

TECHNICAL REPORT



by:

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## ABSTRACT

Title: Metal concentrations in sediments and selected biota from Gastineau Channel, Juneau, Alaska

Abstract: The city of Juneau is located on the shoreline of Gastineau Channel and a commercial fuel dock, boat harbors, cruise ships, and recreational boat traffic contribute to contaminant input. The channel also has a deposit area for incinerated sewage sludge on a former municipal landfill site. There are currently three permitted outfalls in Gastineau Channel and numerous influxes of urban nonpoint source runoff. Tailings and waste rock from hardrock gold mines were deposited into Gastineau Channel from 1880 to 1944 and formed beaches along parts of both Juneau and Douglas Island. Many marine species including, migratory salmonids, waterfowl, and shorebirds use the channel, and bald eagles are year-round residents. The channel is a major recreational crabbing area.

This study, conducted in 1991, found potentially toxic concentrations of metals in sediment and some resident biota in the channel. Sediment samples were collected from 20 locations across and down the channel for an eight-km distance. Fish and shrimp were collected by mid-channel trawl. Blue mussels and cockles were collected at a low tide from six locations in an area composed of old tailings. Freshwater fish were taken from a small stream adjacent to the former Treadwell Mine site on Douglas Island. Metal concentrations in the channel were plotted as 3-D spike plots and reveal strong distribution patterns for arsenic, cadmium, copper, and zinc with the lowest metal sediment concentrations found near the mouth of the channel. The combination of tailings and present urban pollution has contributed to the current situation based on examination of the spike plots.

Concentrations of arsenic, copper, lead, and zinc in sediments were higher than concentrations detected in sediments from many locations in Southeast Alaska where similar measurements have been made. Concentrations of arsenic, copper, mercury, and lead in more than 50 percent of Gastineau Channel sediment samples exceeded Effects Range-Low (ER-L) concentrations for sediments as reported by NOAA's National Status and Trends Program. No Effects Range-Median (ER-M) values were exceeded. Tissue concentrations for whole fish indicate that lead and zinc are elevated compared to fish from a baseline site, Bostwick Inlet on Gravina Island, near Ketchikan, Alaska. Molluscs' metal concentrations were similar to concentrations reported elsewhere in Southeast Alaska indicating that metal contamination of sediments is not bioaccumulating in molluscs. Proposals for adding metals to the channel through permitted effluents should be carefully considered with respect to these data.

Key words: marine sediments, metals, fish, molluscs, mine tailings

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## INTRODUCTION

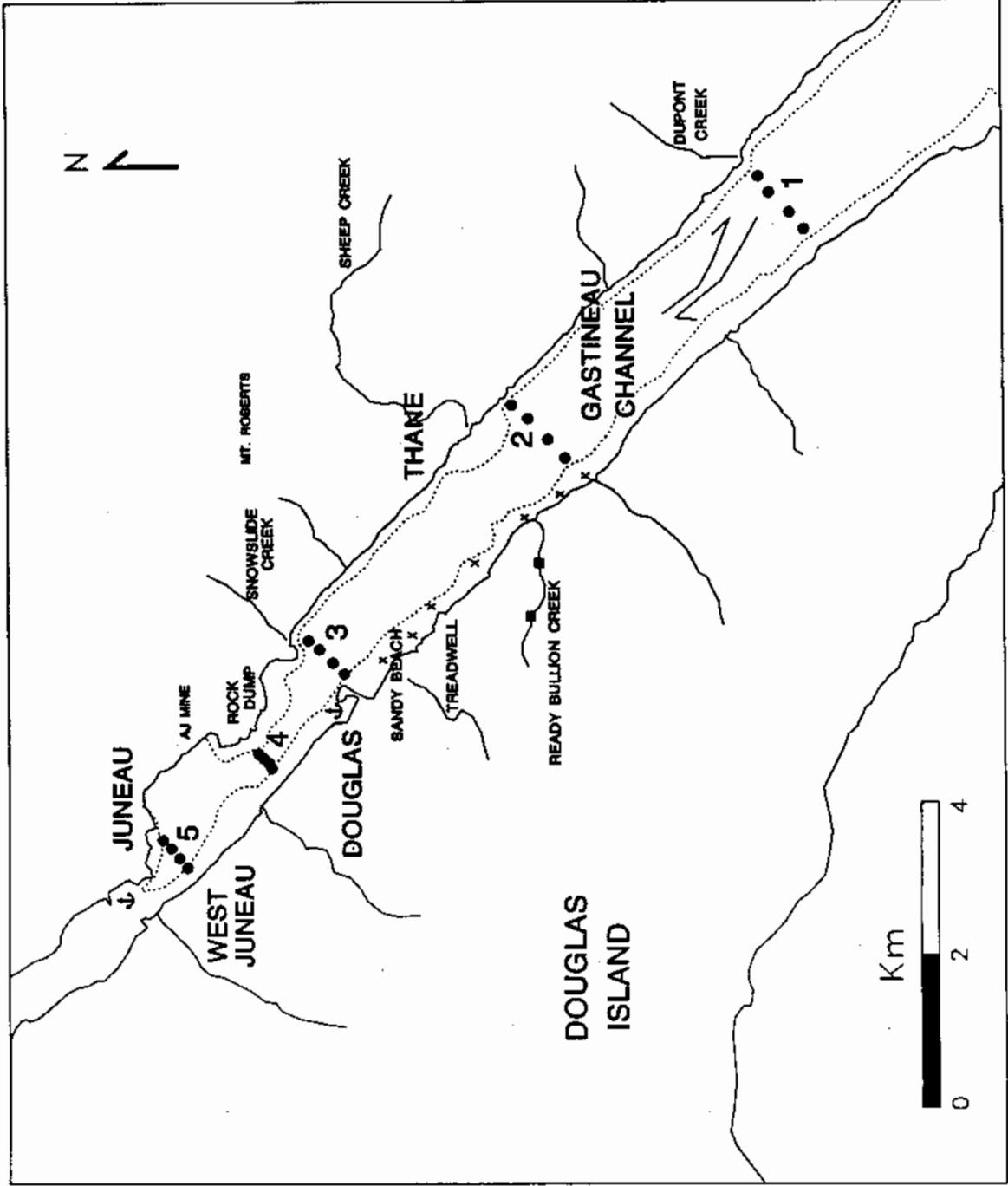
Gastineau Channel is approximately 20 km long and varies in width from 0.6 to 1.3 km. The channel depth at its center is from 35 to 40 m. The shoreline is generally steep-sided and the coastal mountains rise 600 to 1100 m above sea level from the channel at an average gradient of 50 percent. Rocky outcrops and localized deltas are located at the mouths of numerous creeks that empty into the channel. Freshwater inflow is minor compared to tidal volume. Tides follow the long axis of the channel and maximum tidal amplitude is 7.6 m.

The channel is a major recreational crabbing area for both tanner (Chionoecetes bairdi) and dungeness crab (Cancer magister) and supports pink (Oncorhynchus gorbuscha), chum (O.keta) and silver salmon (O.kisutch) roadside fisheries. Protected waters of the channel are the wintering area for numerous species of waterfowl including, scaup (Aythya affinis), scoters (Melanitta nigra, M.fusca, M.perspicillata), goldeneyes (Bucephala islandica, B.clangula), bufflehead (B.albeola) and harlequin ducks (Histrionicus histrionicus). Many other species of waterfowl and shorebirds move through the channel during spring and fall migration and many other marine species are present during various times of the year. Bald eagles (Haliaeetus leucocephalus) are very common residents and their nests are found along Gastineau Channel. River otter (Lutra canadensis) and mink (Mustela vison) feed along the shoreline.

Juneau's downtown commercial and residential area is located approximately halfway up the channel; other populated areas are Douglas and West Juneau (Figure 1). The marine fuel dock is located just south of downtown Juneau. Fuel tanks and barge docking facilities are located at the Rock Dump. There are three boat harbors on the channel, Douglas, Harris, and Aurora, which have recreational and commercial boats. A downtown dock is used for seasonal cruise ships and offshore anchoring is common. Other docking facilities are located in the immediate area.

Three major hardrock mine areas have existed in Juneau: the Treadwell Complex, located on Douglas Island; the Alaska Gastineau Mine, located at Thane, about six km south of downtown Juneau; and the A-J Mine, located within Mt. Roberts. The Juneau waterfront is built on rock fill from the former A-J Mine and the Douglas waterfront is adjacent to old tailings deposits. The Treadwell Complex tailings form broad, exposed flats during low tide along the Douglas Island shore of Gastineau Channel south of Douglas. One of Juneau's commercial areas is situated on the A-J Rock Dump. The Rock Dump is also the site of a former landfill and deposit area for sewage sludge (E. Emswiler, ADEC, pers. comm.). The area is presently a repository for incinerated sewage sludge from the municipal sewer system. There are three outfalls along Gastineau Channel permitted under the National Pollution Discharge Elimination System administered by the U.S. EPA.

Figure 1. Gastineau Channel from Juneau, Alaska south to the mouth of the channel, showing sediment and biota sample locations.



LEGEND

- Sediment transect stations
- x Mollusc samples
- Freshwater fish
- ↗ Trawl path
- ↓ Boat harbor
- 10 fm contour
- 1 Numbers denote transect code  
Station D is SW  
Station J is NE  
(see Appendix A)

Tailings and waste rock from the mines were dumped either by barge into Gastineau Channel or by train and conveyor belt to the waterfront. During the 1930s, there was concern that the dumping of mine tailings was impairing navigation in the channel and tailings were then barged and dumped into deeper waters in the center of the channel (Stone and Stone 1980). The Treadwell Complex tailings created a 1200 m beach along Douglas Island (Sandy Beach). The Alaska Gastineau Mine sent 12,000 tons of tailings per day to the beach near Thane. A total of 90 million tons of ore and rock were moved from the A-J Mine from 1893 to 1944. Tailings were deposited without compaction and as a result often have a low density.

The tailings from the A-J mine range in size from coarse gravel to silt and contain elevated amounts of barium, lead, zinc, cadmium, and arsenic (Ecology and Environment 1990). A 1987 study of A-J tailings found lead ranging from 69 to 226 ppm and zinc concentrations at 186 to 588 ppm (Golder Associates 1987). Rock dump (Fig. 1) sediments have salt water percolation. Groundwater from wells located in the tailings had relatively high salinity and was most likely composed of estuary and fresh water (Golder Associates 1987). Treadwell Complex tailings had significantly elevated concentrations of arsenic, cadmium, copper, iron, lead, mercury, and selenium, as reported by Ecology and Environment (1991). Arsenic and lead were found to be elevated in tailings from the Thane area (Ecology and Environment 1988).

In 1989, an application was filed to reopen the A-J Mine and resume gold mining operations. The company's proposal was to pump tailings to an impoundment in a nearby mountain valley and construct an outfall pipe into Gastineau Channel for excess tailings water (Bureau of Land Management 1992). These plans are currently being revised to address the option of submarine tailings disposal approximately nine miles south of Juneau.

#### **STUDY OBJECTIVES**

Objectives of this study were to (1) determine the concentration of potentially toxic metals in sediment from Gastineau Channel; (2) to determine concentrations of metals in a sample of resident biota of the channel; (3) to compare metal concentrations with data from other locations in Southeast Alaska and National Oceanic and Atmospheric Administration (NOAA) National Status and Trends data (Long and Morgan 1990, Long et al. 1995); and (4) determine if concentrations present a risk to resident biota.

#### **MATERIALS AND METHODS**

##### *Sediment Samples*

Sediment samples were collected on April 23-24, 1991, along five transects across Gastineau Channel from downtown Juneau to 12 km south of Juneau

(Fig.1). Four stations were established per transect. Stations for each transect were located near the 10 m contour on both sides of the channel and halfway to mid-channel from each shore (Appendix A). Sample station locations and nearby Gastineau Channel environs were obtained by digitizing x-y coordinates from the marked locations on a 1:40,000 U.S. Department of Commerce (NOAA) 1984 Mercator Projection of Gastineau Channel (Fig. 1).

Samples were collected using a 0.1 m<sup>3</sup> Smith McIntyre dredge. Three grabs were taken at each station. A station sample was made as a composite of the three grabs, mixed with a stainless steel spoon. Each composite was mixed in a stainless steel pan that was rinsed between stations with ambient seawater. Between each station, all traces of sediment were rinsed from the dredge and spoon using ambient seawater. Each composite station sample was split to form three replicate subsamples that were placed in precleaned jars (I-Chem<sup>®</sup> 200 series, 125 ml) and refrigerated.

#### Biota Collection

Fish and shrimp were collected by a mid-channel trawl on April 25, 1991, (Fig.1). Blue mussels (Mytilus trossulus) and cockles (Clinocardium nuttallii) were collected by hand at low tide from six locations in the vicinity of the former Treadwell Complex on Douglas Island on June 28, 1991. Freshwater fish, Dolly Varden (Salvelinus malma), and sculpins (family Cottidae), were collected from June 21-24, 1991, using minnow traps in Ready Bullion Creek which flows through the former Treadwell mine site. Fish samples were identified to species (except for sculpins and shrimp), weighed, measured, and wrapped in foil before freezing. (See Appendix B for fish measurements and percent moisture - laboratory determined). Mussels and cockles were depurated for 12 hours in seawater; tissues were removed from shells using precleaned stainless steel knives and put into precleaned I-Chem<sup>®</sup> jars and frozen. All but three marine fish samples were composites of three or more individuals of the same species or genus. Two of the three freshwater fish samples were composites of small sculpins; the third sample was an individual Dolly Varden. Gastineau Channel fish, shrimp, and mollusc tissue metal concentrations were compared to previously collected biota samples from other locations.

Whole fish were analyzed in this study to highlight the investigation on uptake of metals through the food chain rather than potential effects on human health. Marine fish sampled were primarily bottom feeders - sole, flounder, and sculpin. Shrimp are also primarily bottom feeders. Migratory species of fish such as salmon were avoided in this study because they are not year-long channel residents.

#### Laboratory Analysis

All samples were sent by Federal Express overnight service to Research

Triangle Institute (RTI), North Carolina, where they were homogenized and portions were freeze-dried for determination of moisture content and then digested with nitric acid in a CEM microwave oven. Graphite Furnace Atomic Absorption metal concentration measurements were made using a Perkin-Elmer Zeeman 3030 atomic absorption spectrophotometer with an HGA-600 graphite furnace and an AS-60 autosampler. Inductively coupled plasma emission spectroscopy (ICP) measurements were made using a Leeman Labs Plasma Spec I sequential spectrometer. Metal concentrations were expressed in parts per million (ppm) dry weight.

#### *Quality Assurance/Quality Control*

Methods for sediment and biota collection generally followed protocols described in the U.S. Fish and Wildlife Service Contaminants Handbook (1985). The Quality Assurance (QA) program for residue data was conducted at Patuxent Analytical Control Facility (PACF) and reviewed Standard Reference Materials (SRM's), duplicates, spike recoveries, and procedural blanks to determine if laboratory data were acceptable. There were five laboratory duplicates per analyte, four of sediment and one of a tissue sample. There were five procedural blanks. Sources of SRM's for this study included the National Institute of Standards and Technology and the National Research Council of Canada. Acceptable accuracy for percent recovery of metals in spiked samples and SRM's by Atomic Absorption was 85 to 115 percent, and by ICP measurements it was 80 to 120 percent (U.S. Fish and Wildlife Service Criteria, Moore 1990). The PACF QA officer reviewed these data to ensure they met U.S. Fish and Wildlife Service standards.

The acidic digestions of sediments performed by RTI release that portion of the total metal content analyte available for release in an acidic environment, (that which is biologically available). Tissue sample digestions were complete, releasing all metals in this matrix.

Detection limits for different matrices varied by element (Table 1).

Table 1. Maximum detection limits for matrices and elements tested from Gastineau Channel.<sup>1</sup>

|                                     | <u>Metal Concentrations (ppm dry weight)</u> |           |           |           |           |           |           |
|-------------------------------------|--|-----------|-----------|-----------|-----------|-----------|-----------|
|                                     | <u>As</u>                                    | <u>Cd</u> | <u>Cu</u> | <u>Hg</u> | <u>Pb</u> | <u>Se</u> | <u>Zn</u> |
| Sediment,<br>marine fish,<br>shrimp | 0.49   | 0.04      | 4.99      | 0.09      | 4.99      | 0.49      | 4.99      |
| Molluscs,<br>freshwater<br>fish     | 0.4  | 0.05      | 2.0       | 0.2       | 0.2       | 0.3       | 3.0       |

<sup>1</sup> Detection limits were slightly lower for some samples depending on sample volume.

#### *Statistical Analysis*

The average of the three replicate measurements for each composite sediment sample (the mean,  $\bar{x}$ ) was reported for each station. Metal concentrations were plotted as 3-D spike plots using SYGRAPH (Wilkinson 1990). Variation among the replicates (i.e., standard deviation [SD] and coefficient of variation [CV=SD/mean]) was calculated to estimate absolute and relative dispersion of the measurements. The variation measured is due to heterogeneity of the composite sample, processing effects, and instrumental (reading and calibration) errors.

Standard errors (SE) of the mean sediment values reported for each station were calculated  $SE(\bar{x}) = SD/\sqrt{n}$ .  $CV(\bar{x})$  was calculated as  $SE(\bar{x})/(\bar{x})$ . The  $CV(\bar{x})$ 's for each station were plotted against their respective means (by element) to explore relationships between these estimates. Also, the distributions of the calculated CV's were illustrated with histograms.

Equal and unequal variance t-tests were conducted to compare the Juneau shoreline sediment samples with the Douglas shoreline sediment samples for each analyte using PC SAS (SAS Inst. Inc. 1985) after logarithmic transformations were applied to normalize the data.

Station J1, the Dupont station, was considered background because it was the furthest station from potential contaminant sources. For the purposes of this study, metal concentrations were considered elevated if they were two times greater than the concentration found at the Dupont station (J1). This criterion was also used to define elevated metal residues in biota. The selection of at least twice background concentrations is a standard value to represent elevated levels and has been used in other local investigations (Ecology and Environment 1988,1990).

## RESULTS

### Sediment Analysis

Of the 60 sediment samples collected (20 stations x 3 subsamples per station), all but one (which was predominately sand), were analyzed. The measurements (Appendix C and D) illustrate a wide range of values by element (Tables 2 and 3).

The range of estimated station values (expressed as the ratio maximum/minimum) was 2.5 for selenium, 3.1 for zinc, 3.4 for copper, 3.8 for mercury, 4.3 for lead, 7.6 for arsenic, and 34 for cadmium (Table 2). The mean and median of the estimated concentrations by station are similar (within 5 percent relative to the mean) for copper, lead, selenium, and zinc, and more diverse for mercury (9%), arsenic (12%), and cadmium (34%).

Measurement error was very low for most samples (Appendix F). Plots of the  $CV(\bar{x})$ 's against their respective means (Fig. 2) shows no tendency of the CV's to depend on the estimated mean (copper, selenium), a tendency for the CV to increase with increasing concentrations (mercury), and possible tendencies for CV's to decrease with increasing concentration (cadmium and perhaps zinc).

The magnitude of three CV's are relatively high, indicating the presence of unusually diverse data values for a station (Figure 2). Values for arsenic at transect 3, station J ( $\bar{x}=47.5$ ,  $CV(\bar{x})=40.3$ ) were 13.1, 50.1 and 79.2, with three diverse values. Values for cadmium at transect 1, station J ( $\bar{x}=0.264$ ,  $CV(\bar{x})=67.0$ ) were 0.616, 0.092 and 0.084, with one relatively high value. Also, values for lead at transect 3, station J ( $\bar{x}=71.3$ ,  $CV(\bar{x})=53.9$ ) were 35.8, 30.1 and 148, with one relatively high value. These few "unusual" values most likely arise due to high heterogeneity of the metals in these samples; however contamination of a subsample, although unlikely, is a possibility that one must always consider.

The lowest mean concentration of each metal was found in the most southern (#1) transect sampled in Gastineau Channel (Table 3, Figures 3-9). The highest mean concentration of each metal was found in one of the most northern three (#5, #4, or #3) transects sampled, and except for lead, occurred in the most northeastern (J and X, Juneau-side) stations. Strong spatial dependencies, or patterns, in the measured concentrations are apparent in the plots, especially for the elements with the largest range of measured values. For example, concentrations of arsenic and cadmium are highest at the northeast stations (J and X) on transect 3, and decline progressively at more distant stations. Comparing concentrations mapped on the spike plots for each of the five transects revealed the transect closest to the mouth of the channel had the lower concentrations for arsenic, copper, lead, and zinc (Figs. 3,5,7,9).

The highest concentrations of arsenic, cadmium, and zinc were found at the Snowslide Creek station (J3). Copper concentrations were highest at the Sandy Beach area station (D3). The highest lead concentrations were at a mid-channel location and the sample point closest to the Juneau waterfront (J5). Mercury concentrations were also highest at the Juneau waterfront

station and near the mouth of the channel.

Metal concentrations in sediments on transects along the Juneau shore (n=5) were not significantly different (p=.05) from those along the Douglas shore (n=5). (Table 4).

Gastineau Channel metal concentrations range from similar to high relative to other mineralized locations in Alaska (Table 5). Gastineau Channel sediments' lead concentrations at 13 stations were similar to those reported from Klag Bay, an area with old tailings from a gold and silver mine (Robinson-Wilson, unpub. data). Zinc concentrations from Gastineau Channel were higher than those in Klag Bay and were one-half of those reported in sediments from Lutak Inlet (Robinson-Wilson and Malinkey, unpub. data). Skagway harbor sediments have extremely high concentrations of copper, lead, and zinc that exceed all other sediment data for Southeast Alaska (Table 5), and are primarily from input of ore dust into the harbor.

Table 2. Summary statistics for concentrations (ppm, dry weight) of arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb), selenium (Se), and zinc (Zn) in Gastineau Channel sediment samples.

-----  
 All 53 analysis: (20 stations x 3 subsamples per all stations but #4N)

|     | As   | Cd    | Cu   | Hg    | Pb   | Se    | Zn   |
|-----|------|-------|------|-------|------|-------|------|
| Min | 5.84 | 0.062 | 19.4 | 0.098 | 14.1 | 0.483 | 53.1 |
| Max | 79.2 | 3.96  | 103. | 0.546 | 148. | 1.38  | 242. |

20 Sampling stations (averages across replicates)

|         | As   | Cd    | Cu   | Hg    | Pb   | Se    | Zn   |
|---------|------|-------|------|-------|------|-------|------|
| Min     | 6.69 | 0.089 | 21.8 | 0.098 | 19.0 | 0.524 | 60.9 |
| Max     | 51.0 | 3.05  | 74.4 | 0.376 | 81.7 | 1.31  | 191. |
| Max/Min | 7.62 | 34.3  | 3.41 | 3.84  | 4.30 | 2.50  | 3.14 |
| Mean    | 22.1 | 0.604 | 51.8 | 0.222 | 54.5 | 0.946 | 124. |
| median  | 19.4 | 0.397 | 51.3 | 0.202 | 57.2 | 0.941 | 122. |

Table 3. Concentrations (ppm, dry weight) of arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb), selenium (Se), and zinc (Zn) in Gastineau Channel sediment samples by transect (Tran) and station.

| Element | Tran <sup>a</sup> | Station <sup>b</sup> |       |       |       |
|---------|-------------------|----------------------|-------|-------|-------|
|         |                   | D                    | N     | X     | J     |
| As      | 5                 | 12.9                 | 12.9  | 23.9  | 25.9  |
|         | 4                 | 17.8                 | 27.7  | 25.3  | 35.4  |
|         | 3                 | 19.8                 | 29.9  | 51.0  | 47.5  |
|         | 2                 | 17.2                 | 19.7  | 19.1  | 18.3  |
|         | 1                 | 9.28                 | 12.5  | 9.72  | 6.69  |
| Cd      | 5                 | 0.316                | 0.362 | 0.509 | 0.544 |
|         | 4                 | 0.501                | 0.913 | 0.676 | 0.960 |
|         | 3                 | 0.433                | 0.803 | 1.31  | 3.05  |
|         | 2                 | 0.349                | 0.230 | 0.247 | 0.267 |
|         | 1                 | 0.089                | 0.160 | 0.090 | 0.264 |
| Cu      | 5                 | 65.9                 | 45.1  | 72.2  | 74.4  |
|         | 4                 | 49.9                 | 53.6  | 48.1  | 49.3  |
|         | 3                 | 70.4                 | 70.2  | 58.9  | 52.6  |
|         | 2                 | 48.8                 | 58.3  | 54.5  | 48.5  |
|         | 1                 | 25.7                 | 41.2  | 26.1  | 21.8  |
| Hg      | 5                 | 0.122                | 0.182 | 0.249 | 0.376 |
|         | 4                 | 0.166                | 0.117 | 0.317 | 0.109 |
|         | 3                 | 0.326                | 0.267 | 0.143 | 0.099 |
|         | 2                 | 0.347                | 0.346 | 0.300 | 0.160 |
|         | 1                 | 0.221                | 0.355 | 0.137 | 0.098 |
| Pb      | 5                 | 37.4                 | 43.6  | 71.3  | 80.5  |
|         | 4                 | 52.7                 | 70.5  | 53.1  | 70.5  |
|         | 3                 | 58.1                 | 81.7  | 66.0  | 71.3  |
|         | 2                 | 62.2                 | 60.5  | 56.2  | 37.0  |
|         | 1                 | 30.9                 | 43.0  | 25.3  | 19.0  |
| Se      | 5                 | 0.613                | 0.85  | 1.31  | 1.16  |
|         | 4                 | 0.923                | 0.935 | 0.870 | 0.880 |
|         | 3                 | 1.06                 | 1.19  | 1.22  | 0.78  |
|         | 2                 | 0.947                | 0.99  | 1.04  | 1.13  |
|         | 1                 | 0.524                | 0.760 | 0.693 | 1.04  |
| Zn      | 5                 | 98.7                 | 94.6  | 151.  | 156.  |
|         | 4                 | 115.                 | 136.  | 124.  | 143.  |
|         | 3                 | 120.                 | 165.  | 181.  | 191.  |
|         | 2                 | 109.                 | 127.  | 135.  | 109.  |
|         | 1                 | 73.9                 | 108.  | 75.5  | 60.9  |

<sup>a</sup> Transect 5 is most northern, transect 1 is most southern.

<sup>b</sup> Station D is most western, station J is most eastern.

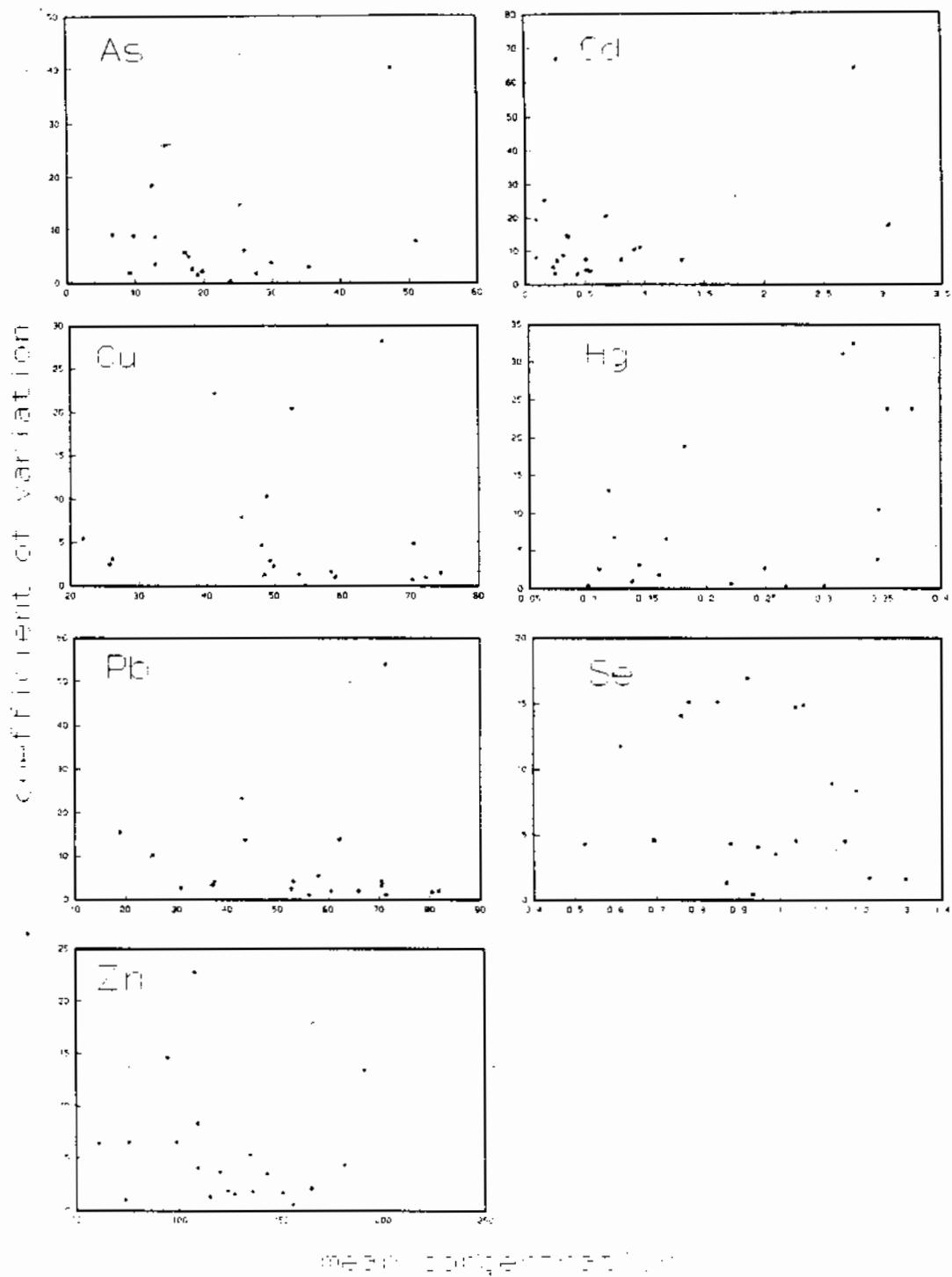


Figure 2. Coefficients of variation for the estimated mean concentrations of metals in Gastineau Channel surface sediments at each station (y axis) versus the estimated mean concentration (x axis), by element.



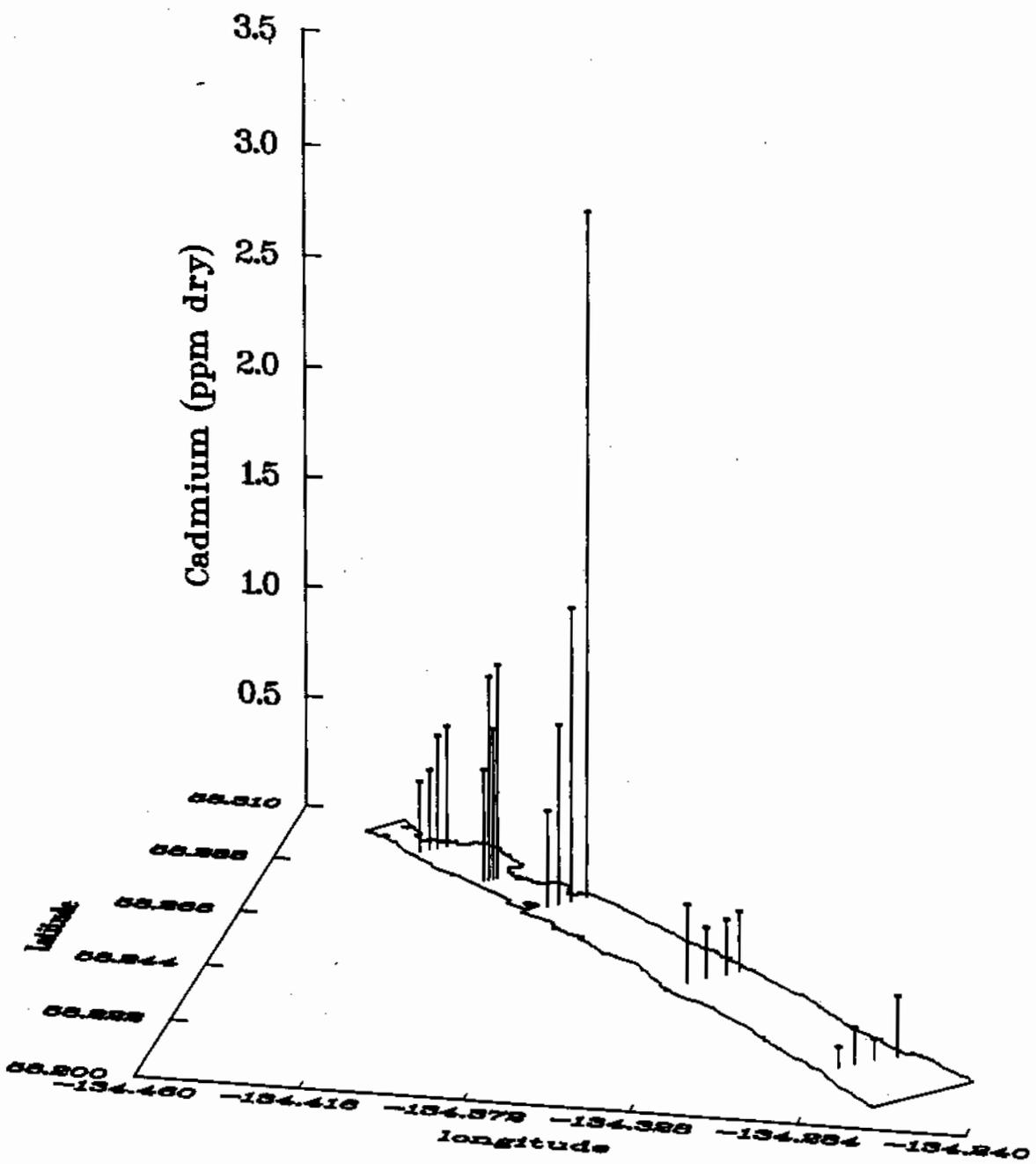


Figure 4. Concentrations of cadmium (ppm dry weight) in Gastineau Channel surface sediment samples plotted by sampling location.

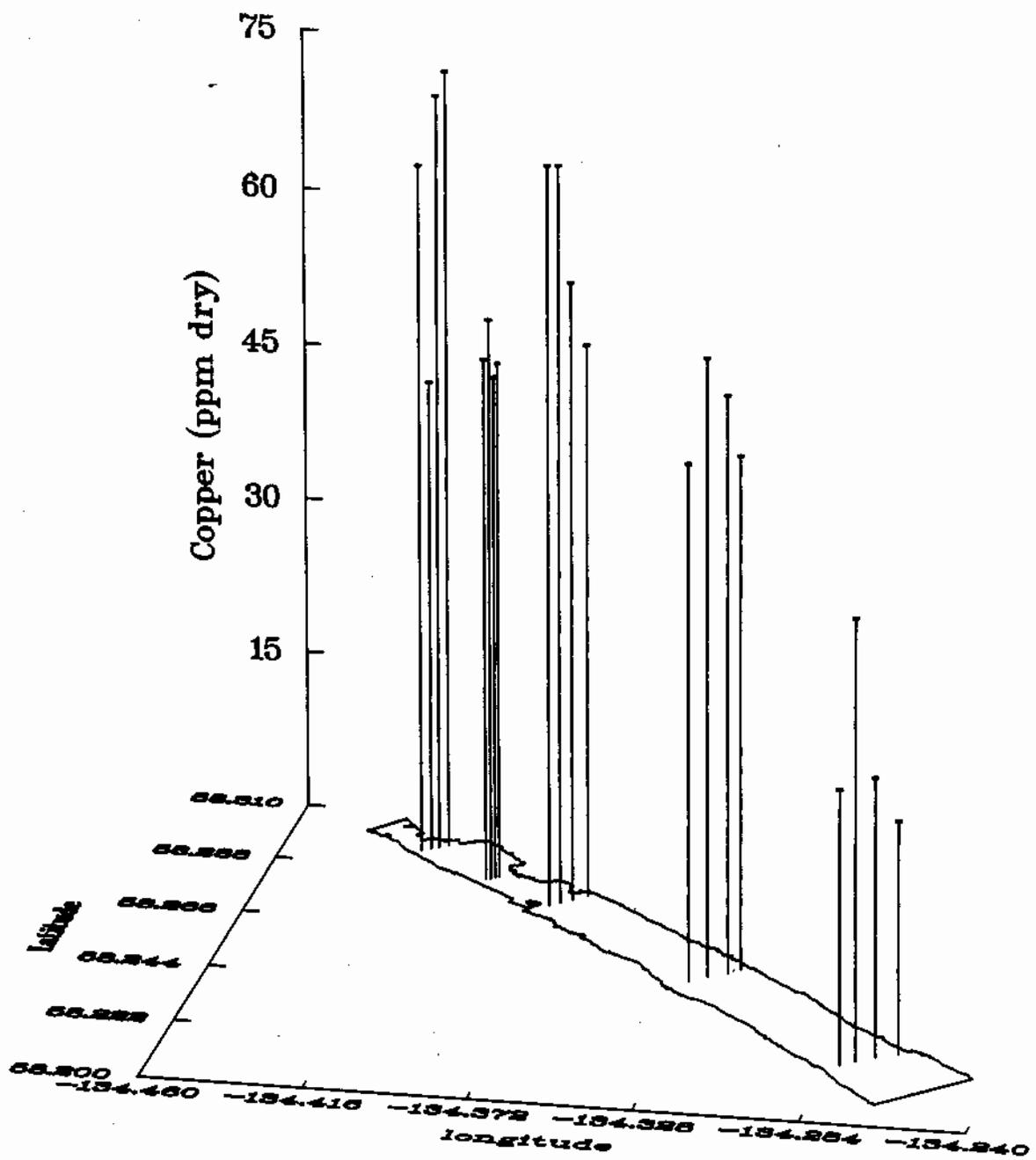


Figure 5. Concentrations of copper (ppm dry weight) in Gastineau Channel surface sediment samples plotted by sampling location.

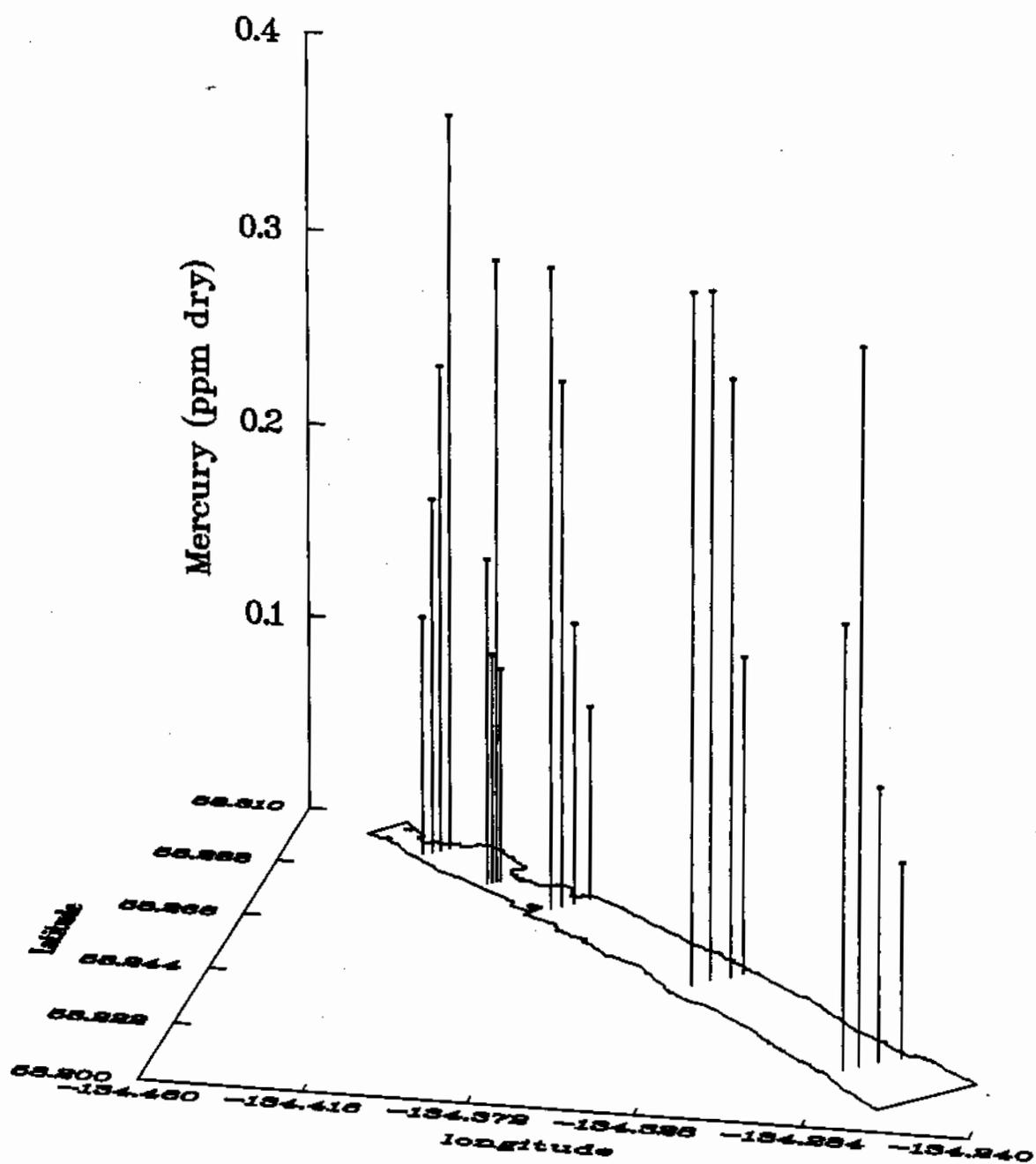


Figure 6. Concentrations of mercury (ppm dry weight) in Gastineau Channel surface sediment samples plotted by sampling location.

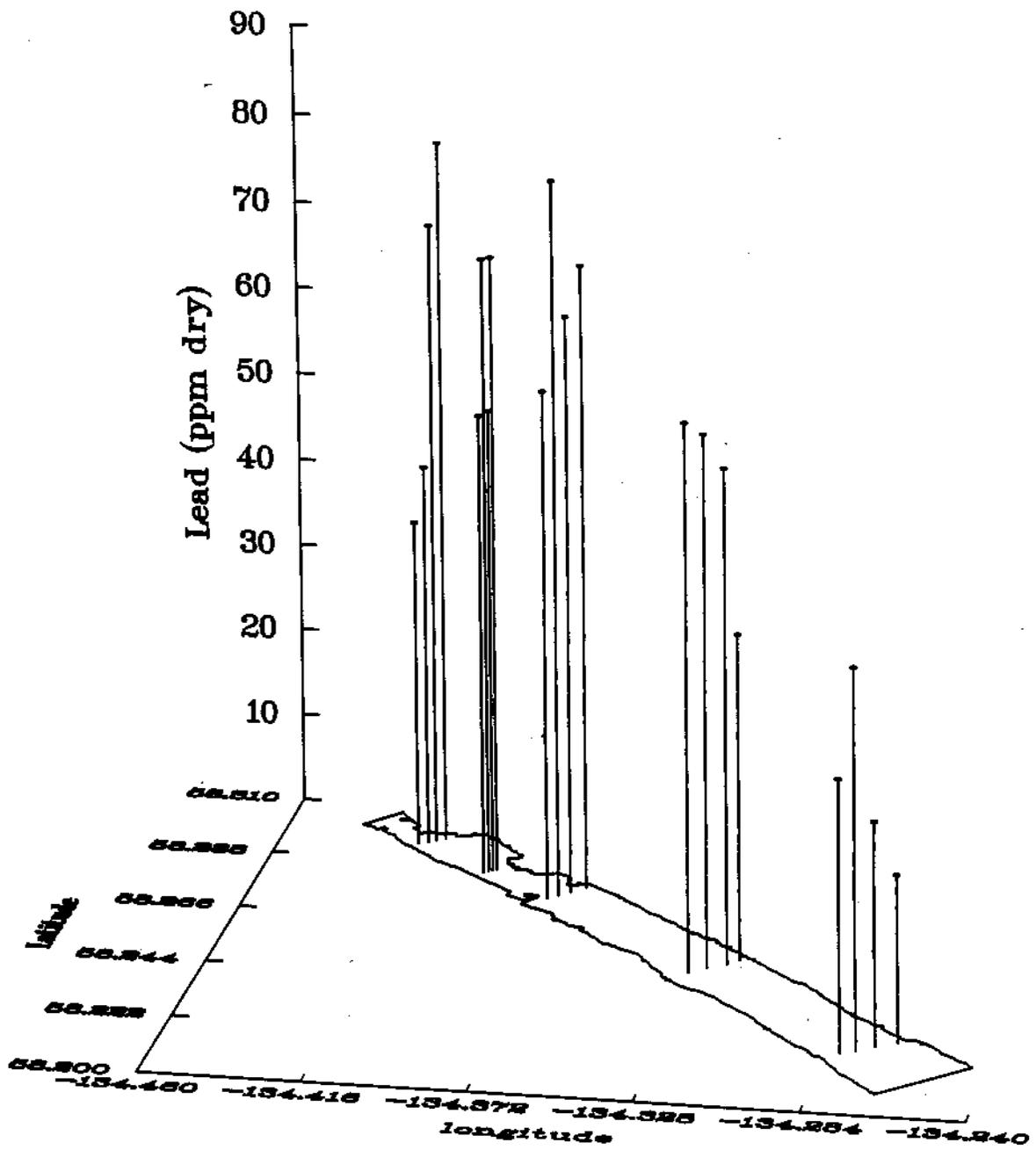


Figure 7. Concentrations of lead (ppm dry weight) in Gastineau Channel surface sediment samples plotted by sampling location.

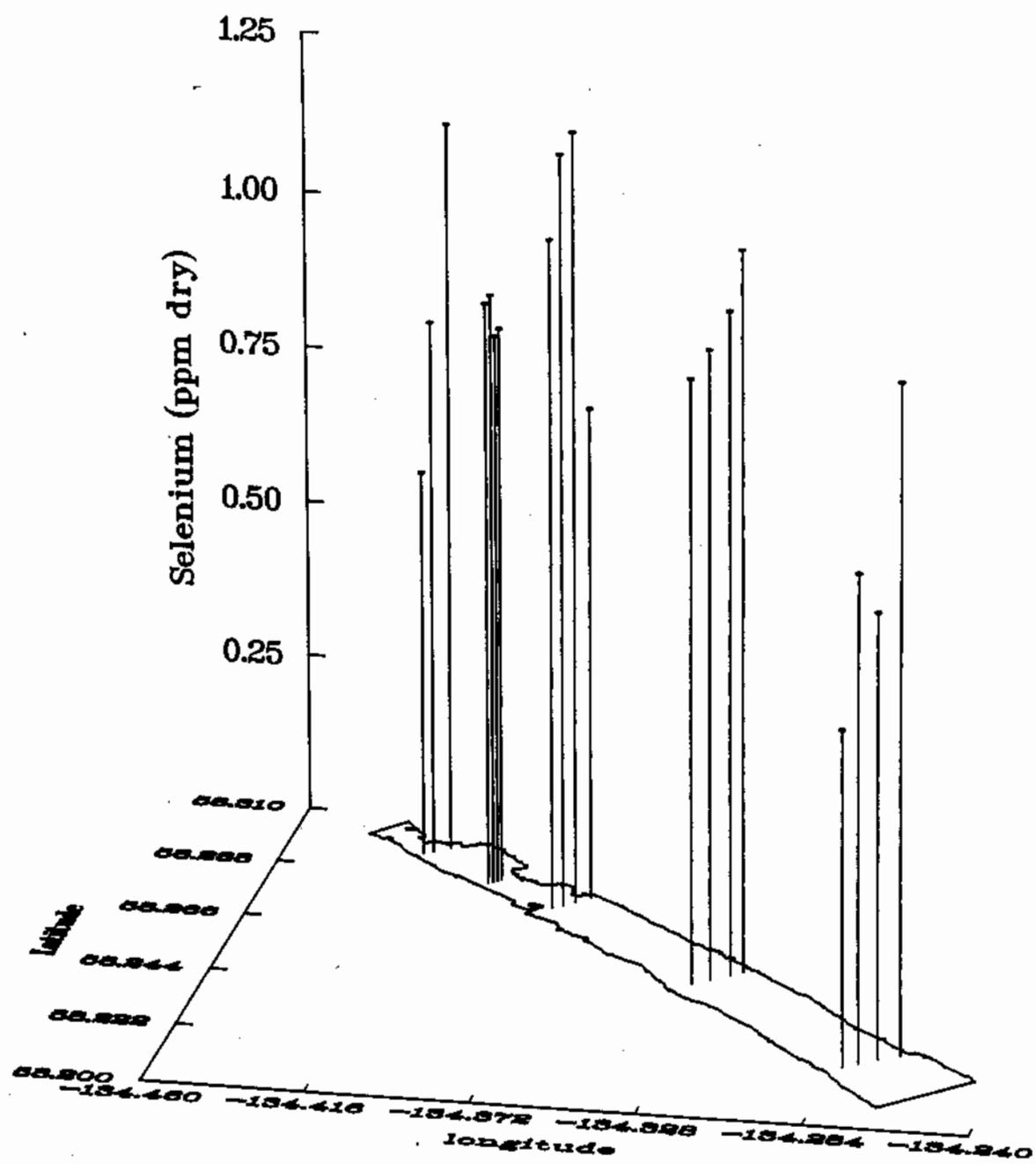


Figure 8. Concentrations of selenium (ppm dry weight) in Gastineau Channel surface sediment samples plotted by sampling location.

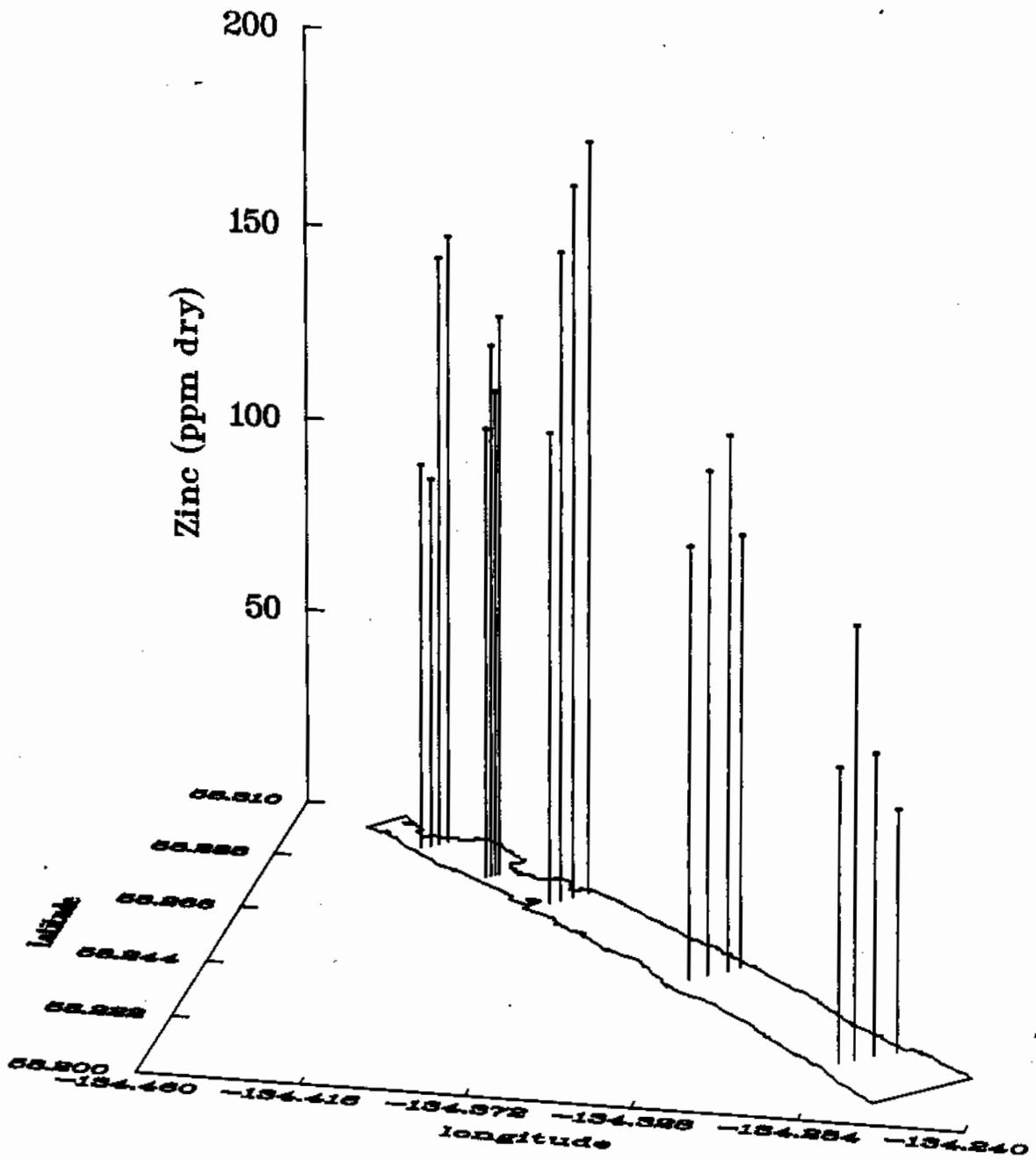


Figure 9. Concentrations of zinc (ppm dry weight) in Gastineau Channel surface sediments plotted by sampling location.

Table 4. Mean metal concentrations (ppm dry weight) in five sediment samples from along the Juneau and Douglas shorelines, respectively.

|                  | As    | Cd   | Cu    | Hg    | Pb    | Se    | Zn    |
|------------------|-------|------|-------|-------|-------|-------|-------|
| Juneau<br>(n=5)  | 22.15 | 0.64 | 45.89 | 0.145 | 49.07 | 0.991 | 123.1 |
| Douglas<br>(n=5) | 14.86 | 0.29 | 44.07 | 0.219 | 46.61 | 0.785 | 101.8 |

### Tissue Analysis

#### Marine fish

Marine fish species analyzed for metal residues were, rock sole (Lepidopsetta bilineata), flathead sole (Hippoglossoides elassodon), yellowfin sole (Limanda aspera), starry flounder (Platichthys stellatus), shortfin eelpout (Lycodes brevipes), and sculpin (family Cottidae) which were not identified to species. A composite of mixed shrimp species (Pandalus spp. and P. dispar) was also collected.

There are very few whole fish data from Alaska for comparison of metal residues. Comparison with metal residues from Pacific herring (Clupea harengus pallasii) from Alaska (Hall et al. 1978) (Table 6) shows Gastineau Channel fish (n=9) had higher whole body concentrations for copper, lead, and zinc than those reported for herring. Arsenic concentrations could be considered elevated only in the yellowfin sole composite sample in this study. Comparison with fish sampled from Bostwick Inlet, an undisturbed area on Gravina Island near Ketchikan, Alaska, shows lead was elevated in most of the channel fish sampled and zinc was elevated in only yellowfin sole. Zinc concentrations were similar to those reported from Klag Bay fish (Robinson-Wilson, unpub. data). No comparative data was found for whole shrimp; data from cleaned, deveined, and deheaded Alaskan sidestripe shrimp (Pandalopsis dispar) (Hall et al. 1978) was included (Table 7) for gross comparison.

#### Molluscs

Metal concentrations and summary statistics for blue mussels and cockles from the Treadwell Complex on Douglas Island are listed in Appendix E. There were no significant differences in metal concentrations between mussels and cockles ( $P < 0.05$ ). Molluscs from the Treadwell Complex tailings had similar mean arsenic, copper, and lead concentrations to metal concentrations in blue mussels from most other mineralized

Table 5. Metal concentrations (ppm dry weight) in Southeast Alaska sediments

|   | As                    | Cd                      | Cu                    | Hg                       | Pb                    | Se                      | Zn                  |
|---|-----------------------|-------------------------|-----------------------|--------------------------|-----------------------|-------------------------|---------------------|
| Gastineau Channel <sup>a</sup><br>(min. and max.)   | 22.1<br>(6.69 - 51.0) | 0.604<br>(0.089 - 3.05) | 51.8<br>(21.8 - 74.4) | 0.222<br>(0.098 - 0.376) | 54.5<br>(19.0 - 81.7) | 0.946<br>(0.524 - 1.31) | 124<br>(60.9 - 191) |
| Klag Bay <sup>b</sup>                               | 209.08 ± 163.61       | 2.8 ± 1.65              | -----                 | 2.28 ± 2.36              | 46.5 ± 22.39          | -----                   | 68.67 ± 21.34       |
| Klag Bay Control <sup>b</sup> C                     | 66.0 ± 8              | 0.6 ± 0.4               | -----                 | .02 ± 0.1                | 3.0 ± 0.3             | -----                   | 7.0 ± 0.4           |
| Skagway <sup>d</sup> C                              | 3.45                  | 0.40                    | 16.90                 | 0.079                    | 52.20                 | 0.15                    | 169                 |
| Taiya Inlet, Skagway<br>(Tetra Tech) <sup>e</sup> C | 14                    | 2.2                     | 5.8                   | 0.23                     | 16.7                  | -----                   | 38.37               |
| Nahku Bay (NOAA) <sup>d</sup> C                     | 1.01                  | 1.09                    | 9.80                  | 0.226                    | 43.30                 | 0.87                    | 191                 |
| Lutak Inlet (ADEC) <sup>f</sup> C                   | 5.0                   | 0.17(ND)                | -----                 | -----                    | 9.66                  | 0.13(ND)                | -----               |
| Lutak Inlet (ADEC) <sup>f</sup><br>(Max. Conc.) C   | 6.66                  | 0.59                    | -----                 | -----                    | 34.5                  | 0.14                    | -----               |
| Lutak Inlet (NOAA) <sup>d</sup> C                   | 1.54                  | 0.64                    | 28.83                 | 0.140                    | 18.27                 | 0.43                    | 180                 |
| Nahku Bay (USFWS) <sup>f</sup> C                    | -----                 | 0.1                     | 9.0                   | 0.9                      | 37                    | -----                   | 257                 |
| Boca de Quadra<br>(NOAA) <sup>d</sup> C             | 1.90                  | 0.44                    | 22.0                  | 0.043                    | 17.87                 | 0.74                    | 104                 |
| Skagway Harbor<br>(Tetra Tech) <sup>e</sup>         | 56.7                  | 13.3                    | 119.6                 | 0.33                     | 2396.7                | -----                   | 3960                |

<sup>a</sup> This study, mean value (n = 20) for each analyte, and (range).

<sup>b</sup> Robinson-Wilson, unpublished USFWS data from 1986 (n = 12). Control located approximately 1.5 km south of Klag Bay on Chichagof Island.

<sup>c</sup> Tetra Tech, 1990. Skagway Harbor Field Investigation. TC 4118-14. Draft Report. (Taiya Inlet value is mean of three reference samples. Skagway Harbor value is mean of three samples.)

<sup>d</sup> NOAA, 1991. Second Summary of Data on Chemical Contaminants in Sediments from the National Status and Trends Program. NOAA Tech. Mem. NOS OPA 59. Raw means from T.O'Connor (pers. comm.) Skagway sample location not in Skagway Harbor.

<sup>e</sup> ADEC, Lutak Inlet Sampling Project Summary, 1990.

C = "Clean" site, no known anthropogenic contaminant input

<sup>f</sup> Unpublished report, E. Robinson-Wilson and G. Malinkey.

<sup>g</sup> ND = non-detect

Table 6. Metal concentrations (ppm dry weight) in whole fish from Gastineau Channel, Klag Bay, and Gulf of Alaska.

|  | As             | Cd             | Cu             | Hg             | Pb             | Se             | Zn              |
|--|----------------|----------------|----------------|----------------|----------------|----------------|-----------------|
| R sole <sup>a1</sup><br>(n = 1)          | 3.76           | 0.05           | 4.04           | 0.21           | 0.90           | 0.90           | 76.4            |
| F sole <sup>a2</sup><br>(n = 3)          | 4.49           | 0.09           | 4.27           | 0.12           | 4.58           | 1.15           | 79.5            |
| Starry flounder <sup>a3</sup><br>(n = 2) | 2.55           | 0.14           | 3.65           | .036           | 1.74           | 1.13           | 73.7            |
| Yf sole <sup>a4</sup><br>(n = 1)         | 4.95           | 0.24           | 2.99           | 0.17           | 1.08           | 1.34           | 111.0           |
| Sculpin <sup>a5</sup><br>spp.<br>(n = 1) | 1.85           | 0.06           | 5.42           | 0.10           | 0.65           | 0.97           | 40.7            |
| Eelpout <sup>a6</sup><br>(n = 1)         | 4.45           | 0.20           | 9.52           | 0.29           | 3.53           | 2.18           | 89.3            |
| x fish <sup>a</sup><br>(n = 9)           | 3.47<br>± 0.37 | 0.11<br>± 0.64 | 4.62<br>± 0.40 | 0.13<br>± 0.73 | 1.62<br>± 0.78 | 1.22<br>± 0.32 | 75.18<br>± 0.34 |
| P. herring <sup>a7</sup>                 | 2.439          | 0.128          | 1.212          | 0.260          | 1.082          | 0.761          | 14.3            |
| Yf sole <sup>c</sup><br>(n = 4)          | 10.575         | 0.60           | ---            | 4.65           | 10.4           | ---            | 80.5            |
| Pacific tomcod <sup>a8</sup><br>(n = 4)  | 13.525         | 0              | ---            | 6.025          | 1.175          | ---            | 51.1            |
| Kelp greenling <sup>a9</sup><br>(n = 4)  | 7.0            | 0              | ---            | 5.775          | 5.4            | ---            | 68.725          |
| Rock sole <sup>d</sup><br>(n = 1)        | 13.0           | 0.11           | 2.5            | 0.079          | 0.4            | ---            | 56.1            |
| Sculpin spp. <sup>d</sup><br>(n = 1)     | 6.7            | 0.12           | 3.9            | 0.24           | 0.4            | ---            | 57.6            |

<sup>a</sup> Gastineau Channel

<sup>a</sup> Hall, R.A., E.G. Zook, and G.M. Meaburn. 1978. National Marine Fisheries Service Survey of Trace Elements in the Fishery Resource. NOAA Tech. Rep. NMFS SSRF - 721.

<sup>c</sup> Klag Bay (Robinson-Wilson, unpub. data, 1986)

<sup>d</sup> Bostwick Inlet (Rudis 1994)

<sup>1</sup> rock sole (Lepidion setta bilineata)  
composite of 2 fish

<sup>5</sup> sculpin species (family Corridae)  
composite of 7 fish

<sup>2</sup> flathead sole (Hippoglossoides elassodon)  
2 composites of 5 fish each; 1 composite  
of 2 fish

<sup>6</sup> shortfin eelpout (Lycodes brevipes)  
composite of 15 fish

<sup>3</sup> starry flounder (Platichthys stellatus)  
2 composites of 3 fish each

<sup>7</sup> Pacific herring (Clupea harengus)

<sup>4</sup> yellowfin sole (Limanda aspera)  
composite of 2 fish

<sup>8</sup> Pacific tomcod (Microgadus proximus)

<sup>9</sup> Kelp greenling (Hexagrammos decagrammus)

Table 7. Metal concentrations (ppm dry weight) in shrimp.

|   | As   | Cd   | Cu   | Hg   | Pb   | Se   | Zn    |
|---|------|------|------|------|------|------|-------|
| Gastineau Channel<br>( <i>Pandalus</i> spp...<br><i>Pandalopsis dispar</i> ) <sup>a</sup> | 30.5 | 0.87 | 72.0 | 0.14 | 1.45 | 1.63 | 65.7  |
| Gulf of Alaska<br>( <i>Pandalopsis dispar</i> ) <sup>b</sup>                              | 4.71 | 0.09 | 5.63 | 0.04 | 0.65 | 0.34 | 13.48 |

<sup>a</sup> Whole shrimp

<sup>b</sup> Cleaned, deveined, deheaded (Hall et al. 1978).

Southeast Alaska locations (USFS, USFWS, Robinson-Wilson, unpub. data) (Table 8). Cadmium concentrations were lower in molluscs from this study than molluscs from Cann Creek and Bostwick Inlet, two other Southeast locations. Zinc was the only metal in Douglas Island mussels that exceeded concentrations in mussels reported from all other Southeast locations (Table 8). However, these values were not considered elevated because they were not two times above the zinc concentrations from areas such as Duncan Canal or Bostwick Inlet, that are considered baseline for this study. Silver Bay and Klag Bay were the only water bodies considered in Table 8 with anthropogenic sources of contamination when sampled in 1986 and 1987. Nahku Bay receives stream-carried sediments that have naturally high metal concentrations of arsenic, chromium, lead, nickel, and zinc (Alaska Department of Natural Resources 1984). The high lead concentrations in mussels from Nahku Bay in Skagway (Robinson-Wilson and Malinkey, unpub. data) may be attributed to these naturally high lead levels in sediments.

#### **Freshwater Fish**

Metal concentrations in freshwater fish are related to conditions in Ready Bullion Creek and not to Gastineau Channel. There are few whole freshwater-fish dry-weight data from Alaskan waters available for comparison, but wet-weight data are available for some Alaskan species. Wet weight concentrations were converted to a conservative dry weight value by multiplying by a factor of three (a 30 percent moisture was estimated based on Dolly Varden from this study). Freshwater fish (Dolly Varden and sculpin species) from Ready Bullion Creek had concentrations of arsenic that were three to five times higher than fish tissue concentrations from other Alaskan locations (Table 9). Cadmium concentrations were comparable to the calculated dry weight values from Neka River sampling (Table 9). Arsenic and lead concentrations are higher in the Dolly Varden sample than in a sample of the same species from Gold Creek in Juneau (Table 9). Zinc and copper concentrations were lower than those reported in Gold Creek fish. The lead concentration of 14.7 ppm in Dolly Varden was very high. Copper and zinc concentrations were much higher than those found in fish sampled from the Neka River in 1992 by the Alaska Department of Environmental Conservation.

### **DISCUSSION**

#### *Sediment Analysis*

Because the Juneau area is heavily mineralized, the high metal values in Gastineau Channel sediments are not unexpected. Indeed, mean metal concentrations are similar to sediment from several Southeast Alaska locations, many of which also receive anthropogenic inputs of metals (Table 5). However, when metal concentrations from individual sampling stations in Gastineau Channel were examined there were some higher than expected values. Choosing concentrations at Dupont (J1) near the mouth of the channel to estimate background conditions, many arsenic, copper, mercury, lead, and zinc concentrations measured were at greater than two times the background concentrations. Coupled with the obvious trends in the distributions of the elements (Figs. 3 - 9) we conclude this suggests

an obvious pattern of contamination. Arsenic, copper, and lead contamination is found at all stations on transects 2, 3, 4, and 5 (Table 3). Cadmium is a contaminant (greater than two times background concentrations) at all but two stations on transect 2 through 5. Mercury is frequently at contaminant concentrations, and zinc is a contaminant at over half of the stations. Selenium is never a contaminant by this definition, even though selenium concentrations in Gastineau Channel sediments ranked number one (Table 5).

The higher sediment metal concentrations in the channel represent contributions from human activities such as old landfills, the municipal sewer outfall, urban nonpoint source pollution, and historic mining. A drift card study (Sturdevant, in prep.) conducted by the National Marine Fisheries Service Auke Bay Laboratory found that the general net direction of surface currents is northwest, up the channel in both ebb and flood tides. This indicated that fine sediment suspended in surface waters would also move in a northwest direction, away from the mouth of the channel.

#### *Other Local Sampling*

The highest concentrations of most metals appears to be localized - across from Sandy Beach and the former Treadwell Mine on Douglas Island - a former tailings deposition site, downtown Juneau, and Snowslide Creek on the Juneau side. The concentrations from transect 5 on the Juneau side of the channel can most likely be attributed to both present day urban activities and the extensive tailings dumping that occurred during the early 1900s. Tailings were also deposited mid-channel. The upland area near Snowslide Creek is the site of the former city landfill and was the municipal sewer system sludge deposit area. The area now receives ash from incinerated sewage sludge. The ash is tested prior to disposal and most metals have been at concentrations below detection levels and well below regulatory levels (E. Emswiler, ADEC). Sewage sludge was deposited in this disposal area until 1988; lead (105 ppm), and cadmium (10.2 ppm) are the only metals that have notably high concentrations. Beneath these layers are unknown landfill wastes and rock disposal which are potential contributors to metal loading in adjacent channel sediments.

Field investigations have been conducted at the Rock Dump, the Thane Mine dump site, and the Sandy Beach/Treadwell Mine area (Ecology and Environment, 1988, 1990, 1991; Versar, Inc. 1989). These site inspections were done for the U.S. Environmental Protection Agency (EPA), the Alaska Department of Environmental Conservation (ADEC), and the City and Borough of Juneau. An earlier study of Rock Dump sediments was conducted in 1987 by Golder Associates.

The 1990 Ecology and Environment Rock Dump study included six on-site soil samples and a background sample. Results indicate that the tailings at the Rock Dump contain, "significantly elevated concentrations of several heavy metals". This was defined as two times the background concentration. Metals of concern were, arsenic (28.8 ppm), cadmium (12.5, 15.8, 15.9 ppm), lead (175, 207 ppm), and zinc (324, 417, 538, 631 ppm). It was concluded that heavy metals from the site could be released to the

surrounding environment through surface water (including high tide submergence) or as airborne particulates.

The Thane Mine tailings site forms an area of approximately 20 ha at the Sheep Creek delta (Ecology and Environment 1988). Thirty-three samples were collected from shallow boreholes at the two tailings dumps. Samples collected north and south of the tailings were considered background with arsenic at 8.9 and 7.5 ppm, lead at 11 and 8.4 ppm, and zinc at 57 and 84 ppm. Elevated (two times background) concentrations of arsenic (means from two tailings dumps of 36.7, 24.4 ppm) and lead (82.7, 47.6 ppm) were found in 19 of the 33 shallow sediment samples. The report concludes that the tailings do not appear to have significant leaching potential but that long-term low concentration leaching is likely. Elevated lead was detected in on-site mussel samples.

The site inspection for the Treadwell Complex on Douglas Island included analyses of soil and sediment samples (Ecology and Environment 1991). Elevated concentrations of arsenic (139 ppm), cadmium (36 ppm), copper (370 ppm), iron (210,000 ppm), lead (450 ppm), mercury (5.9 ppm), and selenium (38.3 ppm) were detected in the lower tailings sample area adjacent to the shoreline (see Figure 2 of Ecology and Environment 1991). The report concluded that there is a potential for contamination of surface runoff, Gastineau Channel, and nearby beaches with heavy metals.

#### *National Status & Trends Program*

Because there are no national sediment criteria at this time, concentrations from the NOAA Status and Trends (NS&T) Program (Long and Morgan 1990), and its revision by Long et al. (1995) were used to compare with values from Gastineau Channel. The values developed by NOAA are not standards or criteria but have been used for comparison in marine sediment studies. An inventory of sediment contamination from nearly 13,500 coastal sediment samples was compiled by the NS&T Program (Daskalakis and O'Connor 1994). A "high" concentration was determined for each analyte. The authors conclude that "high" concentrations could only be natural under unusual circumstances such as mineral deposits. Examination of other Southeast Alaska sediment data reveals that Gastineau Channel sediments are higher in arsenic, cadmium, copper, lead, selenium and zinc than most nonpolluted locations (Table 5). Comparison of elevated concentrations from this study (2 x station J1) with NS&T "high" concentrations show surprisingly similar parallels (Table 10).

Table 8. Metal concentrations (ppm dry wt. means,  $\pm$  SD) in blue mussels (*Mytilus trossulus*) from locations throughout Southeast Alaska. Locations receiving local anthropogenic inputs of metals include Silver Bay and Klag Bay. Nahku Bay receives sediments from highly mineralized streams.

|   | As               | Cd              | Cu                           | Hg                    | Pb                           | Zn                  |
|---|------------------|-----------------|------------------------------|-----------------------|------------------------------|---------------------|
| Douglas Is.<br>(n = 6)                  | 9.40 $\pm$ 1.14  | 2.44 $\pm$ 0.73 | 8.87 $\pm$ 0.81              | <0.2(ND) <sup>a</sup> | 1.60 $\pm$ 0.49              | 111.34 $\pm$ 13.77  |
| Silver Bay <sup>a</sup><br>(n = 9)      | -----            | -----           | 9.178 $\pm$ 3.079            | 0.216 $\pm$ 0.022     | 0.796 $\pm$ 0.260            | 72.889 $\pm$ 14.598 |
| Klag Bay <sup>a</sup><br>(n = 12)       | 12.66 $\pm$ 4.48 | 4.5 $\pm$ 2.24  | -----                        | 6.6 $\pm$ 1.30        | 105.43 $\pm$ 80.12           | 82.33 $\pm$ 13.36   |
| Hawk Inlet <sup>a</sup><br>(n = 15)     | -----            | -----           | 10.047 $\pm$ 1.520           | 0.138 $\pm$ 0.022     | 0.745 $\pm$ 0.298            | 98.733 $\pm$ 1.52   |
| Duncan Canal <sup>a</sup><br>(n = 18)   | -----            | -----           | 7.528 $\pm$ 3.898            | 0.132 $\pm$ 0.018     | 2.128 $\pm$ 0.242            | 64.0 $\pm$ 24.807   |
| Boca de Quadra <sup>a</sup><br>(n = 21) | -----            | -----           | 8.514 $\pm$ 7.087            | 0.661 $\pm$ 0.973     | 2.271 $\pm$ 0.598            | 68.048 $\pm$ 7.087  |
| Nahku Bay <sup>b</sup>                  | -----            | -----           | 4.7/23.5 <sup>c</sup>        | ND                    | 27/135 <sup>c</sup>          | 96/480 <sup>c</sup> |
| Carrn Creek <sup>a</sup>                | 12.30 $\pm$ 0.58 | 7.6 $\pm$ 0.83  | 6.87 $\pm$ 0.42              | 0.08 $\pm$ 0.01       | 0.57 $\pm$ 0.38              | 70.33 $\pm$ 8.62    |
| Douglas Island<br>cockle <sup>d</sup>   | 10.44 $\pm$ 0.17 | 0.28 $\pm$ 0.49 | 7.04 $\pm$ 0.37 <sup>e</sup> | <0.2(ND)              | 2.08 $\pm$ 0.23 <sup>c</sup> | 99.43 $\pm$ 0.17    |
| Bostwick Inlet<br>(n = 2)               | 8.5              | 6.11            | 9.7                          | 0.043                 | 0.3                          | 85.2                |

<sup>a</sup> Robinson-Wilson, unpublished USFWS data from 1986.

<sup>f</sup> Rudis 1994

<sup>b</sup> Unpublished report, E. Robinson-Wilson and G. Malinkey

<sup>g</sup> ND = non-detect

<sup>c</sup> Approximate dry weight calculations = wet weight x 3 (dry wt./wet wt.)

<sup>d</sup> *Clinoocardium nuttalli* (this study)

<sup>e</sup> Unpublished USFWS data, 1993 sampling on Chichagof Island

Table 9. Metal concentrations (ppm) in whole freshwater fish from Alaska.

| Species   |                      | As          | Cd                      | Cu          | Hg          | Pb          | Zn              |
|---|----------------------|-------------|-------------------------|-------------|-------------|-------------|-----------------|
| Rainbow trout <sup>a</sup><br>( <i>Salmo gairdneri</i> )      | wet wt.              | 0.10 - 0.16 | <0.05 - 0.07            | -----       | 0.05 - 0.06 | -----       | -----           |
|   | dry wt. <sup>b</sup> | 0.30 - 0.48 | 0.15 - 0.21             | -----       | 0.15 - 0.18 | -----       | -----           |
| Brown trout <sup>a</sup><br>( <i>Salmo trutta</i> )           | wet wt.              | <0.05       | <0.05                   | -----       | 0.07 - 0.21 | 0.19 - 0.20 | -----           |
|   | dry wt. <sup>b</sup> | <0.15       | <0.15                   | -----       | 0.21 - 0.63 | 0.57 - 0.6  | -----           |
| Lake trout <sup>a</sup><br>( <i>Salvelinus namaycush</i> )    | wet wt.              | 0.06 - 0.11 | <0.05                   | -----       | 0.18 - 0.23 | ---         | -----           |
|   | dry wt. <sup>b</sup> | 0.18 - 0.33 | <0.15                   | -----       | 0.54 - 0.69 | ---         | -----           |
| Arctic grayling <sup>a</sup><br>( <i>Thymallus arcticus</i> ) | wet wt.              | <0.05       | ND <sup>e</sup> - <0.05 | -----       | 0.05 - 0.06 | 0.19 - 0.23 | -----           |
|   | dry wt. <sup>b</sup> | <0.15       | <0.15                   | -----       | ---         | 0.57 - 0.69 | -----           |
| Dolly Varden <sup>c</sup><br>( <i>Salvelinus malma</i> )      | wet wt.              | <1.0(ND)    | 0.41                    | 0.6         | 0.03        | 0.05(ND)    | 5.29            |
|   | dry wt. <sup>b</sup> | ----        | 1.23                    | 1.8         | 0.9         | ----        | 15.87           |
| Dolly Varden <sup>c</sup><br>( <i>Salvelinus malma</i> )      | wet wt.              | 0.46        | 0.34                    | 1.61        | 0.101       | 3.57        | 30.37           |
|   | dry wt. <sup>b</sup> | 1.9         | 1.38                    | 6.63        | 0.414       | 14.7        | 125             |
| Sculpin species <sup>d</sup>                                  | wet wt.              | 0.245       | 0.024                   | 1.23        | 0.15        | 0.96        | 28.69           |
|   | dry wt. <sup>b</sup> | 0.78        | 0.078                   | 3.945       | 0.5         | 3.11        | 91.15           |
| Dolly Varden <sup>e</sup><br>( <i>Salvelinus malma</i> )      | wet wt.              | ND - 0.115  | ND - 0.18               | 1.5 - 4.7   | <0.04(ND)   | ND - 0.37   | 39 - 64         |
|   | dry wt. <sup>b</sup> | ND - 0.637  | ND - 0.841              | 6.7 - 26.13 | <0.21(ND)   | ND - 1.63   | 204.15 - 283.51 |

<sup>a</sup> Walsh, D.F., B.L. Berger, and J.R. Bean. 1977. Residues in fish, wildlife, and estuaries. Mercury, arsenic, lead, cadmium, and selenium residues in fish, 1971-1973. National Pesticide Monitoring Program. Pesticide Monitoring Journal 2(1):5-34. Sample sources: Arctic grayling - Chena River; Lake, Rainbow trout - Kenai River; Brown trout - Rio Grande, CO.

<sup>b</sup> Approximate dry weight calculated from wet weight x 3.

<sup>c</sup> Neka River, Alaska, ADEC, Neka Bay, Port Frederick Fish Kill Investigation Final Report. August 1992.

<sup>d</sup> Ready Bullion Creek, Douglas, Alaska. (This study)

<sup>e</sup> Gold Creek, Juneau, Alaska. (n = 6). 1994 Gold Creek Fish Kill. USFWS.

<sup>f</sup> ND = non-detect

Table 10. High metal concentrations (ppm dry weight) from Gastineau Channel sediments (2 x station J1) and the NS&T Program (Daskalakis and O'Connor 1994).

| Analyte | NS&T "High" | 2 x Station J1 |
|---------|-------------|----------------|
| As      | 13          | 13             |
| Cd      | 0.54        | 0.52           |
| Cu      | 42          | 42             |
| Hg      | 0.22        | 0.19           |
| Pb      | 45          | 38             |
| Se      | 0.92        | 2.1            |
| Zn      | 135         | 122            |

NOAA developed effects-based sediment quality values from chemical sediment concentrations associated with adverse biological effects. Chemical concentrations observed or predicted by different methods to be associated with biological effects were sorted in ascending order. The Effects Range-Low (ER-L) is the low value of the range of concentrations in which effects were observed or predicted. ER-Ls are infrequently indicative of sediment toxicity. The median was identified as an Effects Range-Median (ER-M), a concentration approximately midway in the range of reported values associated with biological effects. Concentrations in the range between ER-L and ER-M were found to occasionally co-occur with effects. Biological effects were frequently or always observed or predicted among species at ER-M values. ER-Ms and concentrations above are indicative of extreme sediment contamination. Relative degrees of confidence in the accuracy of the ER-L and ER-M values vary by contaminant. The ER-L values are primarily based on the Bioeffects/Contaminant Co-Occurrence Analysis (COA) Approach (Long and Morgan 1990) which does not attempt to prove cause and effect.

The NS&T database (Long and Morgan 1990) was refined by Long et al. (1995) when freshwater studies were excluded and new data was incorporated. A revised set of ER-L and ER-M guideline values for trace metals was developed from that data set, reflecting a database more focused on saltwater organisms.

All metals except cadmium were higher than ER-Ls (Long et al. 1995) at some Gastineau Channel sampling stations. Arsenic, copper, mercury, and lead concentrations in Gastineau Channel sediment samples were above the ER-Ls for these metals in more than 50 percent of the samples. Confidence in the ER-L values is considered high for copper (34.0 ppm) and lead (46.7 ppm), but low for mercury (0.15 ppm). Sediment cadmium concentrations at all stations but J3 and X3 were much lower than the ER-L (1.2 ppm). There are no Effects Range values for selenium in the NS&T Program. No Gastineau Channel sediment samples exceeded the ER-M values for any metal tested.

In another analysis, Daskalakis and O'Connor (1995) reviewed EPA data from the Estuarine Component of the Environmental Monitoring and

Assessment Program (EMAP/EC), where chemical analyses were linked with toxicity tests. Their analysis of the EMAP data set indicated that metal concentrations in sediments are not particularly strong predictors of chronic toxicity to amphipods (ten-day exposure). The frequency of toxicity increased with concentration, but concentrations in the highest range did not correspond to more than about a 50 percent frequency of toxicity. Some concentrations in the lowest range tested as toxic in about 15 percent of the cases.

Cadmium did not occur at concentrations in sediment that have generally been reported to cause toxicity to marine organisms (Long and Morgan 1990).

The range of selenium in ocean sediments was reported at 0.34 to 4.8 ppm by Goeij et al. (1974 in Eisler 1985). The range in this study was 0.52 to 1.31 ppm. Other Southeast Alaska sediment selenium concentrations were comparable (Table 5).

Sediment arsenic concentrations in this study ranged from 6 to 51 ppm. Comparison with other Southeast Alaska sediments (Table 5) shows Gastineau Channel sediments to be higher in arsenic than most other locations, except for Skagway Harbor (impacted by lead mine ore dust), Klag Bay (an old mine site), and a reference location for that study. Mean sediment arsenic values for 1984 through 1987 from Elliott Bay, Washington (an industrial area) were 21.89 ppm (NOAA 1988).

The ER-L for copper is 34 ppm (Long et al. 1995). Most biological effects occurred when sediment copper concentrations exceeded 270 ppm (Long et al. 1995). Copper concentrations in Gastineau Channel sediments ranged from 21 to 74 ppm, concentrations that were found to cause adverse effects in nine to 29 percent of toxicity studies reviewed (Long et al. 1995). Copper concentrations were much lower than were reported from Skagway Harbor (Table 5).

Mercury was reported (Eisler 1987) to be the most toxic trace metal to aquatic organisms, with lethal concentrations ranging from 0.1 to 2.0 ppm of medium. Sediment mercury concentrations detected in this study ranged from 0.098 to 0.376 ppm. The ER-L is 0.15 ppm. Most sediment mercury data from Southeast Alaska (Table 5) are above the ER-L. Toxicity of mercury is increased in the presence of lead and zinc, both of which were detected in Gastineau Channel at concentrations that could cause adverse effects to some marine organisms.

Lead concentrations from Gastineau Channel sediments ranged from 19 to 81 ppm with 65 percent of the samples exceeding the ER-L of 46.7 ppm. The incidence of effects for concentrations at the ER-L was 8 percent and 35 percent for the ER-M (Long et al. 1995). Sediment lead concentrations at uncontaminated Southeast Alaska locations ranged from 3 to 48 ppm (Table 5). Sediments are known to be sinks for lead, and may act as a source of lead to aquatic biota after the original source has subsided (Knowlton et al. 1983).

The ER-L value for zinc is 150 ppm. The ER-L was exceeded at four of twenty stations in this study. Where zinc concentrations were below the ER-L, biological effects to marine organisms occurred in only 6 percent of studies reviewed (Long et al. 1995). Nahku Bay and Lutak Inlet also had sediment zinc values above the ER-L (Table 5).

Biological effects occur in sediments that are often contaminated by a number of organic and inorganic substances. This study did not examine organic compounds in sediments. None of the metal concentrations in sediments from Gastineau Channel reported in this study suggest a severe contamination problem, however, concentrations of arsenic, copper, lead, mercury, and zinc do indicate a "stressed" system that would be aggravated with additional metals input.

#### *Tissue Analysis*

##### **Molluscs**

Data from the NOAA Mussel Watch sites (O'Connor 1992) were used to compare mean metal concentrations; "high" values were defined by O'Connor (1992) as the mean plus one standard deviation (Table 11).

Metal concentrations in molluscs from Treadwell/Sandy Beach area on Douglas Island were comparable to mean concentrations reported nationwide in NOAA's Mussel Watch program. Arsenic, copper, lead, and zinc concentrations in this study were comparable to concentrations in molluscs from other locations in Southeast Alaska (Table 8). Cadmium concentrations in molluscs from this study were lower. Mercury concentrations in molluscs (this study) were below detection limits. Correlations between metals and mussel tissue data from 53 sites were examined by O'Connor and Ehler (1991). Considering metals from this study, they found positive correlations for only copper, mercury, and lead with mussel tissue. Molluscs can be agents for resuspension of metals from the sediment to the water column and other biota. Metal concentrations in molluscs and sediment in this study did not show comparable concentrations, indicating contamination is not bioavailable to these invertebrates.

Table 11. Metal concentrations (ppm dry weight) in mussel tissue from Douglas Island and NOAA Mussel Watch (O'Connor 1992).

| Element | Douglas Island | NOAA Geometric Mean | NOAA "High" <sup>a</sup> |
|---------|----------------|---------------------|--------------------------|
| As      | 9.4            | 10                  | 17                       |
| Cd      | 2.4            | 2.7                 | 5.7                      |
| Cu      | 8.8            | 8.9                 | 11                       |
| Hg      | ND             | 0.094               | 0.24                     |
| Pb      | 1.6            | 1.8                 | 4.3                      |
| Zn      | 111.3          | 130                 | 190                      |

<sup>a</sup> "High" concentrations correspond to the means plus one standard deviation of the logarithms of individual site means.

### Shrimp

Examining the data by species indicates that shrimp accumulated the highest concentrations of arsenic and copper. Copper is a component of the blood system in shrimp, and lead accumulates in the shell (Knowlton et al. 1983). The copper concentration was 72.0 ppm dry weight (17.57 ppm wet wt.) in the composite shrimp sample in this study (Table 8). Bryan (1968) reported copper at 30 to 32 ppm wet weight in whole shrimp from Great Britain; an Oregon study reported a mean concentration of 18.8 and a maximum of 26 ppm dry weight in pink shrimp (*Pandalus jordani*), (Cutshall and Holton 1972 in Jenkins 1980). Lead concentrations in that study ranged from 1.3 to 3.5 ppm dry weight, lead was measured at 1.45 ppm dry weight in shrimp from the channel.

Crustacean tissues normally contain arsenic residues of several to more than 100 ppm dry weight (Fowler and Unlu 1978, Lunde 1977). Arsenic concentrations (dry weight) in whole shrimp from Texas were 0.6 ppm and 3.8 ppm, (Sims and Presley 1976), and 16.0 ppm in Great Britain (Leatherland and Burton 1974). Because arsenic occurs as arsenobetaine in marine organisms and the potential risks associated with consumption of seafood containing this organoarsenical appears to be minor (Eisler 1988b), this metal does not present a problem in the concentrations (30.5 ppm dry weight) measured in Gastineau Channel shrimp.

### Marine fish

Concentrations of lead and zinc in marine fish from Gastineau Channel (Table 6) were higher than concentrations found in whole fish from Bostwick Inlet on Gravina Island (Pb <0.4 ppm DW [ND], Zn 54.0 ppm DW, n=4) (Rudis 1994) and Pacific herring collected along coastal Alaska in 1978 (Hall et al. 1978). Because the Bostwick Inlet fish samples are similar or the same species, and were analyzed by the same laboratory using the same procedures, they are the most appropriate samples to use

for comparison. Arsenic, cadmium, and mercury concentrations in Gastineau Channel samples were comparable to concentrations in fish from both of these other studies. Copper was elevated (9.52 ppm) only in the eelpout sample, a bottom-dwelling fish.

Mean lead concentrations in fish sampled in Gastineau Channel were similar to those reported for Pacific herring but far exceeded the nondetect concentration (detection level at 0.4 ppm) for the Bostwick Inlet fish. All four samples from that study were at nondetect for lead. Flathead sole (4.58 ppm) and eelpout (3.53 ppm) samples from this study represented the highest lead values in channel fish (Table 6). All fish species sampled from Gastineau Channel are primarily bottom feeders. It is unknown why these two species showed the highest lead levels. Lead is concentrated by biota from water, and there is little evidence that it is transferred through food chains (EPA 1979).

In contrast to lead uptake, aquatic organisms obtain zinc concentrations from diet rather than seawater (Eisler 1984). Zinc concentrations in marine fish from Gastineau Channel ranged from 40 to 111 ppm. Fish from Bostwick Inlet had zinc concentrations of 46 to 57 ppm. Only the yellowfin sole sample from Gastineau Channel had high enough zinc values (111 ppm) to be considered elevated. Other zinc concentrations in fish were comparable to Klag Bay samples (Table 6).

#### **Freshwater fish**

Metal concentrations in fish from Ready Bullion Creek indicate that this creek is contributing metals to resident fish. Arsenic at 0.46 ppm and lead at 3.57 ppm wet weight concentrations in Dolly Varden are above expected values compared to Gold Creek fish (USFWS 1994, in Table 9). Data from freshwater fish from the National Contaminant Biomonitoring Program (Lowe et al. 1985) reported whole body wet weight arsenic concentrations of 0.14 - 0.16 ppm. Nationwide, lead concentrations were as high as 6.73 ppm wet weight (Lowe et al. 1985). Because fish excrete lead rapidly (Sorenson 1991), elevated lead levels indicate continual exposure to metal concentrations in water. Water quality testing in Ready Bullion Creek is needed to determine trace metal concentrations.

#### **SUMMARY**

Gastineau Channel has a number of potential sources of metals contamination: tailings present for 75 years or more in combination with urban nonpoint source pollution including highway runoff, boat harbors, sewage outfall, and old landfill activities. Concentrations of arsenic, copper, lead, and zinc are elevated in some channel sediments. Metals concentrations are at low, rather than moderate, toxic levels when compared to data from NOAA's NS&T Program. Mapping reveals hot-spot locations, and provides a sound basis for designing future studies to describe the spatial trends in greater detail (Cressie 1991). Tissue data demonstrate that copper, lead, and zinc in sediments may be bioavailable to some bottom-feeding fish, but have not bioaccumulated in molluscs from

the Treadwell tailings. Additional mollusc samples should be collected throughout the channel to characterize metal uptake. More information is needed on resident fish to examine pathways of fish uptake. Sediment bioassays are recommended to determine sediment toxicity to aquatic organisms. Proposals for Gastineau Channel to receive metal-bearing effluent from industrial development and future mining activity should be carefully considered with respect to these results.

#### LITERATURE CITED

- Alaska Department of Natural Resources. 1984. Report of the investigations 84-31, Geology and Geochemistry of the Skagway B-2 Quadrangle, Southeastern Alaska. Div. of Geol. and Geophys. Surveys.
- Bureau of Land Management. 1992. Final Environmental Impact Statement for the Proposed Reopening of the A-J Mine, Juneau, Alaska. Vol. I. BLM-AK-ES-92-028-2800-980.
- Brooks, R.R., and D. Rumsey. 1974. Heavy metals in some New Zealand commercial fishes. *N.Z. Journ. Mar. & Freshwat. Res.* 8(1):155-166.
- Bryan, G.W. 1968. Concentrations of zinc and copper in tissues of decapod crustaceans. *J. Mar. Biol. Assn. U.K.* 48:303-321.
- Cressie, N. 1991. *Statistics for Spatial Data.* John Wiley. New York, N.Y.
- Cutshall, N., and R. Holton. 1972. Metal analysis in IDOE baseline samples. In: IDOE Workshop on Baseline Studies of Pollutants in Marine Environment. Brookhaven Nat. Lab. pp.67-82. May 1972.
- Daskalakis, K.D., and T.P. O'Connor. 1994. Inventory of Chemical Concentrations in Coastal and Estuarine Sediments. NOAA Tech. Mem. NOS ORCA 76. 66 pp.
- Daskalakis, K.D., and T.P. O'Connor. 1995. Distribution of Chemical Concentrations in Coast and Estuarine Sediments. *Mar. Environ. Res.* 40:381-398.
- de Goeij, J.J.M. V.P. Guinn, D.R. Young, and A.J. Mearns. 1974. Neutron activation analysis trace-element studies of Dover sole liver and marine sediments. In *Comparative studies of food and environmental contamination.* Int. Atomic Energy Agency, Vienna. Pages 189-200.
- Ecology and Environment, Inc. May 1988. Site Inspection Report for Thane Mine Dump Site Juneau, Alaska. prepared for U.S. EPA Region X Seattle, WA.
- Ecology and Environment, Inc. June 1990. Site Inspection Report for Alaska Juneau Dump Juneau, Alaska. submitted to: Alaska Dept. of Environmental Conservation, Juneau, AK
- Ecology and Environment, Inc. Sept.1991. Site Inspection Report for Treadwell Mine Juneau, Alaska. submitted to: Alaska Dept. of Environmental Conservation, Juneau, AK
- Eisler, R. 1984. Trace metal changes associated with age of marine invertebrates. *Biol. Trace Element Res.* 6:165-180.

- \_\_\_\_\_. 1985. Selenium hazards to fish, wildlife, and invertebrates: a synoptic review. Biol. Rep. 85(1.5). Laurel, MD: USFWS, DOI. 57 pp.
- \_\_\_\_\_. 1987. Mercury hazards to fish, wildlife, and invertebrates: a synoptic review. Biol. Rep. 85(1.10). Laurel, MD: USFWS, DOI. 90 pp.
- \_\_\_\_\_. 1988a. Lead hazards to fish, wildlife, and invertebrates: a synoptic review. Biol. Rep. 85(1.14). Laurel, MD: USFWS, DOI. 134 pp.
- \_\_\_\_\_. 1988b. Arsenic hazards to fish, wildlife, and invertebrates: a synoptic review. Biol. Rep. No. 85(1.12). Laurel, MD: USFWS, DOI. 92 pp.
- EPA. 1979. The health and environmental impacts of lead and an assessment of a need for limitations. U.S. Environ. Protection Agency Rep. 560/2-79-001. 494 pp.
- Fowler, S.W., and M.L. Unlu. 1978. Factors affecting bioaccumulation and elimination of arsenic in the shrimp *Lysmata seticudata*. Chemosphere 9:711-720.
- Golder Associates, Inc. Dec. 1987. Environmental audit investigation of A.J. Mine Rock Dump, Juneau, Alaska. Submitted to Bank of CA. Seattle, WA.
- Hall, R.A., E.G. Zook, and G.M. Meaburn. 1978. National Marine Fisheries Service Survey of Trace Elements in the Fishery Resource. NOAA Tech. Rep. NMFS SSRF - 721.
- Jenkins, D.W. 1980. Biological Monitoring of Toxic Trace Metals. Vol. 2. Toxic Trace Metals in Plants and Animals of the World. Part I - II.
- Knowlton, M.F., T.P. Boyle, and J.R. Jones. 1983. Uptake of lead from aquatic sediment by submersed macrophytes and crayfish. Arch. Environ. Contam. Toxicol. 12:535-541.
- Leatherland, T.M., and J.D. Burton. 1974. The occurrence of some trace metals in coastal organisms with particular reference to the Solent region. J. Marine Biol. Assn. UK. 54:457-468.
- Long, E.R. and L.G. Morgan. 1990. The potential for biological effects of sediment-sorbed contaminants tested in the National Status and Trends Program. NOAA Tech. Memo. NOS OMA 52. Seattle, WA. 175 pp.
- Long, E.R., D.D. MacDonald, S.L. Smith and F.D. Calder. 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ. Manage. 19(1)81-97.

- Lowe, T.P., T.W. May, W.G. Brumbaugh, and D.A. Kane. 1985. National Contaminant Biomonitoring Program: Concentrations of seven elements in fresh-water fish, 1978-1981. Arch. Environ. Contam. Toxicol. 14:363-388.
- Lunde, G. 1977. Occurrence and transformation of arsenic in the marine environment. Environ. Health Perspec. 19(47-52).
- Moore, J. editor. 1990. PACF Reference Manual. June 1990. Patuxent Analytical Control Facility, USFWS, Laurel, MD.
- NOAA. 1987. A summary of selected data on chemical contaminants in tissues collected during 1984, 1985, and 1986. NOAA Tech. Memo. NOS OMA 38.
- O'Connor, T.P. 1992. Mussel Watch Recent Trends in Coastal Environmental Quality. NOAA. 46p.
- O'Connor, T.P. and C.N. Ehler. 1991. Results from the NOAA National Status and Trends Program on Distribution and Effects of Chemical Contamination in the Coastal and Estuarine United States. Environ. Monitor. and Assmt. 17:33-49.
- Robinson-Wilson, E.F. 1986 (unpub. mss.). Klag Bay Study. USFWS, Juneau, Alaska.
- Robinson-Wilson, E.F., and G. Malinkey. October 1985 (unpub. mss.). Trace metals contamination at an ore loading facility in Skagway, Alaska. USFWS and ADEC, Juneau, Alaska. 17 pp.
- Rudis, D. 1994. An investigation of Metals in Sediment and Biota of Marine Ways Bay at U.S. Coast Guard Base Ketchikan. Prepared for U.S. Coast Guard, Engineering Div. Juneau, AK. USFWS, ES, Juneau, AK 19 p. and app.
- SAS Institute Inc. 1985. SAS user's guide: statistics. Version 5. SAS Inst. Inc., Cary, N.C. 956pp.
- Sims, R.R. Jr., and B.J. Presley. 1976. Heavy metal concentrations in organisms from an actively dredged Texas bay. Bull. Environ. Contam. & Toxicol. 16:520-527.
- Sorensen, E.M. 1991. Metal Poisoning in Fish. CRC Press. 374 pp.
- Stone, D. and B. Stone. 1980. Hard Rock Gold, the Story of the Great Mines That Were the Heartbeat of Juneau. Seattle, WA. Vanguard Press.
- Tetra Tech, Inc. 1985. Commencement Bay nearshore/tideflats remedial investigation. Vol.3. Appendices I-V, TC-3752, 371 pp. Vol.4. Appendices VI-XV. 556pp. Bellevue, WA: Tetra Tech, Inc.

USFWS, 1994. Gold Creek Fish Kill - March 3, 1994. Metals Residues in Dolly Varden. 9 p.

Versar, Inc. 1989. Site Investigation of Selected Mine Sites near Juneau, Alaska. Prepared for the City and Borough of Juneau and Alaska Electric and Power Company. Job No. 6147.1.

Walsh, D.F., B.L. Berger, and J.R. Bean. 1977. Residues in fish, wildlife, and estuaries. Mercury, arsenic, lead, cadmium, and selenium residues in fish, 1971-1973. National Pesticide Monitoring Program. Pesticide Monitor. J. 2(1):5-34.

Wilkinson, L. 1990. SYGRAPH: The system for graphics. SYSTAT, Inc. Evanston, IL

## Appendix A

Latitude and longitude of sediment sampling stations in Gastineau Channel.

| <u>Transect</u> | <u>Station</u> | <u>Latitude</u> | <u>Longitude</u> | <u>Nearby Location</u> |
|-----------------|----------------|-----------------|------------------|------------------------|
| 5               | D              | 58.2946         | 134.4218         | West Juneau            |
| 5               | N              | 58.2955         | 134.4194         |                        |
| 5               | X              | 58.2963         | 134.4175         |                        |
| 5               | J              | 58.2973         | 134.4153         | Government Dock        |
| 4               | D              | 58.2846         | 134.3999         | Douglas Shore          |
| 4               | N              | 58.2851         | 134.3987         |                        |
| 4               | X              | 58.2856         | 134.3977         |                        |
| 4               | J              | 58.2860         | 134.3967         | Rock Dump              |
| 3               | D              | 58.2760         | 134.3790         | Sandy Beach            |
| 3               | N              | 58.2773         | 134.3765         |                        |
| 3               | X              | 58.2789         | 134.3737         |                        |
| 3               | J              | 58.2810         | 134.3702         | Snowslide Cr.          |
| 2               | D              | 58.2500         | 134.3311         | Douglas Is.            |
| 2               | N              | 58.2520         | 134.3268         |                        |
| 2               | X              | 58.2542         | 134.3221         |                        |
| 2               | J              | 58.2560         | 134.3193         | Sheep Cr. Delta        |
| 1               | D              | 58.2222         | 134.2808         | Douglas Is.            |
| 1               | N              | 58.2238         | 134.2771         |                        |
| 1               | X              | 58.2260         | 134.2726         |                        |
| 1               | J              | 58.2278         | 134.2671         | Dupont Pier            |

Appendix B

Fish samples from Gastineau Channel and Ready Bullion Creek, 1991 - number in composite sample, species, percent moisture and total length.

| Sample Number | Number of Fish | Species* | Percent Moisture | Total Length (cm) |      |           |
|---------------|----------------|----------|------------------|-------------------|------|-----------|
|               |                |          |                  | Min.              | Max. | $\bar{x}$ |
| T01           | 2              | RS       | 78.2             | 10.8              | 30.3 | 20.6      |
| T02           | 2              | FS       | 78.4             | 15.2              | 10.1 | 12.6      |
| T05           | 7              | SC       | 81.3             | 9.5               | 22   | 12.8      |
| T06A          | 5              | FS       | 78.4             | 14                | 32   | 20.9      |
| T06B          | 5              | FS       | 78.8             |                   |      |           |
| T07A          | 2              | YF       | 76.4             | 29                | 30   | 29.5      |
| T09A          | 3              | SF       | 80.5             | 35                | 38   | 36.3      |
| T09B          | 3              | SF       | 78.1             |                   |      |           |
| T10           | 15             | EP       | 81.1             | 14                | 23   | 17.5      |
| T13           | >50            | SH       | 75.6             | -                 | -    | -         |
| RB01          | 1              | DV       | 75.7             | 13.9              | -    | -         |
| RB02          | 6              | SS       | 70.2             | 6.0               | 8.7  | 6.9       |
| RB03          | 7              | SS       | 66.3             | 6.0               | 9.1  | 7.1       |

\*RS = rock sole  
 FS = flathead sole  
 YS = yellowfin sole  
 SF = starry flounder

SC = sculpin species  
 EP = shortfin eelpout  
 SH= shrimp species

DV = Dolly Varden  
 SS = sculpin species

## Appendix C

Concentration (ppm, DW) of arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb), selenium (Se), and zinc (Zn) in Gastineau Channel sediment samples.

| Element | Station | As   | Cd    | Cu   | Hg    | Pb   | Se    | Zn   |
|---------|---------|------|-------|------|-------|------|-------|------|
| 1       | J       | 5.84 | 0.616 | 22.7 | 0.098 | 24.3 | 1.02  | 65.0 |
| 1       | J       | 6.36 | 0.092 | 23.2 | 0.098 | 18.5 | 1.13  | 64.6 |
| 1       | J       | 7.86 | 0.084 | 19.4 | 0.098 | 14.1 | 0.970 | 53.1 |
| 1       | X       | 9.90 | 0.122 | 27.7 | 0.136 | 30.5 | 0.750 | 85.3 |
| 1       | X       | 11.1 | 0.085 | 25.4 | 0.135 | 22.8 | 0.690 | 70.9 |
| 1       | X       | 8.15 | 0.062 | 25.1 | 0.139 | 22.6 | 0.640 | 70.3 |
| 1       | N       | 17.0 | 0.126 | 36.6 | 0.359 | 38.1 | 0.950 | 94.2 |
| 1       | N       | 9.33 | 0.113 | 28.2 | 0.207 | 28.5 | 0.580 | 155. |
| 1       | N       | 11.1 | 0.241 | 58.7 | 0.499 | 62.3 | 0.750 | 73.5 |
| 1       | D       | 9.02 | 0.103 | 24.5 | 0.220 | 30.2 | 0.483 | 72.8 |
| 1       | D       | 9.19 | 0.079 | 25.8 | 0.220 | 32.6 | 0.530 | 73.5 |
| 1       | D       | 9.62 | 0.086 | 26.7 | 0.224 | 30.0 | 0.560 | 75.4 |
| 2       | J       | 18.8 | 0.243 | 48.6 | 0.154 | 34.6 | 1.08  | 102. |
| 2       | J       | 17.4 | 0.254 | 47.3 | 0.163 | 38.7 | 0.980 | 108. |
| 2       | J       | 18.8 | 0.304 | 49.5 | 0.162 | 37.6 | 1.32  | 117. |
| 2       | X       | 19.6 | 0.244 | 54.5 | 0.300 | 55.5 | 1.30  | 127. |
| 2       | X       | 18.6 | 0.262 | 54.4 | 0.301 | 57.4 | 1.04  | 128. |
| 2       | X       | 19.0 | 0.235 | 54.5 | 0.298 | 55.8 | 0.770 | 149. |
| 2       | N       | 20.0 | 0.207 | 57.4 | 0.333 | 61.2 | 0.930 | 127. |
| 2       | N       | 18.9 | 0.246 | 57.3 | 0.332 | 58.1 | 1.05  | 123. |
| 2       | N       | 20.2 | 0.238 | 60.2 | 0.372 | 62.2 | 0.980 | 130. |
| 2       | D       | 18.1 | 0.384 | 51.4 | 0.366 | 65.8 | 0.890 | 116. |
| 2       | D       | 18.2 | 0.414 | 55.8 | 0.399 | 75.0 | 1.02  | 119. |
| 2       | D       | 15.2 | 0.248 | 39.1 | 0.277 | 45.7 | 0.930 | 90.5 |
| 3       | J       | 13.1 | 3.12  | 71.5 | 0.098 | 35.8 | 0.710 | 169. |
| 3       | J       | 79.2 | 3.96  | 34.4 | 0.099 | 30.1 | 0.620 | 242. |
| 3       | J       | 50.1 | 2.08  | 51.9 | 0.099 | 148. | 1.01  | 162. |
| 3       | X       | 49.9 | 1.13  | 58.2 | 0.134 | 63.7 | 1.26  | 165. |
| 3       | X       | 58.4 | 1.44  | 60.1 | 0.147 | 65.8 | 1.19  | 188. |
| 3       | X       | 44.6 | 1.37  | 58.4 | 0.148 | 68.4 | 1.22  | 189. |
| 3       | N       | 27.7 | 0.922 | 70.6 | 0.265 | 82.8 | 1.16  | 170. |
| 3       | N       | 30.7 | 0.738 | 70.8 | 0.268 | 83.9 | 1.04  | 166. |
| 3       | N       | 31.2 | 0.750 | 69.1 | 0.267 | 78.5 | 1.38  | 158. |
| 3       | D       | 20.7 | 0.456 | 76.9 | 0.496 | 64.2 | 1.35  | 128. |
| 3       | D       | 19.3 | 0.431 | 68.9 | 0.349 | 56.9 | 1.01  | 118. |
| 3       | D       | 19.5 | 0.411 | 65.4 | 0.132 | 53.3 | 0.810 | 113. |
| 4       | J       | 37.1 | 1.04  | 46.5 | 0.106 | 69.4 | 0.870 | 139. |
| 4       | J       | 33.5 | 0.751 | 50.4 | 0.107 | 65.9 | 0.820 | 137. |
| 4       | J       | 35.7 | 1.09  | 51.1 | 0.115 | 76.2 | 0.950 | 153. |
| 4       | X       | 17.8 | 0.549 | 45.0 | 0.121 | 48.7 | 0.850 | 123. |
| 4       | X       | 29.1 | 0.954 | 46.8 | 0.402 | 55.7 | 0.890 | 128. |
| 4       | X       | 29.0 | 0.524 | 52.5 | 0.429 | 55.0 | 0.870 | 120. |

- continued -

Appendix C (continued). Concentration (ppm, DW) of arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb), selenium (Se), and zinc (Zn) in Gastineau Channel sediment samples.

| Element | Station | As   | Cd    | Cu   | Hg    | Pb   | Se    | Zn   |
|---------|---------|------|-------|------|-------|------|-------|------|
| 4       | N       | 28.3 | 1.03  | 52.7 | 0.135 | 67.7 | 0.940 | 139. |
| 4       | N       | 27.1 | 0.796 | 54.5 | 0.098 | 73.2 | 0.930 | 133. |
| 4       | D       | 16.2 | 0.533 | 51.9 | 0.150 | 51.2 | 0.720 | 112. |
| 4       | D       | 17.9 | 0.543 | 47.9 | 0.187 | 55.3 | 0.820 | 116. |
| 4       | D       | 19.2 | 0.426 | 50.0 | 0.162 | 51.7 | 1.23  | 117. |
| 5       | J       | 23.0 | 0.507 | 72.8 | 0.244 | 77.6 | 1.20  | 155. |
| 5       | J       | 26.2 | 0.582 | 73.8 | 0.338 | 82.8 | 1.06  | 158. |
| 5       | J       | 28.4 | 0.542 | 76.5 | 0.546 | 81.2 | 1.23  | 156. |
| 5       | X       | 23.7 | 0.544 | 73.4 | 0.261 | 72.9 | 1.32  | 156. |
| 5       | X       | 24.0 | 0.470 | 72.0 | 0.246 | 71.0 | 1.34  | 147. |
| 5       | X       | 24.0 | 0.514 | 71.1 | 0.239 | 70.0 | 1.27  | 150. |
| 5       | N       | 15.0 | 0.458 | 51.0 | 0.248 | 52.8 | 1.09  | 117. |
| 5       | N       | 12.4 | 0.345 | 45.7 | 0.164 | 45.8 | 0.810 | 97.3 |
| 5       | N       | 11.2 | 0.282 | 38.7 | 0.134 | 32.3 | 0.650 | 69.6 |
| 5       | D       | 13.6 | 0.292 | 47.5 | 0.111 | 35.1 | 0.740 | 89.1 |
| 5       | D       | 12.1 | 0.286 | 103. | 0.116 | 36.8 | 0.490 | 111. |
| 5       | D       | 13.1 | 0.371 | 47.1 | 0.138 | 40.3 | 0.610 | 96.1 |

Appendix D

Laboratory Quality Assurance Quality Control data

Catalog: 7040005

Lab Name: RTI

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PROCEDURAL BLANKS

| Analyte | Lab Sample Number | Result Total UG |
|---------|-------------------|-----------------|
| As      | 124351            | .09             |
|         | 124352            | .11             |
|         | 124353            | .03             |
|         | 124354            | 0               |
|         | 124356            | 0               |
| Cd      | 124351            | 0               |
|         | 124352            | .09             |
|         | 124353            | 0               |
|         | 124356            | 0               |
| Cu      | 124351            | .21             |
|         | 124352            | .15             |
|         | 124353            | .19             |
|         | 124354            | .22             |
|         | 124355            | .16             |
|         | 124356            | .37             |
| Hg      | 124351            | 0               |
|         | 124352            | 0               |
|         | 124353            | 0               |
|         | 124354            | 0               |
|         | 124356            | 0               |
| Pb      | 124351            | 4.46            |
|         | 124352            | 0               |
|         | 124353            | .33             |
|         | 124354            | 1.16            |
|         | 124355            | .33             |
|         | 124356            | 0               |
| Se      | 124351            | .04             |
|         | 124352            | .12             |
|         | 124353            | .03             |
|         | 124354            | .08             |

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PROCEDURAL BLANKS (Cont.)

| Analyte | Lab Sample Number | Result Total UG |
|---------|-------------------|-----------------|
| Se      | 124356            | .06             |
| Zn      | 124351            | 3.65            |
|         | 124352            | 3.45            |
|         | 124353            | .4              |
|         | 124354            | .28             |
|         | 124355            | .41             |
|         | 124356            | .24             |

Appendix D. Laboratory quality assurance quality control data. (continued)

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DUPLICATES

| Analyte | Sample Number | Sample Matrix | Initial Result (ppm / %) | Duplicate Result (ppm / %) | Average  | Relative % Difference |
|---------|---------------|---------------|--------------------------|----------------------------|----------|-----------------------|
| As      | 9101S01A      | Sediments     | 5.84 Dry                 | 5.89 Dry                   | 5.865    | 0.85                  |
|         | 9101S09B      | Sediments     | 79.2 Dry                 | 76.1 Dry                   | 77.65    | 3.99                  |
|         | 9101S10C      | Sediments     | 44.6 Dry                 | 46.4 Dry                   | 45.5     | 3.96                  |
|         | 9101S18A      | Sediments     | 23 Dry                   | 24.6 Dry                   | 23.8     | 6.72                  |
|         | 9101T01       | Whole Body    | 3.76 Dry                 | 4.36 Dry                   | 4.06     | 14.78                 |
| Cd      | 9101S01A      | Sediments     | .616 Dry                 | .667 Dry                   | 0.6415   | 7.95                  |
|         | 9101S09B      | Sediments     | 3.96 Dry                 | 3.87 Dry                   | 3.915    | 2.3                   |
|         | 9101S10C      | Sediments     | 1.37 Dry                 | 1.34 Dry                   | 1.355    | 2.21                  |
|         | 9101S18A      | Sediments     | .507 Dry                 | .557 Dry                   | 0.532    | 9.4                   |
|         | 9101T01       | Whole Body    | < .0499 Dry              | < .0492 Dry                | 0.024775 | 1.41                  |
| Cu      | 9101S01A      | Sediments     | 22.7 Dry                 | 21.4 Dry                   | 22.05    | 5.9                   |
|         | 9101S09B      | Sediments     | 34.4 Dry                 | 36.3 Dry                   | 35.35    | 5.37                  |
|         | 9101S10C      | Sediments     | 58.4 Dry                 | 64.6 Dry                   | 61.5     | 10.08                 |
|         | 9101S18A      | Sediments     | 72.8 Dry                 | 72 Dry                     | 72.4     | 1.1                   |
|         | 9101T01       | Whole Body    | 4.04 Dry                 | 4.63 Dry                   | 4.335    | 13.61                 |
|         | 9101T068      | Whole Body    | 5.19 Dry                 | 5.17 Dry                   | 5.18     | 0.39                  |
| Hg      | 9101S01A      | Sediments     | < .0984 Dry              | < .0994 Dry                | 0.04945  | 1.01                  |
|         | 9101S09B      | Sediments     | < .0986 Dry              | < .0984 Dry                | 0.04925  | 0.2                   |
|         | 9101S10C      | Sediments     | .148 Dry                 | .155 Dry                   | 0.1515   | 4.62                  |
|         | 9101S18A      | Sediments     | .244 Dry                 | .253 Dry                   | 0.2485   | 3.62                  |
|         | 9101T01       | Whole Body    | .21 Dry                  | .268 Dry                   | 0.239    | 24.27                 |
| Pb      | 9101S01A      | Sediments     | 24.3 Dry                 | 22.3 Dry                   | 23.3     | 8.58                  |
|         | 9101S09B      | Sediments     | 30.1 Dry                 | 28.3 Dry                   | 29.2     | 6.16                  |
|         | 9101S10C      | Sediments     | 68.4 Dry                 | 67.1 Dry                   | 67.75    | 1.92                  |
|         | 9101S18A      | Sediments     | 77.6 Dry                 | 75.1 Dry                   | 76.35    | 3.27                  |
|         | 9101T01       | Whole Body    | .898 Dry                 | .758 Dry                   | 0.828    | 16.91                 |
| Se      | 9101S01A      | Sediments     | 1.02 Dry                 | .7 Dry                     | 0.86     | 37.21                 |
|         | 9101S09B      | Sediments     | .62 Dry                  | .62 Dry                    | 0.62     | 0                     |
|         | 9101S10C      | Sediments     | 1.22 Dry                 | 1.17 Dry                   | 1.195    | 4.18                  |

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DUPLICATES (Cont.)

| Analyte | Sample Number | Sample Matrix | Initial Result (ppm / %) | Duplicate Result (ppm / %) | Average | Relative % Difference |
|---------|---------------|---------------|--------------------------|----------------------------|---------|-----------------------|
| Se      | 9101S18A      | Sediments     | 1.2 Dry                  | 1.28 Dry                   | 1.24    | 6.45                  |
|         | 9101T01       | Whole Body    | .9 Dry                   | .78 Dry                    | 0.84    | 14.29                 |
| Zn      | 9101S01A      | Sediments     | 65 Dry                   | 58 Dry                     | 61.5    | 11.38                 |
|         | 9101S09B      | Sediments     | 242 Dry                  | 358 Dry                    | 300     | 38.67                 |
|         | 9101S10C      | Sediments     | 189 Dry                  | 187 Dry                    | 188     | 1.06                  |
|         | 9101S18A      | Sediments     | 155 Dry                  | 154 Dry                    | 154.5   | 0.65                  |
|         | 9101T01       | Whole Body    | 76.4 Dry                 | 78.5 Dry                   | 77.45   | 2.71                  |
|         | 9101T068      | Whole Body    | 77.5 Dry                 | 80.8 Dry                   | 79.15   | 4.17                  |

Appendix D. Laboratory quality assurance quality control data. (continued)

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Lab Name: RTI

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Purchase Order: 85800-1-3461

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REFERENCE MATERIALS

| Analyte | Lab Sample Number | S.R.M. ID   | S.R.M. Name            | * Certified Reference Value (ppm / %) | 95% Confidence Interval | Result (ppm / %) | Percent Recovery |
|---------|-------------------|-------------|------------------------|---------------------------------------|-------------------------|------------------|------------------|
| As      | 124361            | NIST 2704   | Buffalo River Sediment | 23.4 Dry                              | .8                      | 20 Dry           | 85.47            |
|         | 124362            | NIST 2704   | Buffalo River Sediment | 23.4 Dry                              | .8                      | 18.6 Dry         | 79.49            |
|         | 124363            | NIST 2704   | Buffalo River Sediment | 23.4 Dry                              | .8                      | 16.3 Dry         | 69.66            |
|         | 124981            | NRCC DOLT-1 | Dogfish Liver          | 10.1 Dry                              | 1.4                     | 8.69 Dry         | 86.04            |
| Cd      | 124361            | NIST 2704   | Buffalo River Sediment | 3.45 Dry                              | .22                     | 3.63 Dry         | 105.22           |
|         | 124362            | NIST 2704   | Buffalo River Sediment | 3.45 Dry                              | .22                     | 3.82 Dry         | 110.72           |
|         | 124363            | NIST 2704   | Buffalo River Sediment | 3.45 Dry                              | .22                     | 3.56 Dry         | 103.19           |
|         | 124981            | NRCC DOLT-1 | Dogfish Liver          | 4.18 Dry                              | .28                     | 3.74 Dry         | 89.47            |
| Cu      | 124361            | NIST 2704   | Buffalo River Sediment | 98.6 Dry                              | 5                       | 91.3 Dry         | 92.6             |
|         | 124362            | NIST 2704   | Buffalo River Sediment | 98.6 Dry                              | 5                       | 97.7 Dry         | 99.09            |
|         | 124363            | NIST 2704   | Buffalo River Sediment | 98.6 Dry                              | 5                       | 86.7 Dry         | 87.93            |
|         | 124364            | NIST 2704   | Buffalo River Sediment | 98.6 Dry                              | 5                       | 93.8 Dry         | 95.13            |
|         | 124981            | NRCC DOLT-1 | Dogfish Liver          | 20.8 Dry                              | 1.2                     | 22.3 Dry         | 107.21           |
|         | 124971            | NRCC DORM-1 | Dogfish Muscle         | 5.22 Dry                              | .33                     | 6.07 Dry         | 116.28           |
| Hg      | 124361            | NIST 2704   | Buffalo River Sediment | 1.44 Dry                              | .07                     | 1.35 Dry         | 93.75            |
|         | 124362            | NIST 2704   | Buffalo River Sediment | 1.44 Dry                              | .07                     | 1.35 Dry         | 93.75            |
|         | 124363            | NIST 2704   | Buffalo River Sediment | 1.44 Dry                              | .07                     | 1.28 Dry         | 88.89            |
|         | 124971            | NRCC DORM-1 | Dogfish Muscle         | .798 Dry                              | .074                    | .72 Dry          | 90.23            |
| Pb      | 124361            | NIST 2704   | Buffalo River Sediment | 161 Dry                               | 17                      | 154 Dry          | 95.65            |
|         | 124362            | NIST 2704   | Buffalo River Sediment | 161 Dry                               | 17                      | 156 Dry          | 96.89            |
|         | 124363            | NIST 2704   | Buffalo River Sediment | 161 Dry                               | 17                      | 143 Dry          | 88.82            |
|         | 124364            | NIST 2704   | Buffalo River Sediment | 161 Dry                               | 17                      | 156 Dry          | 96.89            |
|         | 124981            | NRCC DOLT-1 | Dogfish Liver          | 1.36 Dry                              | .29                     | 1.45 Dry         | 106.62           |
| Se      | 124361            | NIST 2704   | Buffalo River Sediment | 1.1 Dry                               |                         | 1.18 Dry         | 107.27           |
|         | 124362            | NIST 2704   | Buffalo River Sediment | 1.1 Dry                               |                         | .99 Dry          | 90               |
|         | 124363            | NIST 2704   | Buffalo River Sediment | 1.1 Dry                               |                         | 1.04 Dry         | 94.55            |

\* Only certified analytes list a confidence interval - all others are considered reference values.

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REFERENCE MATERIALS (Cont.)

| Analyte | Lab Sample Number | S.R.M. ID   | S.R.M. Name            | * Certified Reference Value (ppm / %) | 95% Confidence Interval | Result (ppm / %) | Percent Recovery |
|---------|-------------------|-------------|------------------------|---------------------------------------|-------------------------|------------------|------------------|
| Se      | 124981            | NRCC DOLT-1 | Dogfish Liver          | 7.34 Dry                              | .42                     | 6.52 Dry         | 88.83            |
| Zn      | 124361            | NIST 2704   | Buffalo River Sediment | 438 Dry                               | 12                      | 387 Dry          | 88.36            |
|         | 124362            | NIST 2704   | Buffalo River Sediment | 438 Dry                               | 12                      | 413 Dry          | 94.29            |
|         | 124363            | NIST 2704   | Buffalo River Sediment | 438 Dry                               | 12                      | 368 Dry          | 84.02            |
|         | 124364            | NIST 2704   | Buffalo River Sediment | 438 Dry                               | 12                      | 399 Dry          | 91.1             |
|         | 124981            | NRCC DOLT-1 | Dogfish Liver          | 92.5 Dry                              | 2.3                     | 90.7 Dry         | 98.05            |
|         | 124971            | NRCC DORM-1 | Dogfish Muscle         | 21.3 Dry                              | 1                       | 20.3 Dry         | 95.31            |

\* Only certified analytes list a confidence interval - all others are considered reference values.

Appendix D. Laboratory quality assurance quality control data. (continued)

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SPIKE RECOVERIES

| Analyte | Sample Number | Sample Matrix | Spike Level (ppm / %) | Amount Recovered (ppm / %) | * Spike / Background | Percent Recovery |
|---------|---------------|---------------|-----------------------|----------------------------|----------------------|------------------|
| As      | 9101S01C      | Sediments     | 20.6 Dry              | 20.44 Dry                  | 2.62                 | 99.22            |
|         | 9101S11B      | Sediments     | 20.3 Dry              | 22.9 Dry                   | 0.66                 | 112.81           |
|         | 9101S18B      | Sediments     | 20.4 Dry              | 21.4 Dry                   | 0.78                 | 104.9            |
|         | 9101T05       | Whole Body    | 20.6 Dry              | 18.95 Dry                  | 11.14                | 91.99            |
| Cd      | 9101S01C      | Sediments     | 197 Dry               | 204.916 Dry                | 2345.24              | 104.02           |
|         | 9101S09C      | Sediments     | 197 Dry               | 231.92 Dry                 | 94.71                | 117.73           |
|         | 9101S11B      | Sediments     | 197 Dry               | 214.262 Dry                | 266.94               | 108.76           |
|         | 9101S18B      | Sediments     | 198 Dry               | 199.418 Dry                | 340.21               | 100.72           |
|         | 9101T05       | Whole Body    | 198 Dry               | 202.936 Dry                | 3093.75              | 102.49           |
| Cu      | 9101S01C      | Sediments     | 200 Dry               | 219.6 Dry                  | 10.31                | 109.8            |
|         | 9101S09C      | Sediments     | 197 Dry               | 225.1 Dry                  | 3.8                  | 114.26           |
|         | 9101S11B      | Sediments     | 197 Dry               | 216.2 Dry                  | 2.78                 | 109.75           |
|         | 9101S18B      | Sediments     | 198 Dry               | 210.2 Dry                  | 2.68                 | 106.16           |
|         | 9101T05       | Whole Body    | 200 Dry               | 225.58 Dry                 | 36.9                 | 112.79           |
| Hg      | 9101S01C      | Sediments     | 2 Dry                 | 2.2 Dry                    | 20.04                | 110              |
|         | 9101S09C      | Sediments     | 1.97 Dry              | 1.92 Dry                   | 19.98                | 97.46            |
|         | 9101S11B      | Sediments     | 1.97 Dry              | 1.922 Dry                  | 7.35                 | 97.56            |
|         | 9101S18B      | Sediments     | 1.98 Dry              | 2.012 Dry                  | 5.86                 | 101.62           |
|         | 9101T05       | Whole Body    | 2 Dry                 | 2.43 Dry                   | 20.04                | 121.5            |
| Pb      | 9101S01C      | Sediments     | 998 Dry               | 1165.9 Dry                 | 70.78                | 116.82           |
|         | 9101S09C      | Sediments     | 986 Dry               | 1062 Dry                   | 6.66                 | 107.71           |
|         | 9101S11B      | Sediments     | 984 Dry               | 1166.1 Dry                 | 11.73                | 118.51           |
|         | 9101S18B      | Sediments     | 990 Dry               | 1177.2 Dry                 | 11.96                | 118.91           |
|         | 9101T05       | Whole Body    | 1160 Dry              | 1179.353 Dry               | 1792.89              | 101.67           |
| Se      | 9101S01C      | Sediments     | 20.4 Dry              | 20.63 Dry                  | 21.03                | 101.13           |
|         | 9101S09C      | Sediments     | 20.1 Dry              | 19.69 Dry                  | 19.9                 | 97.96            |
|         | 9101S11B      | Sediments     | 20.1 Dry              | 18.86 Dry                  | 19.33                | 93.83            |

\* For a spike to be a valid measure of method accuracy, this ratio must be higher than 1.0.

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SPIKE RECOVERIES (Cont.)

| Analyte | Sample Number | Sample Matrix | Spike Level (ppm / %) | Amount Recovered (ppm / %) | * Spike / Background | Percent Recovery |
|---------|---------------|---------------|-----------------------|----------------------------|----------------------|------------------|
| Se      | 9101S18B      | Sediments     | 20.2 Dry              | 20.64 Dry                  | 19.06                | 102.18           |
|         | 9101T05       | Whole Body    | 20.4 Dry              | 20.33 Dry                  | 21.03                | 99.66            |
| Zn      | 9101S01C      | Sediments     | 200 Dry               | 215.9 Dry                  | 3.77                 | 107.95           |
|         | 9101S09C      | Sediments     | 197 Dry               | 156 Dry                    | 1.22                 | 79.19            |
|         | 9101S11B      | Sediments     | 197 Dry               | 199 Dry                    | 1.19                 | 101.02           |
|         | 9101S18B      | Sediments     | 198 Dry               | 220 Dry                    | 1.25                 | 111.11           |
|         | 9101T05       | Whole Body    | 200 Dry               | 221.3 Dry                  | 4.91                 | 110.65           |

\* For a spike to be a valid measure of method accuracy, this ratio must be higher than 1.0.

| <b>Appendix E. Metal concentrations (ppm, dry wt.) in blue mussels and cockles from the Treadwell Complex, Douglas Island, Alaska, 1991.</b> |                              |               |                        |               |               |
|--|------------------------------|---------------|------------------------|---------------|---------------|
| <b>ANALYTE</b>   | <b>MUSSEL</b>                | <b>COCKLE</b> | <b>ANALYTE</b>         | <b>MUSSEL</b> | <b>COCKLE</b> |
| <b>Arsenic (As)</b>  | 8.83                         | 9.67          | <b>Lead (Pb)</b>       | 1.48          | 3.00          |
|  | 8.74                         | 8.60          |                        | 1.67          | 1.69          |
|  | 11.40                        | 11.90         |                        | 1.48          | 1.91          |
|  | 9.13                         | 13.00         |                        | 1.34          | 1.76          |
|  | 8.40                         | 9.66          |                        | 1.30          | 2.27          |
|  | 10.20                        |               |                        | 2.61          |               |
| <b>Geometric mean</b>  | 9.40                         | 10.44         | <b>Geometric mean</b>  | 1.60          | 2.08          |
| <b>Arithmetic mean</b>   | 9.45                         | 10.57         | <b>Arithmetic mean</b> | 1.65          | 2.13          |
| <b>Count</b>   | 6.00                         | 5.00          | <b>Count</b>           | 6.00          | 5.00          |
| <b>Std. Dev</b>  | 1.14                         | 1.82          | <b>Std. Dev</b>        | 0.49          | 0.54          |
| <b>Cadmium (Cd)</b>  | 2.49                         | 0.62          | <b>Selenium (Se)</b>   | 2.36          | 2.48          |
|  | 2.73                         | 0.20          |                        | 2.19          | 1.93          |
|  | 3.64                         | 0.18          |                        | 2.66          | 3.00          |
|  | 1.66                         | 0.24          |                        | 2.18          | 2.12          |
|  | 1.79                         | 0.30          |                        | 2.26          | 1.66          |
|  | 2.86                         |               |                        | 2.34          |               |
| <b>Geometric mean</b>  | 2.44                         | 0.28          | <b>Geometric mean</b>  | 2.33          | 2.19          |
| <b>Arithmetic mean</b>   | 2.53                         | 0.31          | <b>Arithmetic mean</b> | 2.33          | 2.24          |
| <b>Count</b>   | 6.00                         | 5.00          | <b>Count</b>           | 6.00          | 5.00          |
| <b>Std. Dev</b>  | 0.73                         | 0.18          | <b>Std. Dev</b>        | 0.18          | 0.52          |
| <b>Copper (Cu)</b>   | 8.54                         | 7.00          | <b>Zinc (Zn)</b>       | 110.00        | 85.40         |
|  | 7.82                         | 5.86          |                        | 108.00        | 122.00        |
|  | 9.38                         | 7.93          |                        | 96.20         | 105.00        |
|  | 8.90                         | 12.00         |                        | 126.00        | 109.00        |
|  | 10.20                        | 4.43          |                        | 131.00        | 81.50         |
|  | 8.58                         |               |                        | 101.00        |               |
| <b>Geometric mean</b>  | 8.87                         | 7.04          | <b>Geometric mean</b>  | 111.34        | 99.43         |
| <b>Arithmetic mean</b>   | 8.90                         | 7.44          | <b>Arithmetic mean</b> | 112.03        | 100.58        |
| <b>Count</b>   | 6.00                         | 5.00          | <b>Count</b>           | 6.00          | 5.00          |
| <b>Std. Dev</b>  | 0.81                         | 2.86          | <b>Std. Dev</b>        | 13.77         | 16.91         |
| <b>Mercury (Hg)</b>  | below detection limits (0.2) |               |                        |               |               |

## Appendix F

Coefficients of variation for the replicated measurements of arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb), selenium (Se), and zinc (Zn) in Gastineau Channel sediment samples by transect (Tran) and station<sup>a</sup>.

| Element | Tran <sup>b</sup> | Station <sup>c</sup> |      |      |      | Average | Median |
|---------|-------------------|----------------------|------|------|------|---------|--------|
|         |                   | D                    | N    | X    | J    |         |        |
| As      | 5                 | 5.91                 | 15.1 | 0.73 | 10.5 | 12.8    | 7.41   |
|         | 4                 | 8.47                 | 3.06 | 25.7 | 5.12 |         |        |
|         | 3                 | 3.82                 | 6.34 | 13.7 | 69.8 |         |        |
|         | 2                 | 9.93                 | 3.55 | 2.6  | 4.41 |         |        |
|         | 1                 | 3.33                 | 32.2 | 15.3 | 15.7 |         |        |
| Cd      | 5                 | 15.0                 | 24.7 | 7.31 | 6.90 | 23.0    | 14.4   |
|         | 4                 | 13.0                 | 18.1 | 35.7 | 19.1 |         |        |
|         | 3                 | 5.21                 | 12.8 | 12.4 | 30.8 |         |        |
|         | 2                 | 25.4                 | 8.94 | 5.57 | 12.2 |         |        |
|         | 1                 | 13.8                 | 44.0 | 33.8 | 116. |         |        |
| Cu      | 5                 | 48.8                 | 13.7 | 1.61 | 2.57 | 10.7    | 4.67   |
|         | 4                 | 4.01                 | 2.38 | 8.14 | 5.02 |         |        |
|         | 3                 | 8.37                 | 1.32 | 1.77 | 35.3 |         |        |
|         | 2                 | 17.8                 | 2.82 | 0.11 | 2.28 |         |        |
|         | 1                 | 4.31                 | 38.3 | 5.46 | 9.49 |         |        |
| Hg      | 5                 | 11.8                 | 32.5 | 4.52 | 41.1 | 15.8    | 6.03   |
|         | 4                 | 11.4                 | 22.5 | 53.8 | 4.51 |         |        |
|         | 3                 | 56.2                 | 0.57 | 5.46 | 0.59 |         |        |
|         | 2                 | 18.2                 | 6.60 | 0.51 | 3.09 |         |        |
|         | 1                 | 1.04                 | 41.1 | 1.52 | 0.00 |         |        |
| Pb      | 5                 | 7.09                 | 23.9 | 2.07 | 3.31 | 14.8    | 6.42   |
|         | 4                 | 4.24                 | 5.52 | 7.26 | 7.43 |         |        |
|         | 3                 | 9.55                 | 3.49 | 3.57 | 93.3 |         |        |
|         | 2                 | 24.1                 | 3.53 | 1.82 | 5.74 |         |        |
|         | 1                 | 4.68                 | 40.5 | 17.8 | 27.0 |         |        |
| Se      | 5                 | 20.4                 | 26.2 | 2.75 | 7.80 | 13.4    | 7.91   |
|         | 4                 | 29.3                 | 0.76 | 2.30 | 7.45 |         |        |
|         | 3                 | 25.8                 | 14.5 | 2.87 | 26.2 |         |        |
|         | 2                 | 7.03                 | 6.11 | 25.6 | 15.5 |         |        |
|         | 1                 | 7.40                 | 24.4 | 7.94 | 7.87 |         |        |
| Zn      | 5                 | 11.3                 | 25.2 | 3.03 | 0.98 | 9.56    | 6.66   |
|         | 4                 | 2.30                 | 3.12 | 3.27 | 6.10 |         |        |
|         | 3                 | 6.38                 | 3.71 | 7.51 | 23.2 |         |        |
|         | 2                 | 14.4                 | 2.77 | 9.23 | 6.93 |         |        |
|         | 1                 | 1.82                 | 39.4 | 11.3 | 11.1 |         |        |

<sup>a</sup> CV = 100 SD / Mean; divide by sq.root(n) to estimate CV( $\bar{X}$ ).

<sup>b</sup> Transect 5 is most northern, transect 1 is most southern

<sup>c</sup> Station D is most western, station J is most eastern.

