



2009 Science Advisory Panel Information Request

Ambient Dissolved Metals and Ammonia Data for Alaska Marine Waters

Requested at 10/21-22/10 Meeting

1. INTRODUCTION

Science Advisory Panel members asked the Alaska Department of Environmental Conservation (ADEC) Cruise Ship Program staff to provide information on the ambient levels of the constituents of concern (ammonia, dissolved copper, dissolved nickel, and dissolved zinc) found in Alaska marine waters, or provide the best available references.

2. METHOD

ADEC staff researched sources suggested by Panel members as well as other potential sources of information for ambient levels of the constituents of concern. A list of sources that were investigated is included below.

3. RESULTS

Ammonia:

A search for ambient ammonia data for Alaska marine waters yielded no recent results. Southeast Alaska EMAP data from 2004 is available for ammonium (NH_4^+) the ionized form of ammonia (NH_3). The chemical equation that drives the relationship between ammonia and ammonium is:



The equation is driven to the left at higher pHs. At a pH of 8.0, the proportion of ammonia is about 10 percent. The activity of aqueous ammonia is also much lower at low temperatures. This means that finding measurable levels of ammonia in the water column in Alaska waters is unlikely.

The average pH from EMAP data from 2004 was equal to 7.93 at an average temperature of 9.3 degrees C and average salinity of 28.4 PSU (practical salinity unit.) The average ammonium concentration from EMAP data was equal to 0.01 mg/L.

Seawater sampling was conducted at nine locations within Gastineau Channel from 1989-1991. Samples were analyzed for Ammonia as N (Echo Bay Alaska, Inc., 1991.)

Year	Ammonia as N (mg/L) - Avg \pm Std Dev
1989	0.025 \pm 0.034 (n=24)
1990	0.023 \pm 0.046 (n=50)
1991	0.007 \pm 0.004 (n=17)
Overall Average	0.021 \pm 0.039 (n=91)

Dissolved Metals:

There is little data available for ambient levels of dissolved metals in Alaska marine waters; however, a few relevant sources were located. In particular, there is a lack of data for dissolved nickel.

Three ocean sites in Hawk Inlet are sampled quarterly to monitor potential water quality effects from the mine (Hecla Greens Creek Mining Company, 2011.) Seawater samples are collected quarterly from the sites on an outgoing tide, with the Chatham Strait sample (Site 106) collected just after low slack water. The two other sites are Station 107, located about mid-way east-west in Hawk Inlet and west of the ship loader facility, and Station 108, located above the 002 diffuser in the mixing zone. Samples at all three locations are taken at a depth of five feet. Dissolved nickel is not monitored at these sites.

Dissolved Metals – Hawk Inlet Water Column Monitoring Results (2006-2010.) N=20 for dissolved copper and N=20 for dissolved zinc at each sampling site.

Site	Dissolved Cu (ug/L) – Avg ± Std Dev	Dissolved Zn (ug/L) – Avg ± Std Dev
106	0.37 ± 0.12	0.97 ± 0.71
107	0.47 ± 0.17	1.31 ± 0.66
108	0.39 ± 0.14	1.24 ± 0.66
Overall	0.41 ± 0.15 (n=60)	1.17 ± 0.69 (n=60)

In a 2007 study of Skagway Harbor surface waters, dissolved metal samples were collected as composite samples from different depths (ADEC and EPA Region 10, 2008.) These samples were not filtered in the field. Dissolved copper and dissolved nickel surface water data were deemed “suspect” due to being in excess of total metal concentrations, and will not be used here. Dissolved zinc levels in Skagway Harbor surface water samples were similar to or below the reference site.

Site	Dissolved Zn (µg/L)
Reference (Taiya Inlet, north of Skagway Harbor)	48
SH-5 – middle of Harbor	31
SH-8 – middle of Harbor	15
SH-10 – side channel of Harbor	55
SH-11 – middle of Harbor	12
SH-12 – middle of Harbor	51
SH-14 – side channel of Harbor	42
SH-15 – mouth of Harbor	63
SH-17 – side channel of Harbor	19
Average	37

In a 2008 study of metals in Skagway Harbor, dissolved copper samples were collected from the surface (n=12,) middle (n=12,) and bottom (n=12) of the harbor (ADEC and EPA Region 10, 2009.) These samples were filtered in the field. Dissolved nickel and dissolved zinc were not measured. Concentrations of dissolved copper were below the detection limit of 2.6 µg/L for all samples with the exception of one of the reference sites, which had a dissolved copper concentration of 5.3 µg/L in the surface water sample. This value was still below the reporting limit.

*Dissolved Metals **Outside** of Alaska Marine Waters – Puget Sound, Washington*

Possession Sound Sampling Site (1999-2000.) All dissolved zinc values were below the Reporting Detection Limit, and the majority were qualified as having zinc detected in the laboratory quality control method blank. Samples from the study that were not analyzed within the 6 month holding time were not considered in this report.

	1999	2000	Overall
Dissolved Cu ($\mu\text{g/L}$) – Avg \pm Std Dev	0.34 \pm 0.05 (n=27)	0.36 \pm 0.04 (n=12)	0.34 \pm 0.05 (n=39)
Dissolved Ni ($\mu\text{g/L}$) – Avg \pm Std Dev	0.42 \pm 0.04 (n=27)	0.46 \pm 0.06 (n=15)	0.44 \pm 0.05 (n=42)
Dissolved Zn ($\mu\text{g/L}$) – Avg \pm Std Dev	0.54 \pm 0.09 (n=27)	0.81 \pm 0.23 (n=15)	0.63 \pm 0.20 (n=42)

***Total Recoverable Metals** in Alaska Marine Waters*

Seawater sampling was conducted at nine locations within Gastineau Channel from 1989-1991. Samples were analyzed for total recoverable (TR) metals (Echo Bay Alaska, Inc., 1991.)

Year	TR Cu ($\mu\text{g/L}$) - Avg \pm Std Dev	TR Ni ($\mu\text{g/L}$) - Avg \pm Std Dev	TR Zn ($\mu\text{g/L}$) - Avg \pm Std Dev
1989	0.99 \pm 0.52 (n=23)	1.44 \pm 0.61 (n=23)	0.83 \pm 0.69 (n=23)
1990	0.66 \pm 0.13 (n=46)	0.84 \pm 0.30 (n=46)	1.98 \pm 1.45 (n=45)
1991	0.59 \pm 0.13 (n=17)	0.71 \pm 0.12 (n=17)	1.64 \pm 0.69 (n=17)
Overall Average	0.73 \pm 0.33 (n=86)	0.97 \pm 0.48 (n=86)	1.60 \pm 1.25 (n=85)

4. SOURCES RESEARCHEDSources referenced above:

ADEC and EPA Region 10 (2008.) Evaluation of Skagway Harbor and Pullen Creek Sediments and Surface Waters. Prepared by Tetra Tech, Inc.

ADEC and EPA Region 10 (2009.) Evaluation of Metals and Petroleum Derivatives in Skagway Harbor and Pullen Creek Sediments and Surface Waters. Prepared by Tetra Tech, Inc.

Echo Bay Alaska, Inc. (1991.) Seawater Monitoring Data. AJ Mine Project Seawater Monitoring Program.

Hecla Greens Creek Mining Company (2011.) Hawk Inlet Monitoring Program 2010 Annual Report.

Metals data from Puget Sound, Washington (1999-2000) provided by Lincoln Loehr.

Southeast Alaska Environmental Monitoring and Assessment Program EMAP (2004.)

Sources that did not yield data:

Draft report entitled “CONTAMINANTS ASSESSMENT OF INTERTIDAL RESOURCES IN SOUTHEAST ALASKA NATIONAL PARKS” Technical Report NPS/SEAN/NRTR (2011.)

This study did not include any water column sampling; only sediment and mussel tissues were sampled. Metals analyzed were: Arsenic, Cadmium, Mercury, Tributyltin.

Gastineau Channel Metals Study Report (1996.) This study did not involve water column sampling; only sediment and biota were sampled.

The USEPA Mussel Watch Program does not include water column sampling, nor the specific metals of interest. Only sediments and tissues were sampled.

Skagway USEPA Cruise Ship (dye plume) Study. No water column sampling for contaminants was performed during this study.

No data has been entered into the Ambient Water Quality Monitoring System (AWQMS) as of the date of this report.

A search of the EPA STORET database for “ammonia in ocean waters” produced no results.

Douglas Harbor Dredging project evaluations included data for mercury (Hg) only.