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Trace Metals Contamination at an Ore Loading Facility in Skagway, Alaska

by

Everett F. Robinson-Wilson
Resource Contaminant Specialist
U.S. Fish & Wildlife Service
Juneau, Alaska

and

Gregg Malinkey
Alaska Department of Environmental Conservation
Juneau, Alaska

ABSTRACT

Trace metals contamination due to an ore loading facility in Skagway, Alaska were measured. Concentrations of lead, zinc, cadmium, copper, and mercury in marine sediments were found to exceed the values for the control area. The infauna found in the marine sediments was much reduced and diversity was correlated with the concentration of lead and zinc in the sediment. Lead and zinc concentrations in blue mussels (mytilus edulis) from the loading basin were significantly higher than concentration from mussels in the control area. The concentrations in the blue mussels paralleled that found in the sediments from the ore loading basin and control area.

INTRODUCTION

The effects of trace metals on aquatic biota in freshwater systems has been extensively studied (Doudoroff and Katz, 1953; McKim et al., 1975), however the effects of these same metals in marine systems has not been as extensively studied. This stems from the idea that the marine systems of the world are so large that trace metal contamination is not a problem. However problems that have occurred very recently have changed that perspective. The occurrence of Minamata Disease in Japanese people living around Minamata Bay was traced to the consumption of fish and shellfish contaminated with mercury from a vinyl chloride and acetaldehyde plant (Fujiki, M. 1980). Studies in Australia have documented increased trace metals concentrations in blue mussels near industrial discharges (Phillips, 1976). Similarly trace metals have been found to accumulate in biota surrounding sewage outfalls (Pringle, et al. 1968; Chow et al., 1976). These along with many other incidents have served to point out that marine waters are not infinite sinks for trace metals.

Recent studies have also shown marked changes in species composition (Lande, 1977; Wong et al., 1978; Nealler and Castolia, 1978; Brown et al., 1977) in marine areas that are contaminated by heavy metals. The discharge of contaminated waters or sediment into the marine environment has pointed out the pausity of data which we have to work with (Klapou and Lewis, 1979) and has lead to statements such as "The available data for total recoverable lead indicate that acute and chronic toxicity to saltwater aquatic life occur at concentrations as low as 668 and 25 ug/l, respectively, and would occur at lower concentrations among species that are more sensitive than those tested"

(U.S. EPA, 1980). The realization that trace metals in sediments are not sequestered from the environment has led to a whole new group of studies dealing with the chemistry of dredged contaminated sediments (Engler, 1979). The study presented here was initiated to determine the extent and severity of trace metal contamination from an ore loading facility in marine waters in Southeast Alaska.

Skagway is located 113 kilometers northeast of Juneau, Alaska, near the terminus of Stephens Passage. The harbor at Skagway includes two large ship berthing facilities, a state ferry berth and a small boat harbor. The northernmost berthing facility is owned by the White Pass and Yukon Railway and is used as a berthing facility for large ore carriers (Figure 1). Ore is loaded via a conveyer from a storage area. Winds blowing around the conveyer carry ore into the water surrounding the dock facility.

The extent of the contamination from the ore lost was studied both in the basin and in adjacent areas. Samples were therefore taken at five stations within the basin (Figure 1 - Stations 1-4 and 7) and five stations adjacent to the basin (Stations 5, 6 and 8-10). Four control stations (11-14), located in Nahku Bay were also sampled. Data pertinent to each station is listed in Table 1.

Three types of samples were taken at each station. They included 3 or 5 Smith-McIntyre oceanic dredge samples for infauna analysis, a water sample taken with a non-metallic Kemmerer Bottle and a sample of the sediment for trace metals analysis.

The infauna samples were washed through a series of screens consisting of 1.75 cm^2, 0.87 cm^2 amd 0.44 cm^2 mesh. All of the organisms in the first two screens were picked by hand and preserved with a 10% buffered formalin seawater solution. The formalin was decanted from the samples within a week and replaced with 90% ethanol. The portion of the sample left on the 0.44 cm^2 screen was preserved in 10% buffered formalin seawater solution and

was later examined using a binocular microscope. All organisms were subsequently transferred to 90% ethanol. Organisms were identified to species when possible and family or genus when no lower taxonomic grouping could be found. The Shannon Weaver diversity index was calculated for each sample (Pielou 1974).

Water samples were stored in pre-cleaned polyethylene bottles at less than $3^{o}C$ for five days and frozen for long term storage. Sediment samples were placed in polyethylene bags and stored frozen at less than -10^{o} C.

Dungeness crabs (Cancer magister), and yellowfin sole (Limanda aspera) were taken in crab pots set in the White Pass and Yukon basin and in the control area. The crabs and fish were removed from the pots, weighed, measured, placed in plastic bags and frozen. Blue mussels (Mytilus edulis) were taken by divers from pilings within the basin and from rocks within the control area. The mussels were allowed to depurate for 24 hours in clean water and were subsequently placed in polyethylene bags and frozen.

Sediment samples were dried to a constant weight at 60^{o} C. A subsample weighing 2 to 10 grams was placed in a beaker with concentrated nitric acid and digested at 60^{o} C overnight. The acid solution plus sediment was transferred to an oxidation tube and irridated with ultra-violet light until the solution cleared. The solution plus sediment was then centriguged at 2000-3000 RPM for one hour, pipetted into a vial and brought up to 100 mls with double distilled water.

Unfiltered water samples were treated with concentrated nitric acid to lower the pH to 2.5 for analysis of total recoverable copper, cadmium and lead the water samples for zinc analysis were inadvertently destroyed. Water samples for mercury analysis were not treated.

Blue mussels were thawed, scrubbed with a stiff brush to remove all the byssal threads and any other material adhering to the shell. The mussels were then measured to the nearest 0.1 cm and weighed. A group of 30 mussels between 5.5 and 7.0 cm was selected from each of the samples for further analysis. Each mussel selected for analysis was opened with a teflon spatula, the tissue was removed, and the shell and tissue were weighed separately. The shell and tissue were dried to a constant weight at $60^{o}C$, then reweighed, and the tissue was stored at -10^{o} C for trace metals analysis.

Shell volume was measured for each of the mussels in the subsample. Each half of the shell was filled with dried screened sand and the volume of the sand was measured. A condition index was calculated by dividing the dry tissue weight by the shell volume (Walne, 1970).

Each of the fish was partially thawed and filleted with a stainless steel knife, each fillet was skinned and washed with distilled water before it was refrozen. The livers were removed from each fish and refrozen. Muscle tissue was removed from each of the crabs and refrozen for later analysis.

Limits of detection for different matrices and elements and storage conditions may be found in table (2).

Muscle tissue from crabs, muscle and livers of fish, and whole soft tissues from mussels were analyzed for copper, cadmium, lead, mercury and zinc. All tissue samples were prepared for analysis in the same manner.

The tissue was freeze dried and ground to a powder with a mortar and pestle. Two to five grams of the powdered tissue was digested in concentrated nitric acid at a temperature of 60^{o} C for 6-8 hours and cooled at room temperature overnight. The solution was transferred to an oxidation tube, hydrogen peroxide was added and the sample was irradiated with ultra-violet light until the solution cleared. The solution was then brought to 100 mls with double distilled water and filtered to remove any residue

Analyses for lead, cadmium, copper and zinc in sediment and tissue were done using flame atomic absorption or graphite furnace methods depending upon the concentration in the matrix. Mercury analyses were done using cold vapor atomic absorption on a Perkin-Elmer Mercury Analyzer System.

Lead, cadmium and copper in water were analyzed using differential pulse anodic stripping voltametry with a Princeton Applied Research Model 374 Polarographic Analyzer and SDME 300 electrode assembly. Samples were run in duplicate and if the difference between the duplicates exceeded 10 percent, third and fourth readings were taken. Mercury was analyzed by cold vapor atomic absorption on a Perkin-Elmer Mercury Analyzer System.

Statistical differences were tested where three or more treatments were present using analysis of variance (ANOVA) programs available through SPSS (Nie et al., 1975). Differences between means were tested using a modified least significant difference test (LSD) to account for different numbers of observations in each cell. Where two means were compared a T-test adjusted for different numbers of observations in each cell was used. Differences were considered significant at $p \leq .05$.

RESULTS

Concentrations of lead, zinc, copper, cadmium and mercury were all significantly higher in marine sediment samples from within the Yukon and White Pass Basin than in samples from outside the basin or from the control area Table (3). Mean lead concentrations within the basin were over 40 times higher than those from the control area and approximately 7 times higher than mean lead concentrations from outside the basin. The mean lead concentrations from outside the basin were 6 times higher than the mean concentrations at the control site. Lead concentrations generally decreased as the distance from the ore loading facility increased. Mean zinc concentrations from within the basin were over 6 times higher than concentrations from the control area, however mean zinc concentrations outside the basin were slightly lower than those from the control area. Mean copper concentrations in sediments from within the basin were over 5 times higher than concentrations from the control area. Mean copper concentrations from outside the basin were 4 times higher than the control, but were not significantly different from the control. Mean mercury concentrations were over 20 times higher within the basin than at the control site. Mercury concentrations outside the basin area were not significantly higher than the control site although the mean was approximately 4 times higher than the control. Cadmium concentrations within the basin area were over twice as high as those at the control site. The mean cadmium concentration outside the basin was slightly lower than the mean concentration at the control site

Marine sediments within the basin are contaminated with lead, zinc, copper, mercury and cadmium. The area outside the main basin is contaminated with

lead, copper and mercury concentrations also appear to be elevated although they are not significantly higher than the concentrations from the control site.

Blue mussels (Mytilus edulis) taken by divers from the wooden piers in the White Pass and Yukon Basin had significantly higher lead and zinc, concentrations than did mussels from the control area Table (4). Mean lead concentrations in mussels from the White Pass and Yukon Basin exceeded the concentrations in mussels from the control area by nearly 40 times. Zinc concentrations were 5 times as high in the Basin as in the control area. The mean cadmium concentration was only slightly higher and the difference was not significant. Copper concentrations were not significantly different between the two sites.

Dungeness crab and yellowfin sole were captured both in the White Pass and Yukon Basin and in Nahku Bay which was the control area. No significant differences were found in any of the metals concentrations in the crabs or sole from within the basin compared to those from Nahku Bay Table (5).

Lead, copper, cadmium and mercury concentrations were measured in water, zinc samples were inadvertently lost before the analysis could be completed. Mean lead, copper and cadmium concentrations were all higher within the White Pass and Yukon Basin than at the control site Table (6). Lead concentrations in water were significantly higher within the basin than at the control site. Neither the copper nor the cadmium water concentrations were significantly different. Mercury concentrations were below the limits of detection in all of the water samples analyzed.

The condition index for mussels from within the basin area (mean of 2.75) was significantly lower than the condition index for mussels from the control area (mean of 4.00).

The infaunal samples from both the Yukon and White Pass Basin and Nahku Bay, the control area, contained mainly polychaete worms. No bivalves were taken in any of the dredge samples from within the White Pass and Yukon Basin. Bivalves (Macoma sp.) were first found at stations 9 and 10 which were outside the White Pass and Yukon Basin near the container ship loading facility. Bivalves (Macoma sp.) were taken in each of the samples from Nahku Bay, the control area. Diversity values for the stations within the basin were significantly lower than the diversity values for the stations outside the basin or the control stations Table (7). The diversity values for stations outside the harbor were also lower than for the control stations. Infauna diversity values were negatively correlated with the lead and zinc concentrations in the sediment (Figure 2). Similarly the number of organisms in each sample was signigicatly lower within the basin than just outside or at the control.

DISCUSSION

Marine sediments from throughout the world exhibit great variation in the concentration of each trace metal we are studying in this paper (Table 8). The lowest concentrations presented may be considered to be a baseline for uncontaminated areas, while the higher concentrations represent areas of known anthropogenic input. The mean concentrations of cadmium, copper, lead, mercury and zinc found within the White Pass and Yukon Basin are certainly greater than the lower concentrations, although they do not approach the highest concentrations. Lead and zinc concentrations within the basin are particularly high, both exceeding concentrations which are found at marine sludge disposal sites in the New York Bight and the lead concentration exceeding the highest concentration found near contaminated areas in Southern California. These results indicate that there is a severe problem in the basin with regard to the concentrations of lead, zinc and copper in the marine sediment. Lead concentrations in areas adjacent to the basin also appear to be elevated and are high enough to cause concern.

The contaminated sediment within the basin has resulted in a less diverse benthic infaunal population, and a shift toward more tolerant species such as polychaetes (Grassle and Grassle, 1974). Contaminated sediments containing much lower concentrations of the metals studied here were found to inhibit burrowing behavior in Macoma balthica (McGreer, 1979), therefore it is not suprising that no bivalves were caught in the grab samples taken within the basin. A number of fish , starry flounder (Platichthys stellatus), halibut (Hippoglossus stenolepsus) and yellowfin sole (Limanda aspera) along with dungeness (Cancer magister) and tanner crabs (Chionoecetes bairdi), were taken in crab pots set in the basin. The concentrations of trace metals in water in

the basin were significaltly higher than those at the control site, but were not as high as concentrations considered to be hazardous to aquatic marine life (U.S.EPA, 1980). Analysis of tissue from these animals indicated that they did not have higher concentrations of heavy metals than fish or crabs from the control areas. Since the fish and crabs are quite mobile and could move in and out of the contaminated area very easily they may not have remained in the contaminated areas long enough to accumulate metals. Furthermore, in other studies where marine fish have been exposed to high lead concentrations, the lead has been found to be associated with the skin and mucus of the fish (Phillips and Russo, 1978). Since we did not include these tissues in our analysis we may have missed the highest lead concentrations. Zinc has been shown to accumulate in marine fish both from water and food, however marine fishes are also able to eliminate zinc very quickly when they are in clean water. Therefore it is not at all suprising that the concentrations of lead and zinc in the fish tissue from the basin were not higher than the concentrations in tissue from the control site. Crustaceans have been shown to accumulate lead, however the major areas of concentration were in the shell not in the tissue (Knowlton et al., 1983).

The concentrations of lead and zinc in the blue mussels from the White Pass and Yukon Basin are very high when compared to the concentrations in the mussels from the control area. Mussels have been shown to accumulate lead from both food and water (Schulz-Blades, 1974). The bioaccumulation ratio (tissue concentration/water concentration) for the mussels with lead is approximately 143,000, which is very high. Such a high bioaccumulation ratio

leads one to suspect that a portion of the Pb concentration in the mussels is coming either from the food or from ingestion of particulate lead during the feeding process. The differences between concentrations in mussels from the basin and the control paralell the differences between the concentration of lead and zinc in the marine sediments. The lead concentration is approximately 40 times the concentration from the control and zinc is 5 times the control which is similar to the differences found in the sediment. Although the mussels were not buried in the sediment, they were close to the bottom and any disturbance of the bottom, by wave or current would carry the sediment to them. Even though the copper concentrations in the marine sediments of the basin were significantly higher than those at the control site, the copper concentrations in mussels were not significantly different. Phillips (1976) noted that the uptake of copper by Mytilus edulis was affected by the uptake of either zinc, cadmium or lead, but that the uptake of zinc, cadmium or lead was not affected by the uptake of copper. Stenner and Nickless (1974) also reported that copper concentrations in mussels could not be related to obvious areas of copper contamination. Phillips (1977) states that Mytilus edulis may not therefore be an acceptable indicator organism for copper.

The lower condition index for mussels found within the White Pass and Yukon Basin as compared to the mussels from Nahku Bay is a result of the high lead and zinc concentrations found in the mussels in the basin. High concentrtions of metals in the blue mussel are not uncommon in mussels from contaminated areas, mussels are apparently able to sequester certain metals in vesicles within cells (Coombs 1977). In this manner the metal is shunted away from major physiological processes and mussels may be able to accumulate high concentrations without dying. However heavy metals have been shown to reduce the growth rate of mussels (Widdows et al. 1981).

While the blue mussel is not an important commercial species it is consumed by a number of seabirds and has been shown to be a contributor to heavy metals contamination in seaducks (Vermeer and Peakall 1979). Furthermore it is harvested and consumed by some native people. The mussels may be an important vector for the movement of the heavy metals from the sediment to other biota.

The area of contamination in Skagway is realtively small at this time, however it is obvious that the Pb contamination is being spread further out into Lynn Canal. Furthermore dredging and disposal of the contaminated marine sediments will be a problem. The dredging of the basin would resuspend large amounts of highly toxic sediments and fish throughout the area would be exposed to very high lead and zinc concentrations. Furthermore disposal of such highly contaminated sediment would require special care.

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Figure 1. Sampling stations within the Yukon and White Pass Basin (Sta. 1-4 and 7) and outside (Sta. 5,6,8-10).

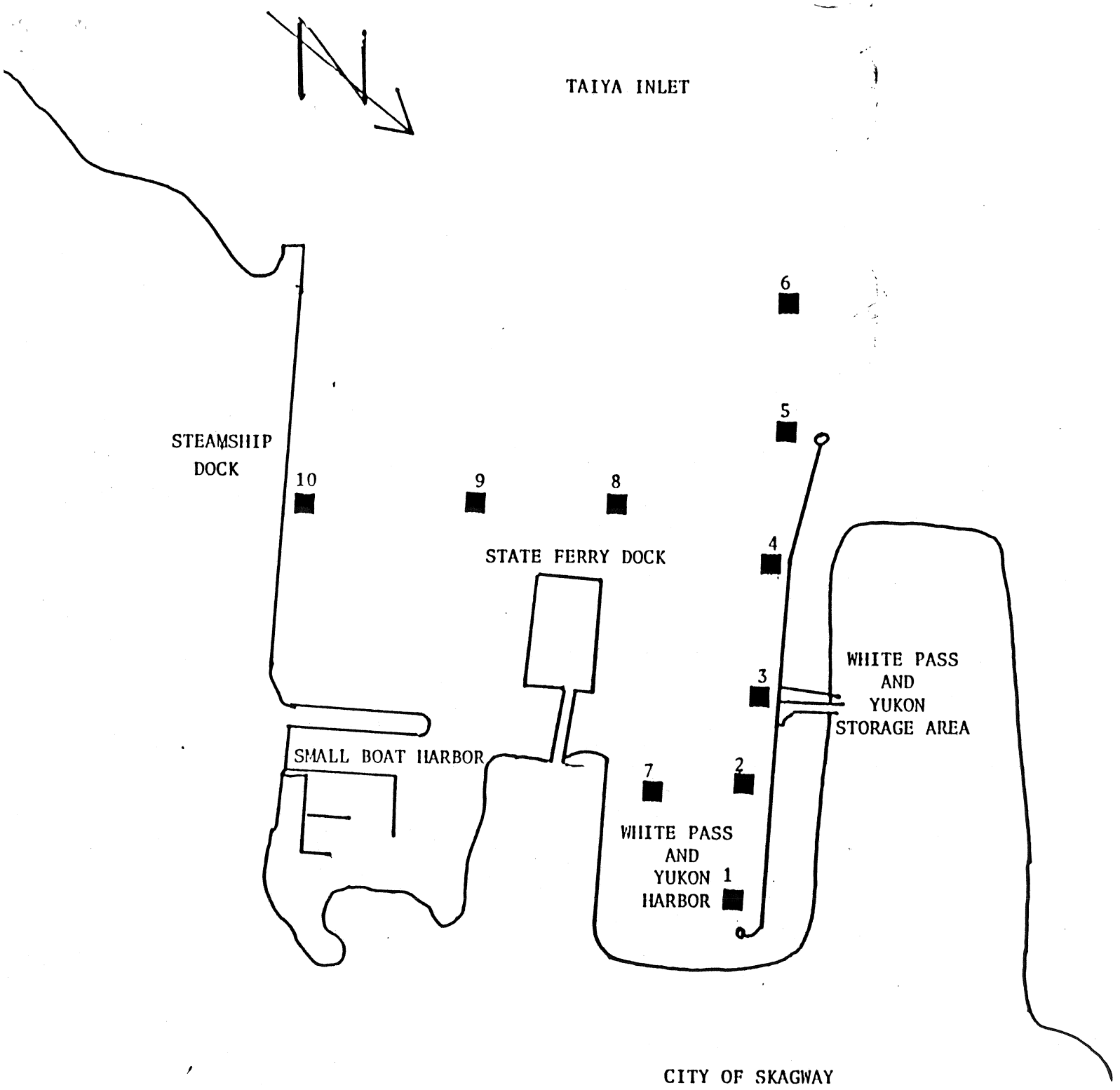
TAIYA INLET
STEAMSHIP DOCK
10
9
8
6
5
4
3
2
1
7
STATE FERRY DOCK
SMALL BOAT HARBOR
WHITE PASS AND YUKON HARBOR
WHITE PASS AND YUKON STORAGE AREA
CITY OF SKAGWAY

Figure 2. *The relationship between benthic infauna diversity and the concentrations of lead and zinc in the sediments.*

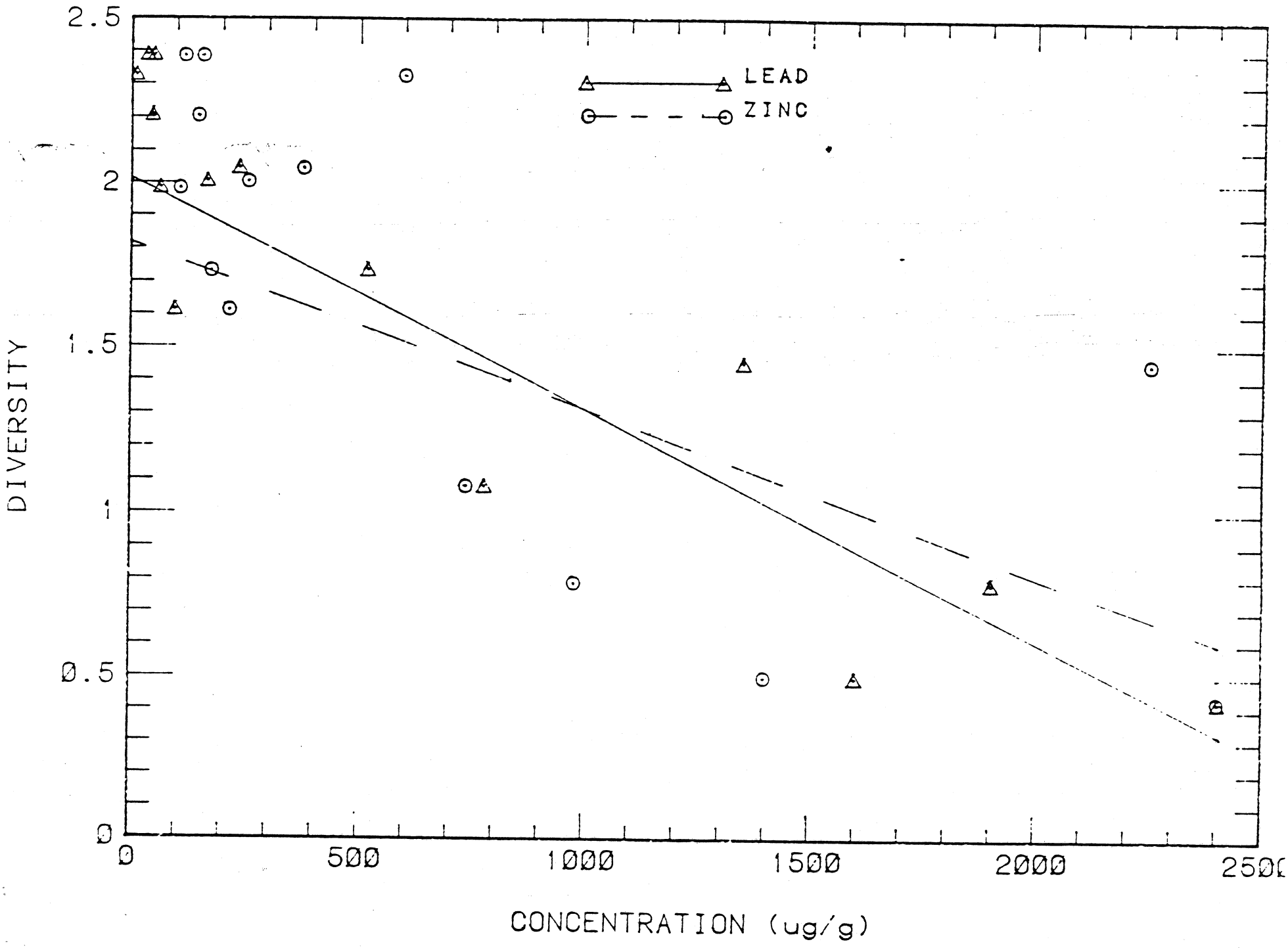
LEAD
ZINC
DIVERSITY
CONCENTRATION (ug/g)
2.5
2
1.5
1
0.5
0
0
500
1000
1500
2000
2500

Table 1. Station Descriptions

Station Number	Location[1]	Number of Infauna Samples	Depth (Meters) (Ref. MLLW)	Distance from the Ore Conveyer (Meters)
1	Within	3	12.2	175
2	Within	3	14.6	75
3	Within	3	15.2	0
4	Within	3	15.2	75
5	Outside	3	36.6	200
6	Outside	3	73.2	315
7	Within	3	15.2	180
8	Outside	3	19.8	200
9	Outside	3	31.1	250
10	Outside	3	29.0	375
11	Control	5	15.2	3,575
12	Control	5	15.2	3,600
13	Control	5	15.2	3,800
14	Control	5	21.3	3,625

[1] Within - refers to those stations within the confines of the Yukon and White Pass basin. Outside refers to stations outside the basin but contiguous to the White Pass and Yukon Basin. The control area was in Nahku Bay.

Table 2.

			Detection Limit for Each Element (PPM)				
Matrix	Treatment	Storage	Lead	Zinc	Copper	Cadmium	Mercury
Tissue	Frozen	-10°C	0.3		0.3	0.1	0.05
Water	Acidified	3°C					
Sediment	Frozen	-10°C	0.3		0.3	0.1	0.05

Table 3. Mean concentrations of heavy metals in marine sediments. Means with different superscripts are significantly different ($p < .05$).

	Concentration (PPM)				
Site	Lead	Zinc	Copper	Mercury	Cadmium
Within	1606^{a}	1554^{a}	55^{a}	1.20^{a}	2.0^{a}
Outside	219^{b}	220^{b}	39^{b}	0.21^{b}	0.7^{b}
Control	37^{c}	257^{b}	9^{b}	0.05^{b}	0.9^{b}

Table 4. Mean concentrations of heavy metals in soft tissues (wet weight) of blue mussels from the "Control" Nahku Bay. Means with different superscripts are significantly different ($p < .05$).

	Concentration (PPM)				
Site	Lead	Zinc	Copper	Mercury	Cadmium
Within	1050^{a}	517^{a}	9.2^{a}	*	5.1^{a}
Control	27^{b}	96^{b}	9.5^{a}	*	4.7^{a}

*Mercury concentrations were below detection limits for more than 50 percent of the samples analyzed.

Table 5. Mean concentrations of heavy metals in tissues from yellowfin sole and Dungeness crab within the Yukon and White Pass harbor and at the control site (Nahku Bay).

			Concentration (ppm) Dry Tissue				
Species	Tissue	Sample Area	Lead	Zinc	Copper	Cadmium	Mercury
Dungeness Crab	Muscle	Within	8.1	190	22	0.58	*
Yellowfin Sole	Muscle	Within	--	98.3	1.3	*	*
Yellowfin Sole	Liver	Within	1.9	56	3.7	0.84	*
Dungeness Crab	Muscle	Control	9.5	170	10	0.57	*
Yellowfin Sole	Muscle	Control	--	26.0	1.1	*	0.4
Yellowfin Sole	Liver	Control	--	155	12.0	6.0	*

*Indicates samples where the concentrations in at least half of the samples was less than the detection limit.

TABLE 6. Mean concentrations of total heavy metals in marine waters from stations . Means with different superscripts are significantly different p_.05.

	CONCENTRATION ug/l				
SITE	LEAD	ZINC	COPPER	MERCURY	CADMIUM
WITHIN	7.34	N.A.	2.69	*	0.32
OUTSIDE	3.48	N.A.	1.71	*	0.21
CONTROL	1.10	N.A.	0.68	*	0.22

* Mercury concentrations were less than the detection limit in all samples.

N.A. Zinc samples were inadvertantly destroyed

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Table 7. Mean number of organisms per m^2 and mean diversity at each station. Means with different superscripts are significantly different p_.05.

Site	Number of Organisms/m^2	Shannon Weaver Diversity
Within	400^b	0.85^c
Outside	690^b	1.8^b
Control	1930^a	2.2^a

Table 8. Concentrations of trace metals found in marine sediments from sites throughout the world.

(ug/g dry wgt)

Element	....Marine ...Sediments*	Nahku Bay	White Pass Yukon Basin	New York Bight	Southern California
Cadmium	.13-9.9	0.9	2.0	0.47-9.6	0.22-140
Copper	1-2424	9.0	55.0	1-320	9-1000
Lead	4.6-11367	37	1606	5-270	7-600
Mercury	.19-5.68	0.05	1.2	0.12-4.9	.04-6.1
Zinc	6-20016	257	1554	4.6-541	44-2900
References	Phillips 1977			Segar and Davis (in Press)	

* Lowest and Highest concentration as cited in Phillips 1977.