MERCURY IN ALASKA MARINE SURFACE SEDIMENTS: A REVIEW OF THE REGIONAL DATA

by

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Final Report
Outer Continental Shelf Environmental Assessment Program
Research Unit 691

February 1989

ACKNOWLEDGMENTS

Thanks to to J. V. Gardner, and L. A, Gardner for sharing unpublished data, and to L. Tobiska, and R, A, Vaa for technical support.

This study was funded by the Minerals Management Service, Department of the Interior, through an Interagency Agreement with the National Oceanic and Atmospheric Administration, Department of Commerce, as part of the Alaska Outer Continental Shelf Assessment Program.

ABSTRACT

Mercury concentrations reported by eight studies of surface sediments varied significantly among regions of the Alaska shelf. Chukchi Sea data indicated the lowest mercury geometric means, .0121ppm and .0127ppm, for sand and mud, respectively. One Beaufort Sea study reported the highest concentrations, with means of .0615ppm and .0877ppm, for sand and mud, respectively.

Mercury levels did not differ significantly between the mud and sand fractions when data were combined among studies. Laboratory and collection methods differed among the studies and may have affected the mercury estimates, but no clear relationship emerged from a comparison of the reports.

INTRODUCTION

Offshore mineral and petroleum developments which disturb surface sediments may increase heavy metal pollution in Alaska marine areas. Gold dredges off Nome and drilling pads in Arctic waters, for example, currently introduce toxic metals into the water column, Whether these activities represent a significant pollution problem is an issue of continuing research in Alaska.

Past sampling data on concentrations of heavy metals in Alaska marine sediments may contribute to an understanding of the source and extent of such pollution. First, the likelihood that development will cause significant pollution varies from place to place as a consequence of geographical differences in heavy metal concentrations. In addition, past estimates of these toxic elements can serve as a basis for measuring future effects of development.

This paper examines mercury concentrations reported by past investigators of Alaska shelf regions. The review establishes estimates for mean mercury levels in several regions and tests whether the samples are adequate for indicating patterns of variation in mercury among regions,

METHODS

Reported concentrations of mercury in surface sediments off the Alaska coast were characterized statistically.

Non-proprietary reports, identified in a search of published and unpublished literature, were selected for examination in this review. Only those reports providing ten or more mercury concentrations exceeding the lower detection limit were selected. Mercury samples which may have been affected by specific industrial activity were omitted from consideration in this review for the two studies which reported such activity, i. e. NORTEC (1982) and Rusanowski et al (1988). For these two local studies, only "control'? mercury samples known to be unaffected by dredging and effluent disposal are included here.

Each sediment specimen was classified as mud, sand, or gravel by applying the grain-size classification criteria of its report. These grain-size classes were then assigned to the individual mercury values from each report. Subsequent statistical treatments of mercury concentrations were carried out within the grain-size classes. Mud is defined as silt and clay combined,

The mercury concentrations were first summarized as geometric means and confidence intervals by back-transforming from natural logarithms. The log values were examined for departure from an expected normal frequency distribution using tests for skewness and kurtosis, Bartlett's test of homogeneity of variances was applied to the samples using the method described by Sokal and Rohlf

(1969:370). Where heterogeneity of variances precluded parametric analysis of variance, a Kruskal-Wallis rank test among studies was performed. Statistical calculations; except Bartlett's test, were carried out with Complete Statistical System, a micro-computer application distributed by Statsoft, Inc., Tulsa, Oklahoma.

All the data reviewed here were taken at face value from the original reports. Data on grain size and mercury concentrations were selected without regard to methods of collection, storage, or laboratory analysis, and were subjected to no modifications other than log transformation.

Mercury concentrations are expressed as parts per million on a dry weight basis. For purposes of statistical calculations, concentrations reported as lower than the lower detection limit were assigned a value equal to the product of the lower detection limit times 0.7.

The alpha level of significance is $P<.05$ for statistical tests.

RESULTS

The reports

Eight reports with unreduced data on concentrations of mercury in sediment were identified for Alaska shelf areas.

Barnes et al (1974) collected sediment with a variety of instruments in 1971 in the Beaufort Sea. The sampled area lay between 143 and 155 degrees west longitude and extended from the coast to approximately 2,000 meters water depth. It encompassed lagoonal areas and depths less than 10 meters. Barnes and his USGS colleagues provided sediments analyzed by Weiss et al (1974) for Beaufort Sea waters outside lagoons, from approximately 10 meters to 2,000 meters depth.

Barnes and Leong (1971) reported mercury levels from the Chukchi Sea collected in 1970. The sampled area extended from Cape Lisburne northward to 70.5 degrees north latitude and westward from Icy Cape to approximately 168 degrees west longitude.

Nelson et al (1972) sampled mercury in the northern Bering Sea, including Norton Sound, St. Lawrence Island, St. Matthew Island, and offshore Seward Peninsula. The investigation collected sediments at various depths with several instruments. For this review, only the material indicated as surficial sediment by the authors was considered.

Gardner et al (1979) collected surface sediments from the greater St. George Basin area of the southeastern Bering Sea employing three collection methods. The area extended from around the Pribilof Islands southeastward to Unimak Pass in the Aleutian Island archipelago, and lay east of the continental slope. The report associated mercury concentration values with a grain-size distribution in 1976 and only that year's data are reviewed here.

Burrell (1978) reported mercury concentrations determined by H. V. Weiss for the shelf area of northeastern Gulf of Alaska, lying between 140 and 150 degrees west longitude. Although no grain size data were reported for the cruise which collected the mercury samples, the mercury values can be associated with the grain sizes for eight of the stations occupied by the vessel Silas Bent earlier in the year (Burrell, 1978: Table 22).

Two studies measured the affects of artificial perturbations on the sea floor, NORTEC (1982) experimented with drilling mud disposal on sea ice east of the Sagavanirktok River delta in 1980. Rusanowski et al (1988) studied mercury concentrations near the Bima dredge off Nome. This review considered only the sediment collected at Endeavor and Resolution Islands before NORTEC's experimental work, and upstream of the dredge at Nome.

Methods differences

Collection methods varied among the seven studies which reported methods of collecting sediment. There was no indication that any of the studies collected sediment from the same depth range below the sediment surface (Table 1). The three studies which reported the collection depth each sampled from unique ranges, Four studies did not report the depth range for collected sediment, and one study (Rusanowski et al, 1988) reported mercury concentrations from stations unassociated with the grain-size collections,

Storage also differed among the studies. For example, Weiss et al (1974), NORTEC (1982), and Burrell (1978) reported that sediment specimens were frozen (Table 1).

Six of the eight studies measured mercury concentrations by means of atomic absorption spectrometry. In contrast, H. V. Weiss employed neutron activation to determine mercury levels reported by Burrell (1978) and by Weiss et al (1974).

Grain-size criteria

Five reports shared similar grain-size classification criteria for the mud and sand fractions (Table 2), Sand and mud were separated at .062mm to .063mm diameter for the Beaufort Sea (Barnes et al, 1974; Weiss et al, 1974), the Chukchi Sea (Barnes and Leong, 1971), the St. George Basin (Gardner et al, 1979), and the northeastern Gulf (Burrell, 1978) . Because Weiss et al (1974) did not report grain sizes, their mercury concentration data are associated in

Table 1. Reported methods for estimating whole-rock concentrations of mercury in surface sediment collected from Alaska shelf areas.

Area & citation	Methods summarized
Beaufort Sea Barnes et al (1974)	Upper 2cm of surface sediment. Stored unfrozen in plastic 4-6 months. Sieved and air dried at room temp. Gentle disaggregation with mortar and pestel. AAS (Vaughn and McCarthy, 1964). Lower detection limit is inferred as .01ppm from the lower boundary of the range.
Beaufort Sea Weiss et al (1974)	Sediments provided by Barnes. Frozen. Neutron activation analysis. No lower detection limit reported.
Chukchi Sea Barnes & Leong (1971)	2-10cm. Sieved and air dried. Gentle disaggregation with mortar and pestel, AAS (Vaughn and McCarthy, 1964). Lower detection limit .01ppm.
No. Bering Sea Nelson et al (1972)	0-10cm. Air dried. Gentle disaggregation with mortar and pestel. AAS (Vaughn and McCarthy, 1964), Lower detection limit .01ppm.
St, Gee. Basin Gardner et al (1979)	0-30cm. Stored moist, air tight at 3 deg C. Air dried, ground to <.149mm. AAS, No lower detection limit reported.
Sag Delta NORTEC (1982)	Pipe dredge. Frozen in plastic bags. Digested with K-permanganate, aqua regia, and K-persulfate; cold vapor AAS. Lower detection limits varied .001 to .003ppm.
Nome Rusanowski et al (1988)	Refrigerated. Digested by EPA method 3050. Perkin-Elmer 603 AAS and EPA method 7471. Lower detection limits varied .002 to .035ppm.
NE Gulf Burrell (1978)	Frozen in polyethylene jars. Neutron activation analysis. No lower detection limit reported.

this review with grain sizes shown on the sediment-type map of Barnes et al (1974) for the same region.

For the three other studies, grain-size classes were defined by unequal criteria. NORTEC (1982) expressed grain-size distributions in detail for each sediment specimen. However, the diameter class boundaries differed from the other studies, and for this review the .045mm boundary was used to distinguish mud and sand, Nelson et al (1972) mapped three sediment classes but did not specify the diameter boundaries of the classes, Rusanowski (et al 1988) reported grain-sizes unassociated with mercury samples.

Mercury levels

Mercury concentrations varied among the studies of Alaska shelf areas. A Kruskal-Wallis non-parametric test of seven data sets indicates a significant difference (Table 3).

The data of Weiss et al (1974) were omitted for the purposes of testing the hypothesis that mercury concentrations are equal among studies. Weiss et al (1974), using neutron activation, reported mercury levels about twice as great as the highest geometric means of the other investigations, including the estimates of Barnes et al (1974) for the same region of the Beaufort Sea and the results of Burrell (1978) derived by neutron activation analysis,

Other than Weiss et al (1974), the report of Gardner et al (1979) sampling in the southern Bering Sea showed the highest mercury concentrations, The lowest geometric means were from the Chukchi Sea, with levels of .0127ppm for mud and .0121ppm for sand. See Table 4 for a comparison of the means. Figure 1 illustrates these regional differences.

A further Kruskal-Wallis test indicates that mercury levels were not significantly different between the mud and sand fractions (P=.12). Table 3 shows the results of this test for the five studies which reported grain sizes.

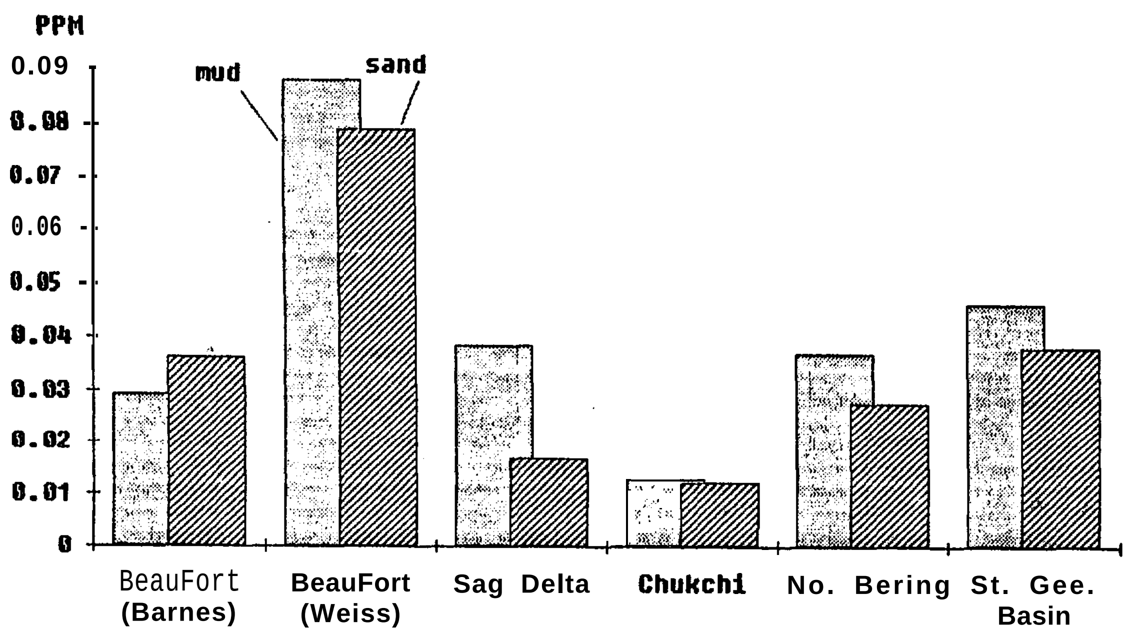

Fig. 1. Geometric mans of mercury (ppm) in Alaska shelf areas.

Table 2. Criteria "for assigning grain-size classes to mercury concentrations in surface sediment collected from Alaska shelf areas.

Area & citation	Maps	Station labels	Percentage wt. in the diameter class
Beaufort Sea Barnes et al (1974)	Sed. type & [Hg]		Mean diam.: silt and clay <.062 sand .062-2.5mm gravel >2.5mm
Beaufort Sea Weiss et al (1974)	[Hg]		None reported. (Criteria are imposed for this review from Barnes (1974).)
Chukchi Sea Barnes & Leong (1971)	Seal. type & & [Hg]		mud >50% <.062mm sand >50% .062-2mm gravel >25% >2mm
No. Bering Sea Nelson et al (1972)	Seal. type	Lat/lon for each [Hg]	Undefined grain diam. classes are mapped as: silt 0%-50% gravel >50% gravel
St. Gee. Basin Gardner et al (1979)	Gr. size classes & [Hg] gr. size	Lat/ lon for each [Hg] &	mud >50% <.063mm sand >50% >.063mm
Sag Delta NORTEC (1982)		labels for each [Hg] & gr. size	mud >50% <.045mm sand >50% >.045mm
Nome Rusanowski et al (1988)		labels for each [Hg]	Not applicable
NE Gulf Burrell (1978)		labels for each [Hg]	Grain size for 8 of 28 stations, mud <.062mm

Table 3, Kruskal-Wallis non-parametric rank tests for grain size affect and study affect on mercury concentrations in mud and sand of the Alaska shelf,

Grain size affect for five studies

Fraction:	Mud	Sand
Sample size:	213	181
Sum of ranks:	43765	34049

Degrees of freedom:	1, 394
Test statistic:	H = 2.320
Probability:	P = .1236 NS

Study affect for seven studies

Study	Sample size	Sum of ranks
Beaufort Sea Barnes et al (1974)	172	38964
Chukchi Sea Barnes & Leong (1971)	51	4283
No, Bering Sea Nelson et al (1972)	49	11311
St. George Basin Gardner et al (1979)	100	28300
Sag Delta NORTEC (1982)	22	4314
Nome Rusanowski et al (1988)	22	3696
NE Gulf Burrell (1978)	28	7921

Degrees of freedom:	6, 444
Test statistic:	H = 96
Probability:	P < .0001

Table 4. Mean mercury concentrations in mud and sand fractions of surface sediment collected from Alaska shelf areas. Mud and sand are defined in the original reports. Sample size is number of sediment specimens. The geometric means and confidence bounds are back-transformed from mean and confidence bounds of the natural logs of the original values. Transformed values of the St. George Basin mercury samples indicated significant skewness (1.04) for mud and significant kurtosis (1.88) for sand. No other samples showed significant departures from normal. Expressed as ppm dry weight of mercury in whole-rock digests.

Area & citation	Fraction	Sample size	Geom, mean	95% Conf. Int.
Beaufort Sea	mud	119	.0293	.0251-.0341
Barnes et al	sand	53	,0362	.0304-00431
(1974)	gravel	7	.0157	.0133-.0221
Beaufort Sea	mud	42	.0877	.0777-.0990
Weiss et al	sand	5	.0615	.0343-.1104
(1974)	gravel	1	,036	---
Chukchi Sea	mud	19	.0127	.0100-.0161
Barnes & Leong	sand	32	.0121	.0101-.0145
(1971)	gravel	12	.0178	.0134-.0237
No. Bering Sea	mud	17	,0369	.0246-.0554
Nelson et al	sand	32	.0277	,0205-.0373
(1972)	gravel	53	.0253	.0206-.0313
St. George				
Basin area	mud	48	.0464	.0424-,0508
Gardner et al	sand	52	.0381	.0354-.0410
(1979)				
Sag Delta	mud	10	.0384	.0281-.0524
NORTEC (1982)	sand	12	.0166	.0104-.0266
Nome				
Rusanowski et al		22	.0147	.0078-.0278
(1988)				
NE Gulf		28	.0402	.0344-.0470
Burrell (1978)				

Heterogeneity of variances

Bartlett's test of the five studies which reported grain sizes indicates significant heterogeneity among the variances within sediment fractions (Table 5).

Figures 2 and 3 show confidence intervals which reflect these regional differences in variance. Figure 4 illustrates the proportion of the total sample contributed by each of the studies.

DISCUSSION

Means

The reported mercury concentrations varied widely among the investigations, although the sources of the variation could not be determined. Proportions of mud and sand were shown to have no significant affect on mercury concentrations, and as a result offer little explanation for the regional differences in mercury levels. Similarly, collection depths, storage methods, and analytical procedures showed no clear relationship with variation in mean mercury levels. Consequently, the variation in mercury concentrations among the studies was not attributable to particular factors, including geographic affects,

Variances

Significant heterogeneity of variances placed additional limits on an attempt to measure regional differences in mercury concentrations. The inequality of variances among studies violated an assumption of parametric methods. As a result, analysis of variance cannot be employed to partition total mercury variation into its components and to estimate the relative strength of geographic and grain-size affects.

Furthermore, because the variances must be considered as representing independent "statistical populations" of mercury, the studies' samples cannot be pooled to achieve a single estimate of an overall mean,

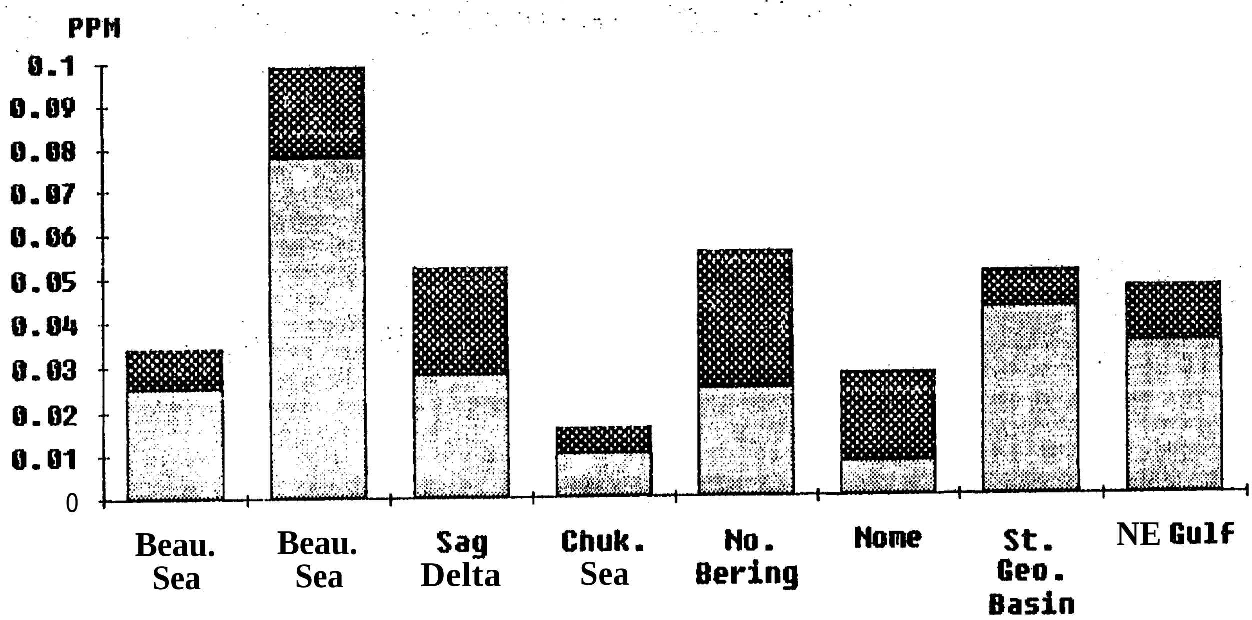

Fig. 2. Confidence intervals (95%) for geometric means of mercury in surface sediments of Alaska shelf areas. Nome and NE Gulf samples are all grain size fractions combined. Other area samples are mud fraction.

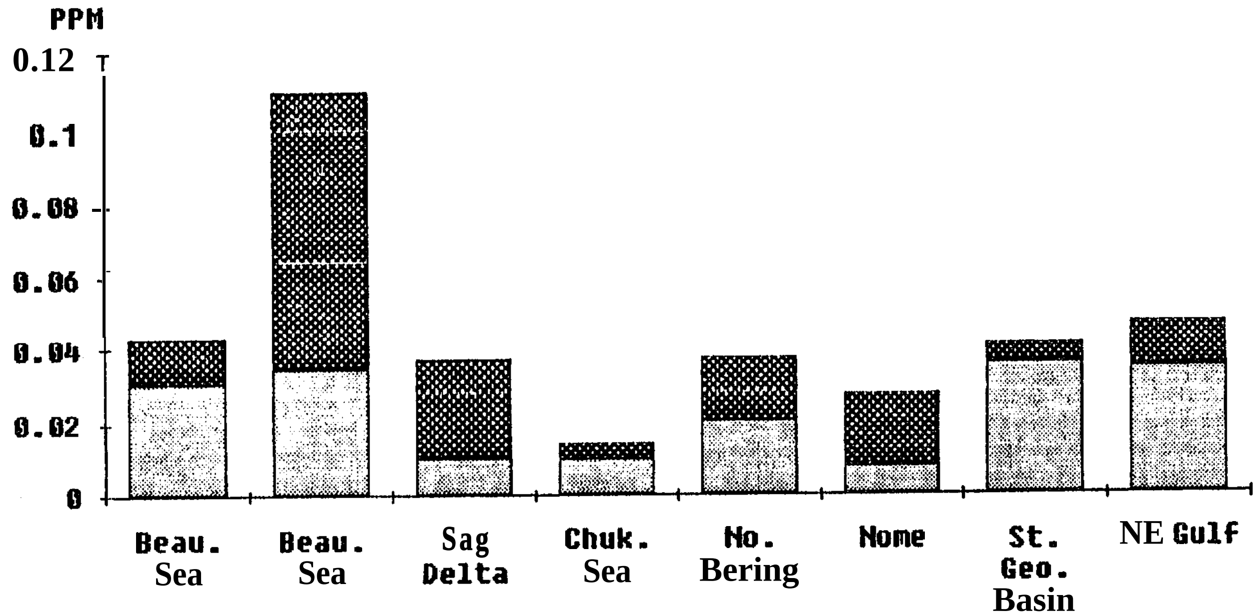

Fig. 3. Confidence intervals (95%) for geometric means of mercury in surface sediments of Alaska shelf areas. Nome and NE Gulf samples are all grain size fractions combined. Other area samples are sand Fraction.

Fig. 4. The proportions of total mud-sand samples for mercury in Alaska shelf areas.

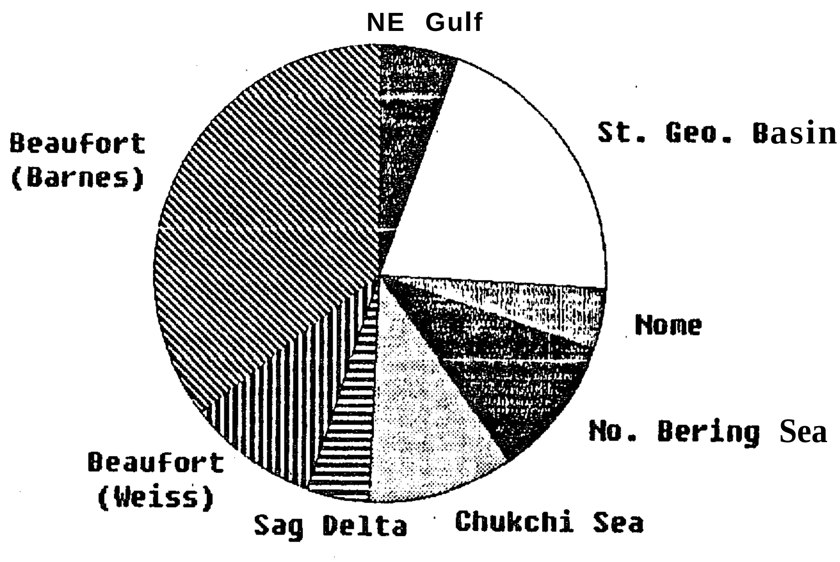

Table 5. Bartlett's test of homogeneity of variances among five studies of mercury concentration in surface mud and sand from the Alaska shelf. Calculations follow Sokal and Rohlf (1969:370). Significant differences in variances are inferred from the test statistics which exceed the critical chi-square of 9.5 for alpha=.05 and df=4 .

Individual studies

	Degrees of freedom	SD
Mud :		
Beaufort Sea	118	.83188
Chukchi Sea	18	.51107
No. Bering Sea	16	.81169
St. Gee. Basin	47	,30995
Sag Delta	9	. 49149
Sand:		
Beaufort Sea	52	.62918
Chukchi Sea	31	,50898
No. Bering Sea	31	.83122
St. Gee. Basin	51	.26156
Sag Delta	11	.77887

Studies combined

	Degrees of freedom	Weighted avg. var.	Test chi-square	
Mud	208	49,8	52,2	S
Sand	176	34.2	55.0	s

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