

## TRACE METAL DISTRIBUTION IN SEDIMENTS FROM THE BERING SEA

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### ABSTRACT

During the summer of 1984, the Second Joint Soviet- American Expedition to the Bering Sea carried out an extensive field study. Sediment samples collected during the expedition were analyzed for Fe, Cu, Mn, Zn, Pb, Hg and Cd. Sediment concentrations of Fe and Pb showed only minor variations throughout the study area. Lead concentrations were very low at all 12 sites analyzed and showed little evidence of pollutant inputs. Manganese values also were uniform over the study area with the exception of one deep-water site where the Mn concentration was 14860 µg/g due to Mn remobilization within the sediment column. Zinc and Hg concentrations varied as a function of water depth. Sediments collected from depths of >2000 meters had on the average ~1.3 and ~3 times more Zn and Hg, respectively, than those from water depths <2000 meters. A similar pattern was observed for Cu. The highest concentration of Cu occurred at the deep-water site where, as with Mn, remobilization within the sediment column is believed to be the primary mechanism. Sediment cadmium values were low except at two shallow-water sites where values of 330 and 445 ng/g were observed. These higher concentrations are believed to result from natural biological inputs rather than a pollution source.

### Acknowledgements

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### Introduction

The Bering Sea is believed to be one of the few bodies of water which is relatively free from pollutants due to a sparse population and limited industrial development in the area. With an expansive continental shelf, the Bering Sea is also home to large quantities of finfish and shellfish important to U.S. as well as foreign fishing fleets (Hood and Kelly, 1974). Increased industrial activity, especially petroleum exploration and production, is proposed for the

future and thus extensive preliminary studies of the area are necessary.

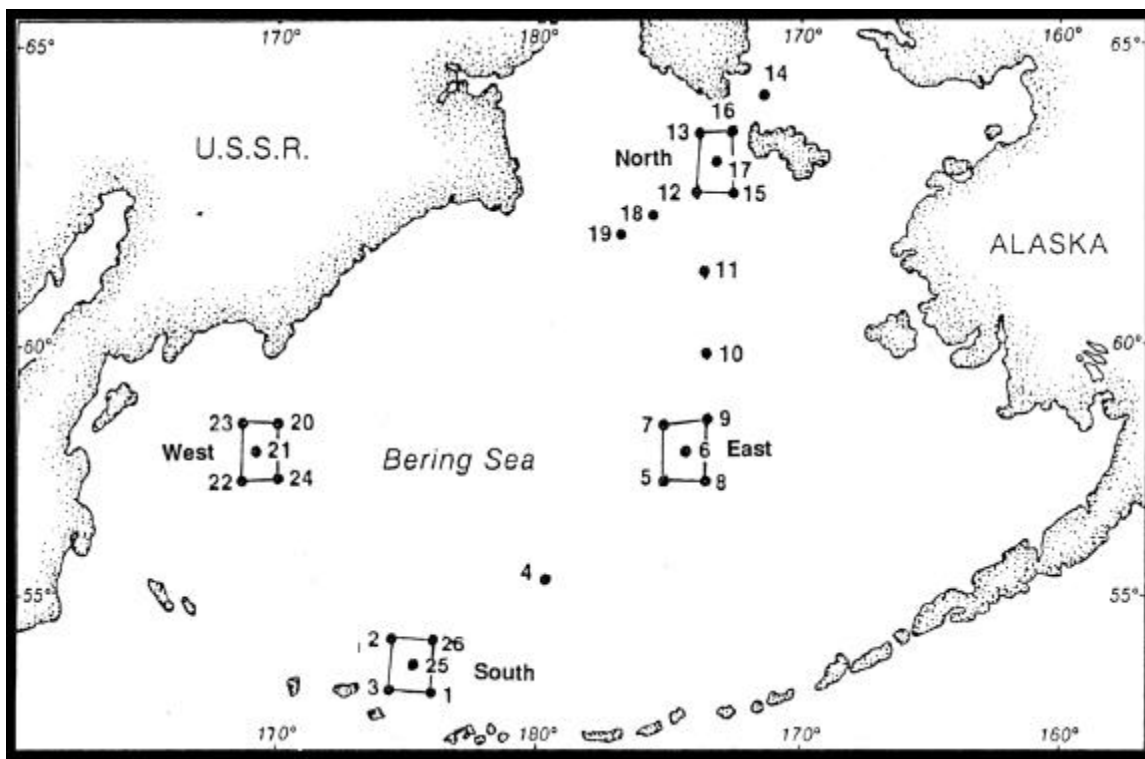
During June and July of 1984, the Second Joint Soviet-American Expedition to the Bering Sea was undertaken to collect biological, chemical and physical baseline data and thereby provide a comprehensive profile of the Bering Sea; to study physiological and ecological characteristics of planktonic organisms; and to assess the relative ecological health of the Bering Sea. This paper discusses the distribution of iron (Fe), copper (Cu), manganese (Mn), zinc (Zn), lead (Pb), mercury (Hg) and cadmium (Cd) in surficial sediments collected from 12 stations sampled during the expedition. Locations of the stations are listed in Table 1 and shown on the area map (Figure 1).

### Methods

#### *Sediment Collection*

Sediment collection was performed from the Soviet Research Vessel *Akademik Korolev*. All sediment samples were obtained using a gravity corer lined with 8-cm diameter cellulose-

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**Fig. 1.** Polygons and sampling stations for the second Joint U.S.-U.S.S.R. Bering Sea Expedition.

acetate-butyrate tubing. The core was split into two sections lengthwise. One section was subsampled and the other was archived. Subsampling was done in one-cm intervals over the top 10 cm and in two-cm intervals below 10 cm.

#### *Laboratory Analysis*

Sediment analysis was performed on 0 - 1 cm intervals collected from each site. These sediment samples were digested in acid-cleaned Teflon® beakers using ~0.4 g aliquots of sample with HClO<sub>4</sub>-HNO<sub>3</sub>-HCl-HF following the process outlined in Trefry and Metz (1984). Sediment solutions and reagent blanks were analyzed for Fe, Cu, Mn and Zn by flame atomic absorption spectrophotometry (AAS) using a Perkin-Elmer® 4000 instrument. Lead and Cd were determined by flameless AAS using a Perkin-Elmer® 4000 instrument equipped with an HGA-400 heated graphite atomizer and an AS-40 autosampler. Deuterium background correction was required for Cu, Mn, Zn, Pb and Cd determinations. Matrix interferences were corrected

by using standard additions analysis when necessary.

Mercury concentrations in each sample were determined by heating ~2 g of wet sediment in a 50 ml polyethylene centrifuge tube with 5 ml of concentrated, redistilled HNO<sub>3</sub> in a 65°C water bath for ~1 h. The centrifuge tubes were then cooled for 12 h and diluted to a volume of 25 ml using distilled, deionized water. A Laboratory Data Control Mercury Monitor® was used for Hg analysis. In this system the sample is treated with stannous chloride to reduce Hg to its elemental state. The elemental Hg is then carried by N<sub>2</sub> from the reaction vessel into a 30-cm path length cell where it is measured by absorption of light at 253.7 nm.

Analytical precision for determination of metal concentrations is expressed as a coefficient of variation and established from analysis of triplicate samples. Precision averaged <5% for Cd, Fe, Hg, Mn and Pb and <1% for Cu and Zn. As

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Table 1. *Sampling station data.*

Station	Location	Core Length (cm)	Date sampled	Water Depths (meters)
4	56°43.8'N 178°32.0'W	60	7/6/1984	>2,000
10	59°58.8'N 174°00.4'W	152	7/10/1984	<100
11	61°30.1'N 173°40.0'W	47	7/11/1984	<100
12	63°30.1'N 173°28.7'W	138	7/12/1984	<100
15	62°58.4'N 172°29.2'W	29	7/14/1984	<100
18	62°44.1'N 174°37.1'W	76.5	7/17/1984	<100
19	62°25.4'N 175°09.7'W	42.5	7/18/1984	<100
20	58°34.0'N 170°27.7'E	173	7/19/1984	600-2,000
21	58°03.4'N 170°02.9'E	175	7/20/1984	600-2,000
22	57°23.0'N 169°31.4'E	90	7/21/1984	>2,000
24	57°28.9'N 170°42.4'E	178	7/23/1984	>2,000
25	53°46.6'N 176°19.1'E	144	7/25/1984	>2,000

a quality control check, U.S. National Bureau of Standards (NBS) estuarine sediment (SRM 1646) was analyzed. Data for trace metals analyzed in SRM 1646 agreed with certified values from NBS.

## Results and Discussion

### *Site Description*

Twelve sediment cores were collected from the Bering Sea and analyzed for trace metals. Four of the twelve cores (stations 4, 22, 24 and 25)

were obtained from water depths >2000 m (Fig. 1). Stations 10, 11, 12, 15, 18 and 19 are located in water depths of less than 100 m. Water depths for the remaining two stations (20 and 21) ranged from 600 to 2000 m. The deepest core obtained was from station 25 at a water depth of 3950 m.

### *Trace Metal Concentrations*

Trace metal concentrations for surficial sediments varied with location and water depth.

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Table 2. Trace metal concentrations for surficial sediments (0-1 cm) from the Bering Sea.

Station	Fe (%)	Cu (µg/g)	Mn (µg/g)	Zn (µg/g)	Pb (µg/g)	Hg (ng/g)	Cd (ng/g)
4	2.27	13	248	102	2.4	70	155
10	2.88	28	397	92	3	36	63
11	3.15	31	407	80	6.4	24	27
12	2.90	17	375	86	3.1	29	330
15	3.04	12	391	68	5.9	21	445
16	3.05	16	370	92	7.7	30	40
19	2.67	16	356	77	3.3	25	89
20	2.90	24	354	85	2.6	20	64
21	3.00	11	355	90	2.6	21	77
22	3.02	49	325	119	2.5	105	215
24	3.04	31	408	110	1.9	58	212
25	2.49	73	14,860	108	2.5	90	16
Mean	2.87	23 <sup>a</sup> [27]	362 <sup>a</sup> [1,571]	92	3.7	44	144
(± SD)	(± 0.26)	(± 12) <sup>a</sup> [(± 18)]	(± 46) <sup>a</sup> [(± 4,185)]	(± 15)	(± 1.9)	(± 30)	(± 134)
Average Continental Crust <sup>b</sup>	5.60	55	950	70	12.5	80	200

<sup>a</sup> excluding station 25

[] Data within brackets shows statistic including station 25

<sup>b</sup> Taylor (1964)

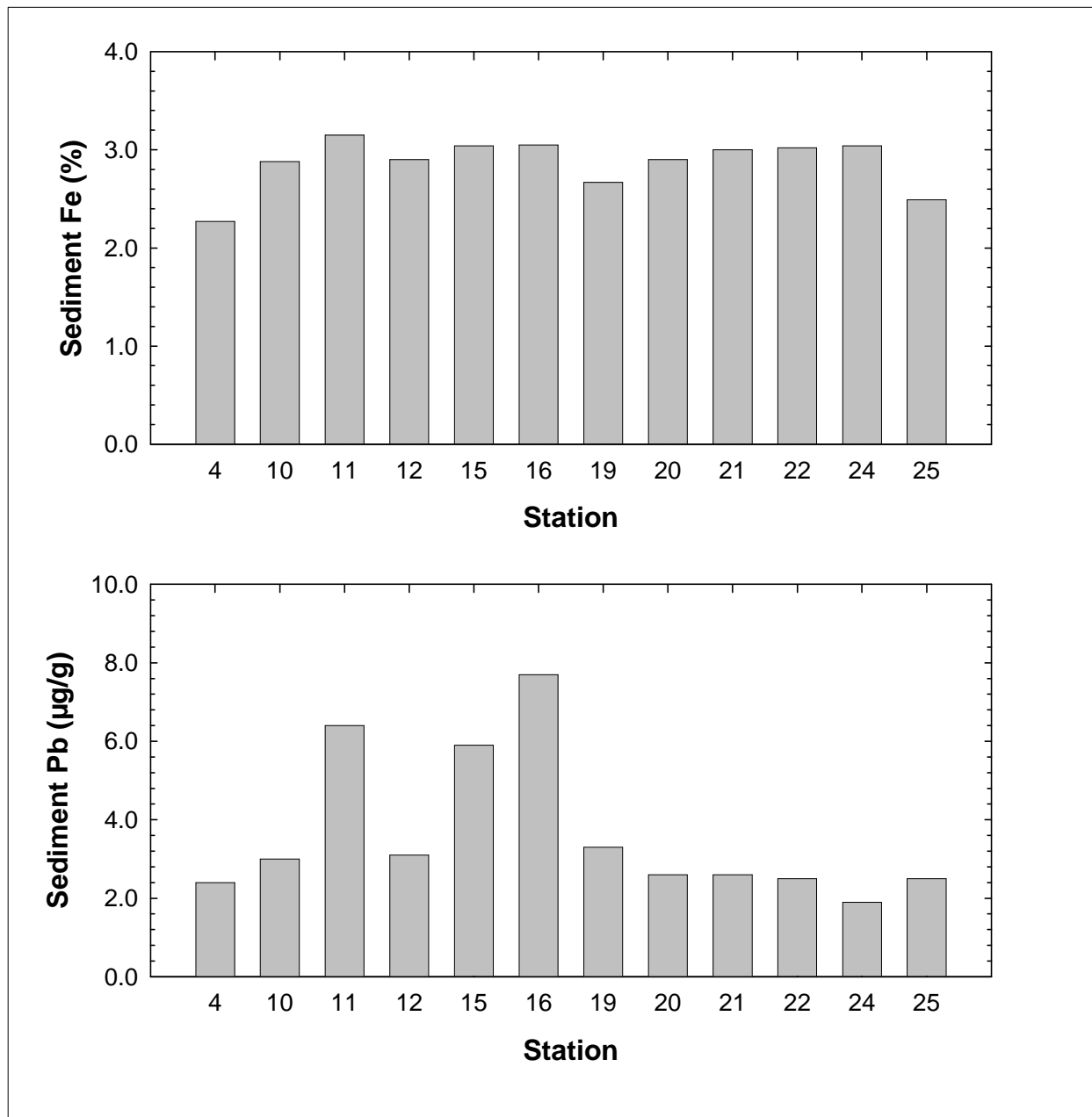
Higher concentrations were generally found for samples collected in deeper water (>2000 meters). Sediments collected in shallower waters (<2000 meters) are believed to contain a mixture of sand and mud.

Iron and Pb concentrations in the sediment varied very little in the study area (Table 2 and Fig. 2). Iron concentrations averaged 2.87% and are only ~50% of continental crust averages (Table 3). However, they are quite comparable with average Fe values of 2.02 to 3.13% reported by Loring (1984) for surficial sediments from Baffin Bay and the sounds leading into the Arctic

Ocean. In the case of Fe, pollution is uncommon and Fe often serve as a useful element to help gain a general picture of sediment composition.

Lead concentrations for Bering Sea sediments are very low everywhere at  $3.6 \pm 1.9 \mu\text{g/g}$  (Table 2 and Fig. 2). Iron concentrations can sometimes be used to normalize other sediment trace metal values and thereby obtain an estimate of natural and anthropogenic contributions of trace metals to the sediments. In the Bering Sea, the ratio of Pb/Fe is  $1.2 \pm 0.6 \times 10^{-4}$ , somewhat

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**Fig. 2.** Concentrations of Fe and Pb in surficial (0-1 cm) sediments from the Bering Sea.

Table 3. Ratios of Cu, Pb, Hg and Cd concentrations to Fe values for surficial sediment (0-1 cm) from the Bering Sea.

Station	Cu/Fe ( $\times 10^{-4}$ )	Pb/Fe ( $\times 10^{-4}$ )	Hg/Fe ( $\times 10^{-7}$ )	Cd/Fe ( $\times 10^{-7}$ )
4	6	1.1	31	68
10	10	1.0	13	22
11	10	2.0	8	9
12	6	1.1	10	114
15	4	1.9	7	146
16	5	2.5	10	13
19	6	1.2	9	33
20	8	0.9	7	22
21	4	0.9	7	26
22	16	0.8	35	71
24	10	0.6	19	70
25	29	1.0	36	6
Mean	10	1.3	16	50
( $\pm$ SD)	( $\pm 7$ )	( $\pm 0.6$ )	( $\pm 11$ )	( $\pm 45$ )
Average Continental Crust <sup>a</sup>	10	2.2	14	36

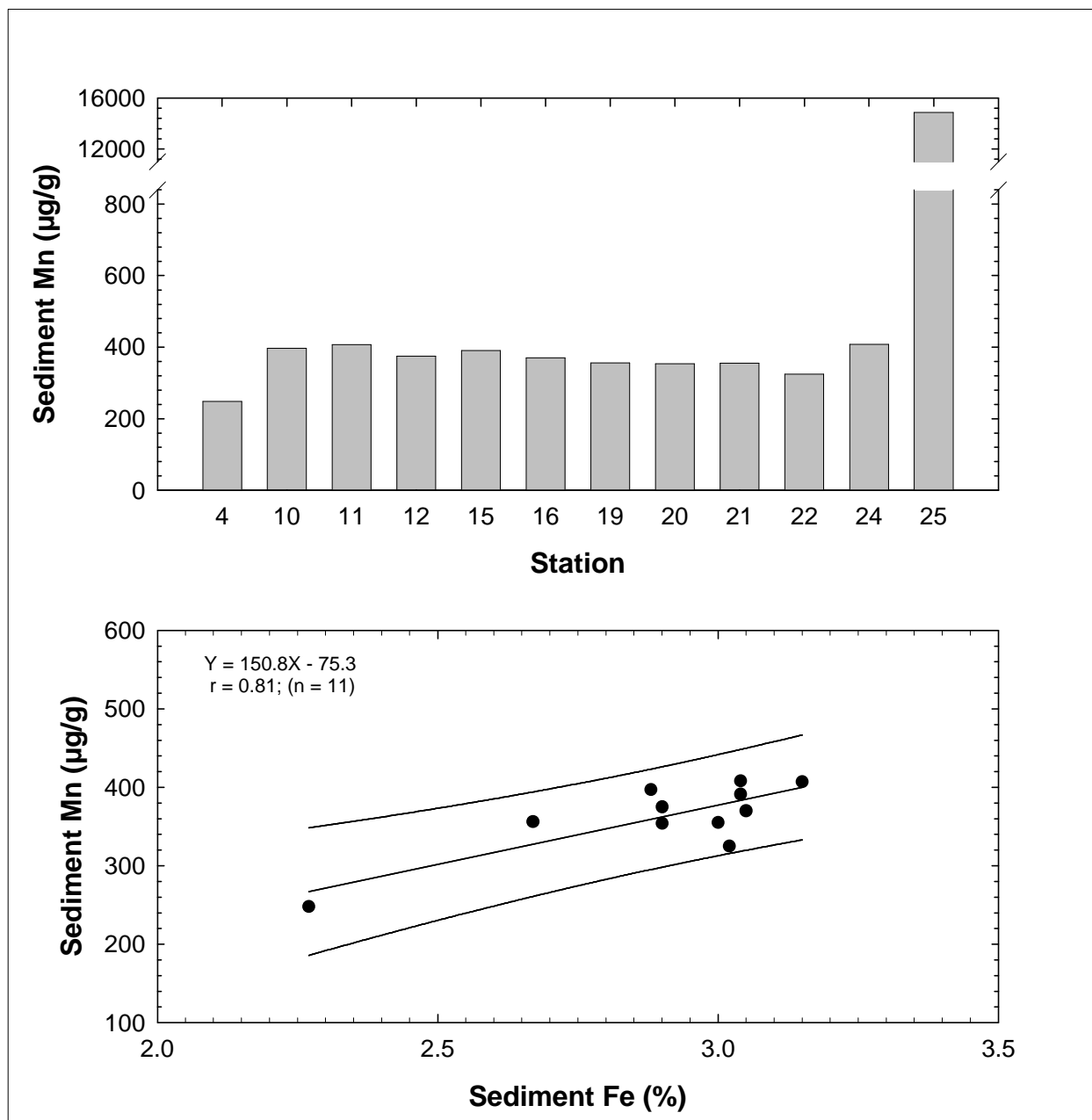
<sup>a</sup> Taylor (1964)

lower than a  $2.2 \times 10^{-4}$  value for continental crust (Table 3). Thus, Pb input into the Bering Sea is believed to be mostly from natural sources at present.

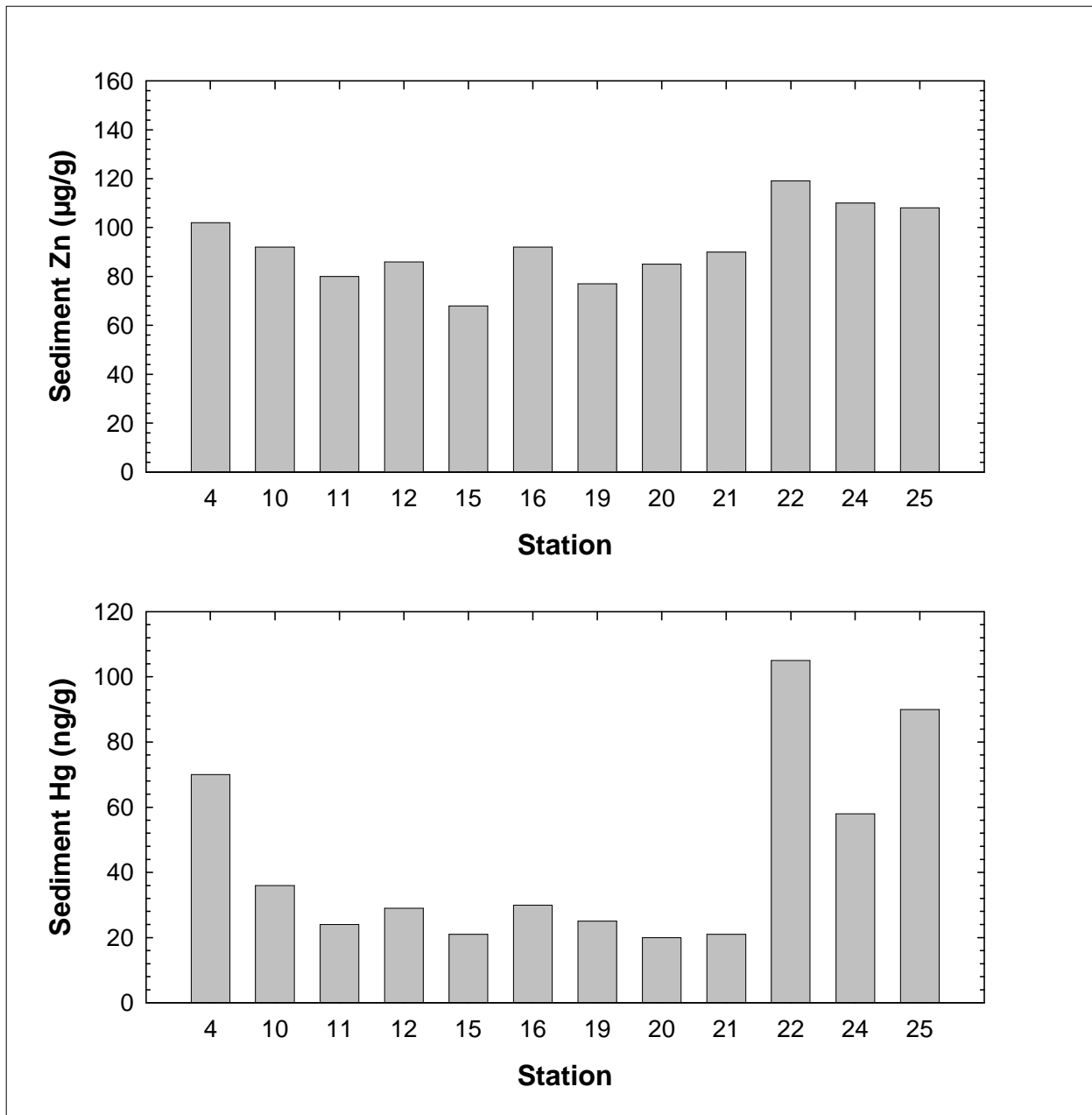
Manganese concentrations were generally uniform at all sites except at station 25 (Table 2 and Fig. 3). Eleven of the 12 Mn values correlate well ( $r = 81$ ) with Fe concentrations (Fig. 3B). Ratios of Mn/Fe for these 11 stations averaged  $\sim 150 \times 10^{-4}$  compared to  $170 \times 10^{-4}$  for continental crust. Manganese values for Arctic

nearshore muds averaged  $340 \mu\text{g/g}$  (Loring, 1984), comparing well with values of  $362 \pm 46 \mu\text{g/g}$  reported for this study. The high Mn concentration of  $14,860 \mu\text{g/g}$  reported for station 25 is believed to result from remobilization of Mn within the sediment column. The top 10-cm of the sediment column from this site had a reddish-brown color identifying an oxidizing layer over a grey (reducing) layer. Under these conditions, Mn is dissolved in the subsurface reducing sediments and then diffuses upward until it

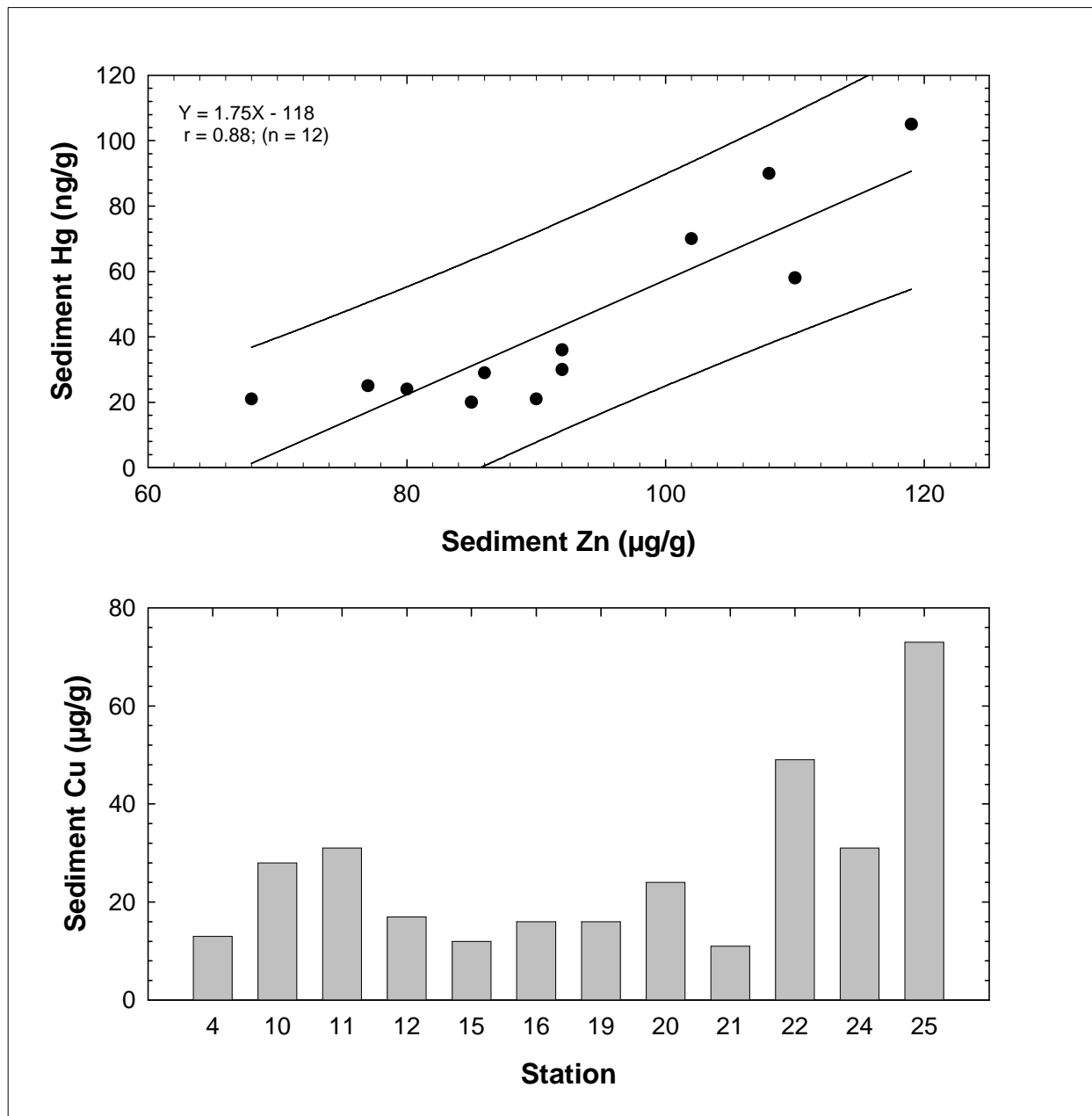
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**Fig. 3.** Concentrations of Mn in surficial (0-1 cm) sediments from the Bering Sea and a plot of sediment Fe vs sediment Mn.



**Fig. 4.** Concentrations of Zn and Hg in surficial (0-1 cm) sediments from the Bering Sea.



**Fig. 5.** Plot of sediment Zn vs. sediment Hg and concentrations of Cu in surficial (0-1 cm) sediments from the Bering Sea.

Table 4. *Comparison of surficial sediment Hg concentrations in the Bering Sea with values recorded elsewhere.*

Location	Hg (ng/g)	Source
Minimata Bay	15,000	Nishimura and Kumagai (1983)
Ebrie lagoon, West Africa	2,250	Kouadio and Trefry (1987)
Arctic nearshore muds	50	Loring (1984)
Baffin Bay deep-sea muds	90	Loring (1984)
Bering Sea	44 ± 30	This Study

precipitates as an oxide phase in the top centimeters of oxidizing sediment. This high concentration of surficial Mn results from natural processes and is similar to values of 2,000 to 13,500 µg/g observed in northwest Pacific sediments (Lynn and Bonatti, 1965). More study of the area around station 25 certainly merits consideration for possible metalliferous deposits.

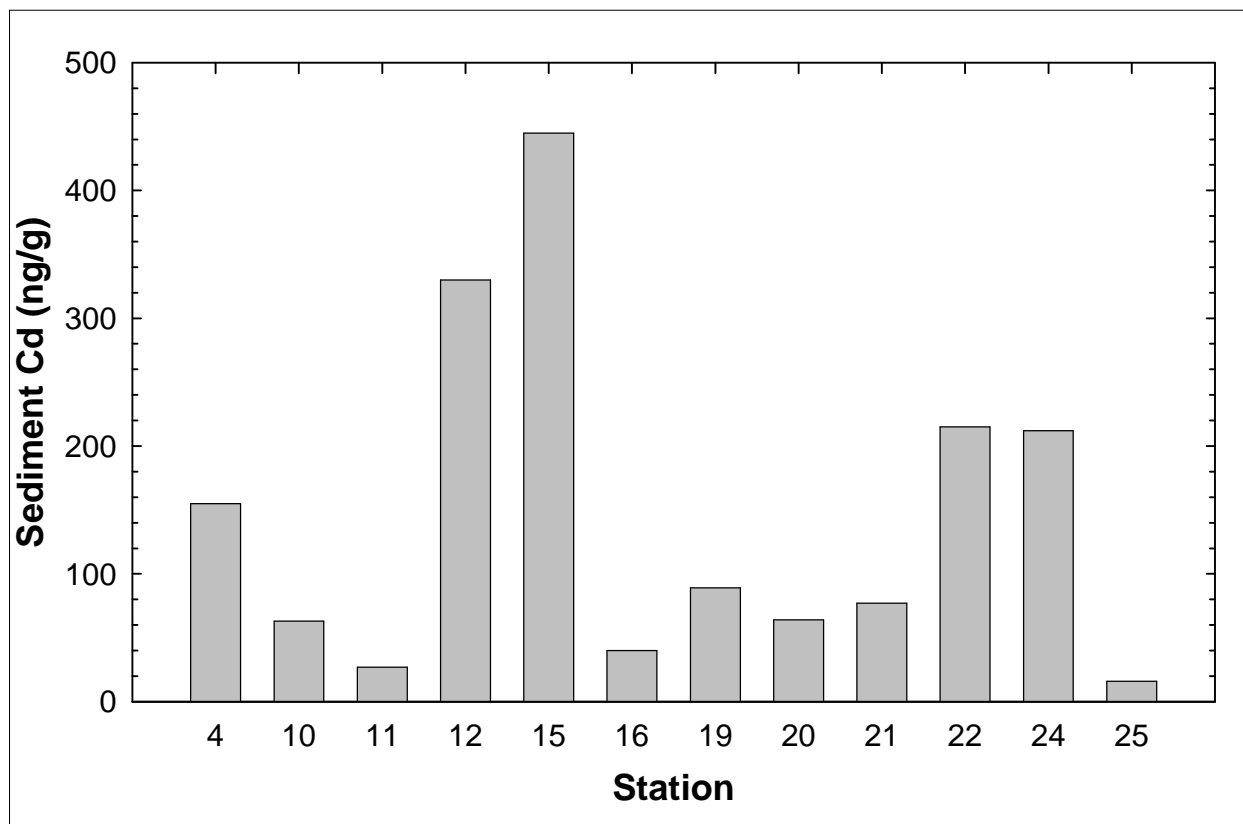
Concentrations of Zn and Hg in Bering Sea sediments showed some variation as a function of water depth. Sediments collected from depths <2000 meters (stations 10 to 21) had Zn levels of 84 ± 8 µg/g and Hg values of 26 ± 6 ng/g (Table 2 and Fig. 4). Sediments collected from deeper waters (stations 4, 22, 24 and 25) had significantly higher concentrations of both Zn (110 ± 7 µg/g) and Hg (84 ± 21 ng/g). These deep-water sediments were all collected from the same sedimentary basin (Fig. 1). A linear relationship ( $r = 0.88$ ) was found for Zn vs. Hg for all sites sampled in the Bering Sea (Fig. 5). Elevated Zn and Hg values from the deep-water sites may be due to some natural mineral source in the southern portion of the study area or long-term scavenging of these metals from

seawater. Although anthropogenic inputs cannot be totally discarded, Hg concentrations for Bering Sea sediments are 140 to 260 times lower than those for Minamata Bay and 20 to 40 times lower than those reported for a contaminated African Lagoon (Table 4). Average Hg concentrations for the Bering Sea were similar to Arctic nearshore muds and ~2 times lower than Baffin Bay deep-sea muds (Loring, 1984; Table 3).

Copper concentrations show some similarity to Zn and Hg values (Table 2). The average Cu concentration for Bering Sea sediments of 27 ± 18 µg/g is similar to concentrations of 9 to 61 µg/g measured in Baffin Bay (Loring, 1984). These values and their ratios to Fe show no evidence of pollutant inputs at this time (Tables 2 and 2). Station 25 had the highest Cu concentration (73 µg/g) relative to the other 11 stations (Fig. 5B). This higher value is believed to result from remobilization of Cu within the sediment column.

The most interesting trace metal studied in Bering Sea sediments is Cd (Fig. 6). Generally, Cd

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**Fig. 6.** Concentrations of Cd in surficial (0-1 cm) sediments from the Bering Sea.

has a similar distribution to both Zn and Hg except for stations 12, 15 and 25 (Table 2). The low Cd values observed at 9 sites suggest no pollutant inputs. Stations 12 and 15 have the highest Cd concentrations (Fig. 6). Both sites are located in an area where the water depth is <65 m and primary productivity is high. The higher Cd concentrations at these sites are most likely due to a downward vertical flux of planktonic organisms and associated biogenic debris. Concentrations of Cd in Pacific Ocean plankton are reported to be 2 to 5  $\mu\text{g/g}$  (dry weight), but values as high as 20  $\mu\text{g/g}$  (dry weight) have been measured (Martin and Broenkow, 1975). Thus, observed high Cd values for these 2 sites are believed to be due to a natural bioconcentration mechanism. At station 25, the Cd concentration is lower than at any of the other sites. It is possible that Cd is diffusing out of the sediments into the overlying water at station 25 resulting in a lower concentration of

Cd in surficial sediment.

## Conclusions

Trace metal concentrations for the Bering Sea were generally quite uniform with some regional variability. Two metals, Pb and Fe, had little or no variability over the entire study area. Lead concentrations were generally very low and showed little evidence of pollutant inputs. Iron concentrations are lower than average continental crust and serve as a useful data set for normalizing other trace metal values.

Zinc and Hg concentrations varied as a function of water depth and correlated well with each other. Deeper water stations had elevated concentrations of both metals. These values are believed to be due to natural sources rather

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than any anthropogenic input.

The distribution of Mn in Bering Sea sediments is uniform except for station 25 where a very high concentration is believed to result from remobilization occurring within the sediment column. A correlation was found to exist between Fe and Mn for all stations except station 25. Copper distribution throughout the study area is similar to Zn and Hg except for station 25. At this site, an elevated Cu concentration in surficial sediments is believed to have resulted from remobilization. All 12 sites show no evidence of pollutant inputs of Cu.

None of the Cd values from the 12 sites suggest pollutant inputs. Stations 12 and 15 had the highest Cd concentrations of all 12 sites sampled, the result of high primary productivity and shallow waters in this area. The primary source of Cd in this area is believed to be biogenic. The lowest Cd concentration was found at station 25 where remobilization may have removed Cd from the sediments.

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