t-test, p = 0.03); however, average concentrations of dissolved Zn did not differ significantly between harbors.

#### Total and Dissolved Nickel (Ni)

Quality Assurance. Results of sample analyses for Ni from samples collected in September 2015 are not reported or used to calculate average harbor concentrations. The laboratory MDL for total and dissolved Ni for samples collected in September 2015 was 1.0  $\mu$ g/L which exceeded the MDL of 0.034  $\mu$ g/L specified within the QAPP. Average harbor concentrations from subsequent samples were < 0.5  $\mu$ g/L. Therefore, the concentration of Ni in blanks reported to be below the MDL of 1.0  $\mu$ g/L could have exceeded average harbor values. Residual total Ni was present in field and equipment blanks at an

average concentration of 0.032  $\mu$ g/L. Residual dissolved Ni was not present in concentrations above MDLs within field and equipment blanks.

Harbor Values. Average total and dissolved Ni concentrations within the Skagway and Juneau Harbors are shown in Figures 16 and 17. Within the Skagway Harbor average total Ni concentrations ranged from 0.21 to 0.47 μg/L, and average dissolved concentrations from 0.14 to 0.45 μg/L. Within the Juneau Harbor average total Ni concentrations ranged from 0.49 to 0.62 μg/L among sampling dates and dissolved Ni from 0.43 to 0.55 μg/L. Average concentrations of dissolved Ni in both harbors were below acute and chronic WQC or 74 μg/L and 8.2 μg/L, respectively. Total and dissolved concentrations were significantly higher in the Juneau Harbor compared to the Skagway Harbor (t-test, p < 0.001).

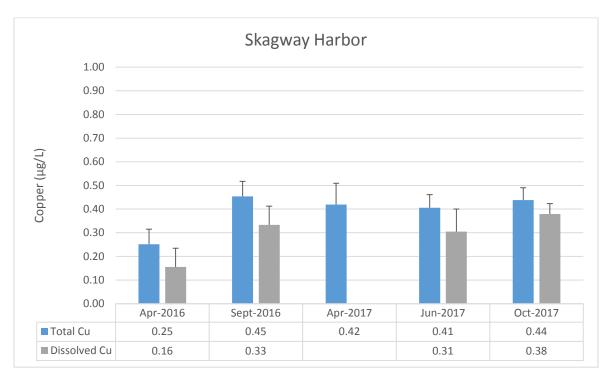


Figure 12. Average total and dissolved Cu concentrations in the Skagway Harbor for all sampling dates. Error bars are one standard deviation.

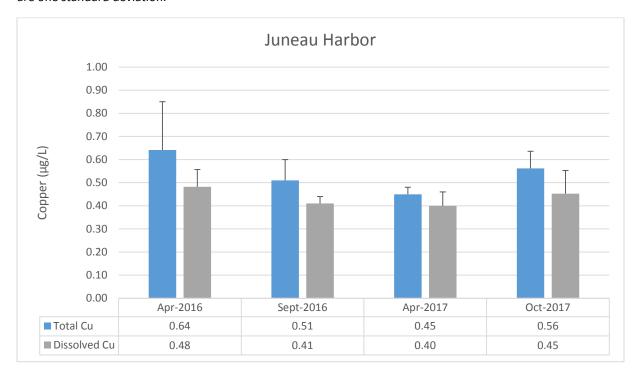


Figure 13. Average total and dissolved Cu concentrations in the Juneau Harbor for all sampling dates. Error bars are one standard deviation.

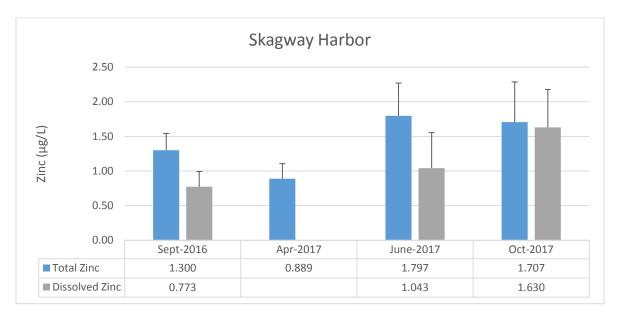


Figure 14. Average concentrations of Zinc within the Skagway harbor on each sampling date. Error bars are one standard deviation.

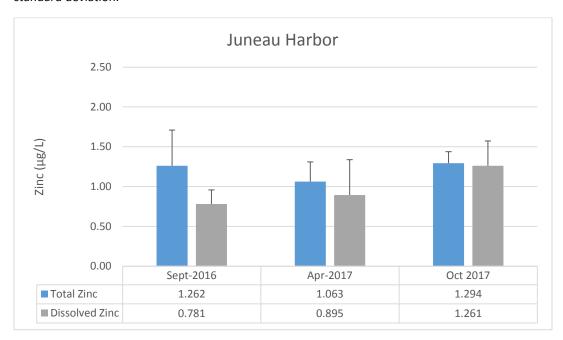


Figure 15. Average concentrations of Zinc within the Juneau harbor on each sampling date. Error bars are one standard deviation.

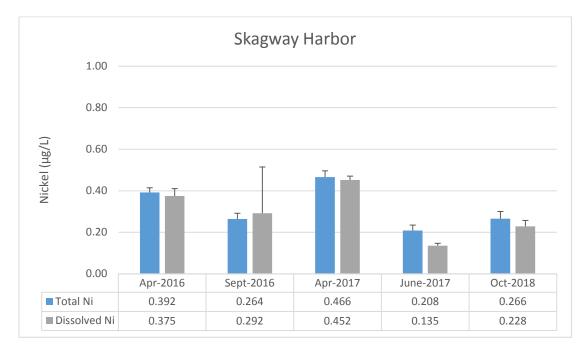


Figure 16. Average total and dissolved Ni concentrations in the Skagway Harbor on each sampling date. Error bars are one standard deviation.

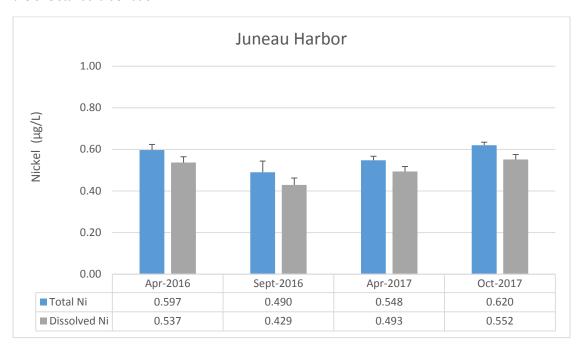


Figure 17. Average total and dissolved Ni concentrations in the Juneau Harbor on each sampling date. Error bars are one standard deviation.

#### Fecal Coliform Bacteria

Total fecal coliform bacteria and *E. coli* abundance in water samples from the Skagway and Juneau Harbors is shown in Table 2. Fecal coliforms were most abundant from samples collected in September 2015, at 76 and 23 cfu/100 ml, for the Skagway and Juneau Harbors, respectively. The abundance of fecal coliforms did not approach these high values on any subsequent sampling date. The number of samples collected within a 30-day period were insufficient to test for WQC exceedances. The most stringent WQC is for marine waters used as a water supply for seafood processing, where 30-day geometric means may not exceed 20 cfu/100 ml and not more than 10% of the samples can exceed 40 cfu/100 ml (18 AAC 70.020(a)(14)(A)(ii)), The geometric means for each harbor, including all samples, were 2.7 cfu/100 ml in the Skagway Harbor and 1.5 cfu/100 ml in the Juneau Harbor.

Table 2. Abundance of fecal coliform and *E. coli* in water samples collected from 3 locations in the Skagway and Juneau Harbors.

	<b>Skagway Harbor</b>			Juneau Harbor	
	Fecal Coliforms	E. coli		Fecal Coliforms	E. coli
	(cfu/100 ml)	(MPN)		(cfu/100 ml)	(MPN)
Sept 2015			Sept 2015		
SK02	1	N/A	JN21	3	3.1
SK23	1	0.5	JN12	8	1.0
SK11	76	N/A	JN02	23	19.7
April 2016			April 2016		
SK08	1	0.5	JN02	1	0.5
SK09	5	0.5	JN13	1	0.5
SK18	1	0.5	JN18	1	0.5
Oct 2016			Oct 2016		
SK20	1	0.5	JN20	1	0.5
SK21	2	2	JN17	1	0.5
SK24	2	1	JN24	1	0.5
April 2017			April 2017		
SK20	1	0.5	JN11	1	0.5
SK21	5	0.5	JN17	1	0.5
SK24	1	0.5	JN20	1	0.5
June 2017			June 2017		
SK24	3	1	N/A	N/A	N/A
SK23	2	0.5	N/A	N/A	N/A
SK16	7	2	N/A	N/A	N/A
Oct 2017			Oct 2017		
SK19	5	0.5	JN03	1	0.5
SK13	7	10	JN11	1	0.5
SK10	7	5	JN24	1	0.5

# Summary

Water quality parameters were variable among sampling dates and between harbors. Water temperatures and pH were lowest in the April and highest in September, whereas, salinity was highest in April and lowest in September. Differences in salinity among sampling dates in the Skagway Harbor may be due to differences in local river discharge (Pullen Creek, Skagway River, Dyea River). There are no large rivers that discharge near the Juneau Harbor and salinity differences among sampling dates may reflect differences in recent precipitation. Since ammonia-N water quality criteria vary with temperature and salinity, more detailed information may be necessary. Salinity and temperature data loggers could be installed to obtain more frequent measures of these parameters.

Average ammonia-N and metals concentrations for the Skagway and Juneau Harbors are shown in Table 3 and results from previous studies are shown in Table 4. Ammonia-N concentrations were slightly low than previously reported. Average harbor total copper and nickel concentrations also were lower than previously reported values, but concentrations of zinc were similar.

Average concentrations of copper and nickel were higher in the Juneau Harbor than in the Skagway Harbor. The average concentrations of ammonia-N and zinc were not significantly different between these two harbors.

Table 3. Average harbor concentrations of ammonia-N and total and dissolved metals with standard error and 95% confidence interval (CI). September 2015 values were not used in calculations of harbor average total and dissolved copper and nickel and September 2015 and April 2016 values were not used to calculate average harbor total and dissolved zinc concentrations due to MDLs above QAPP quality objectives.

Skagway Harbor	Average	Standard Error	95% CI
Ammonia-N (mg/L)	0.025	0.002	0.005
Total Copper (μg/L)*	0.39	0.012	0.025
Dissolved Copper μg/L)*	0.29	0.015	0.031
Total Nickel (μg/L)*	0.33	0.015	0.030
Dissolved Nickel (µg/L)	0.31	0.023	0.047
Total Zinc (μg/L)*	1.42	0.775	0.156
Dissolved Zinc (μg/L)*	1.15	0.095	0.193
Juneau Harbor	Average	Standard Error	95% CI
Juneau Harbor Ammonia-N (mg/L)	Average 0.022	Standard Error 0.001	95% CI 0.003
Ammonia-N (mg/L)	0.022	0.001	0.003
Ammonia-N (mg/L) Total Copper (μg/L)*	0.022 0.54	0.001 0.020	0.003 0.039
Ammonia-N (mg/L) Total Copper (µg/L)* Dissolved Copper µg/L)*	0.022 0.54 0.44	0.001 0.020 0.011	0.003 0.039 0.022
Ammonia-N (mg/L) Total Copper (µg/L)* Dissolved Copper µg/L)* Total Nickel (µg/L)*	0.022 0.54 0.44 0.56	0.001 0.020 0.011 0.009	0.003 0.039 0.022 0.017

<sup>\*</sup> Result estimated and bias high due to blank contamination on some sampling dates.

Table 4. Historic concentrations of metals within Gastineau Chanel and Skagway Harbor (Science Advisory Panel 2009). TR is total recoverable, and D is dissolved.

Date	Location	NH <sub>3</sub> -N (mg/L)	Cu (µg/L)	Ni (μg/L)	Zn (μg/L)
1989	Gastineau Channel	0.025	0.99 (TR)	1.44 (TR)	0.83 (TR)
1990	Gastineau Channel	0.023	0.66 (TR)	0.84 (TR)	1.98 (TR)
1991	Gastineau Channel	0.007	0.59 (TR)	0.71 (TR)	1.64 (TR)
Average	Gastineau Channel	0.018	0.75	1.00	1.43
2006-2010	Hawk Inlet		0.41 (D)		1.17 (D)
2007	Skagway Harbor				37 (D)
2008	Skagway Harbor		< 2.6 (D)		

# Reference

State of Alaska Department of Environmental Conservation. 2008. Alaska Water Quality Criteria Manual for Toxic and other Deleterious Organic and Inorganic Substances, as Amended through December 12, 2008.