OCS Study
MMS 90-0010

ALASKA OCS REGION

Concentrations of Metals in Norton Sound Seawater Samples and Human Hair Samples, 1989

U.S. Department of the Interior
Minerals Management Service
Alaska OCS Region

April 1990

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering the wisest use of our land and water resources, protecting our fish and wildlife, preserving the environmental and cultural values of our national parks and historical places, and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to assure that their developement is in the best interest of all our people. The Department also has a major responsibility for American Indian reservation communities and for people who live in Island Territories under U.S. Administration.

March 3, 1849

U.S. Department of the Interior Minerals Management Service

DISCLAIMER

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE MEMORIAL INSTITUTE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

OCS Study
MMS 90-0010

CONCENTRATIONS OF METALS IN NORTON SOUND SEAWATER SAMPLES AND HUMAN HAIR SAMPLES, 1989

Prepared for:

U.S. Department of the Interior
Minerals Management Service
Alaska OCS Region
949 East 36th Avenue, Room 110
Anchorage, Alaska 99508-4302
Under Interagency Agreement No. 14-35-0004-60143

Report Preparation by:

E. A. Crecelius
C. W. Apts
B. K. Lasorsa

Battelle/Marine Sciences Laboratory
439 West Sequim Bay Road
Sequim, Washington 98382

April 1990

SUMMARY

A limited survey conducted in the summer of 1989 indicated that concentrations of seven metals (Ag, Cd, Cu, Hg, Ni, Pb, Zn) in Norton Sound seawater are typical of coastal seawater. Of particular interest was Hg, which was determined to be in the range of 1 to 2 ng/L. Previous monitoring studies, which used a less sensitive U.S. Environmental Protection Agency (EPA) method, reported values one hundred times higher.

There was no indication of horizontal or vertical gradients in the concentrations of metals. The Snake River, which enters Norton Sound at Nome, Alaska, does not appear to be a significant source of metals to Norton Sound.

Seawater samples collected in the turbidity plume of the BIMA gold dredge contained elevated concentrations of total metals as a result of suspended sediment. However, dissolved metals were not significantly elevated in seawater down-current of the gold dredge.

Sediment elutriate tests conducted on three sediments indicated As and Ni may be released during sediment resuspension processes. A comparison was made between the EPA Method 3005 for Total Recoverable metals in water and chemical oceanographic methods for metals in seawater. The Total Recoverable digestion method causes significant contamination of the seawater for some metals. The EPA methods for analysis of metals in water are not sensitive enough to quantify the natural concentrations of metal in coastal seawater.

The concentrations of Hg and As in hair samples from Nome women were below the levels of concern for human health. The ingestion rate of methylmercury by these 200 women of Nome is estimated to be much lower than had been predicted from data on other populations that consume significant quantities of fish and marine mammals.

CONTENTS

TABLES

INTRODUCTION

The U.S. Department of the Interior Minerals Management Service is proposing to lease submerged federal lands in Norton Sound, which is near Nome, Alaska, for placer mining of gold. The Department believes that recovery of minerals and protection of the environment are compatible. Minerals Management Service contracted with the Pacific Northwest Laboratory (PNL)[a] to investigate the concentrations of selected metals in environmental samples from Norton Sound.

Trace-metal data for seawater in Norton Sound available through November 1988 suggested that elevated concentrations of trace metals may be the result of either present and past mining activities or natural sources. These data were suspected to be inaccurate because the methods used for sampling and analysis were not state-of-the-art and were believed to reflect contamination; therefore, the methods were not deemed appropriate for the quantification of trace metals in coastal seawater.

Pacific Northwest Laboratory staff sampled seawater near Nome in June and September 1989. These seawater samples and sediment samples were analyzed for trace metals with the following objectives: 1) to determine the concentrations of metals in surface and bottom water within 30 miles of Nome, 2) to determine the concentrations of metals up-current and down-current of the BIMA gold dredge while the dredge was operating, 3) to compare the U.S. Environmental Protection Agency (EPA) total recoverable digestion technique for the analysis of metals in seawater with other analytical-chemical methods, and 4) to determine the concentrations of metals in sediment elutriates.

In a related issue, few data were available on the levels of mercury and arsenic in Nome residents through 1988. To fill this data need, samples of hair collected from Nome women of child-bearing age were analyzed to determine the concentrations of mercury and arsenic.

(a) Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

FIELD SAMPLING

WATER AND SEDIMENT

Water samples were collected on June 19 and 20, 1989, and on September 6, 1989, from several regional stations and from near the BIMA gold dredge (Figure 1). The station locations are given in Table 1. In June, the Snake River, which flows through Nome, was sampled. The water samples were collected using "clean" techniques, which included using plastic hydroline, plastic-coated hydroweight, and acid-cleaned Teflon®-coated GO-FLO (General Oceanics, Miami, Florida) water-sampling bottles, and storing water samples in acid-cleaned Teflon bottles. All water samples were acidified in the field with hydrochloric acid to a pH of approximately 1.8. A few water samples were filtered in the field through an acid-cleaned 0.4-μm pore-size membrane filter before being acidified.

Sediment samples, of approximately the top 10 cm, were collected on two different occasions (see Figure 1 and Table 1 for locations). In October 1988, the University of Alaska collected sediment samples at Stations 3 and 10, using a HAPS corer. These two sediment samples were stored frozen until elutriate tests were conducted by PNL in the fall of 1989. On September 15, 1989, Western Gold Exploration and Mining Company collected a surface-sediment sample using a Van Veen grab from a recently dredged area near the gold dredge. This sample was stored at 4°C for several weeks before the elutriate test was conducted.

HAIR

The Norton Sound Health Corporation collected hair samples in September and October 1989 from 200 Nome women of child-bearing age. A bundle of 10 to 20 strands of hair, approximately 6 to 18 in. long, were cut near the scalp and the total length of hair was cut into pieces as the hair was placed in a precleaned glass vial which was then sealed with a Teflon lid.

® Teflon is a registered trademark of E. I. Du Pont de Nemours, Wilmington, Delaware.

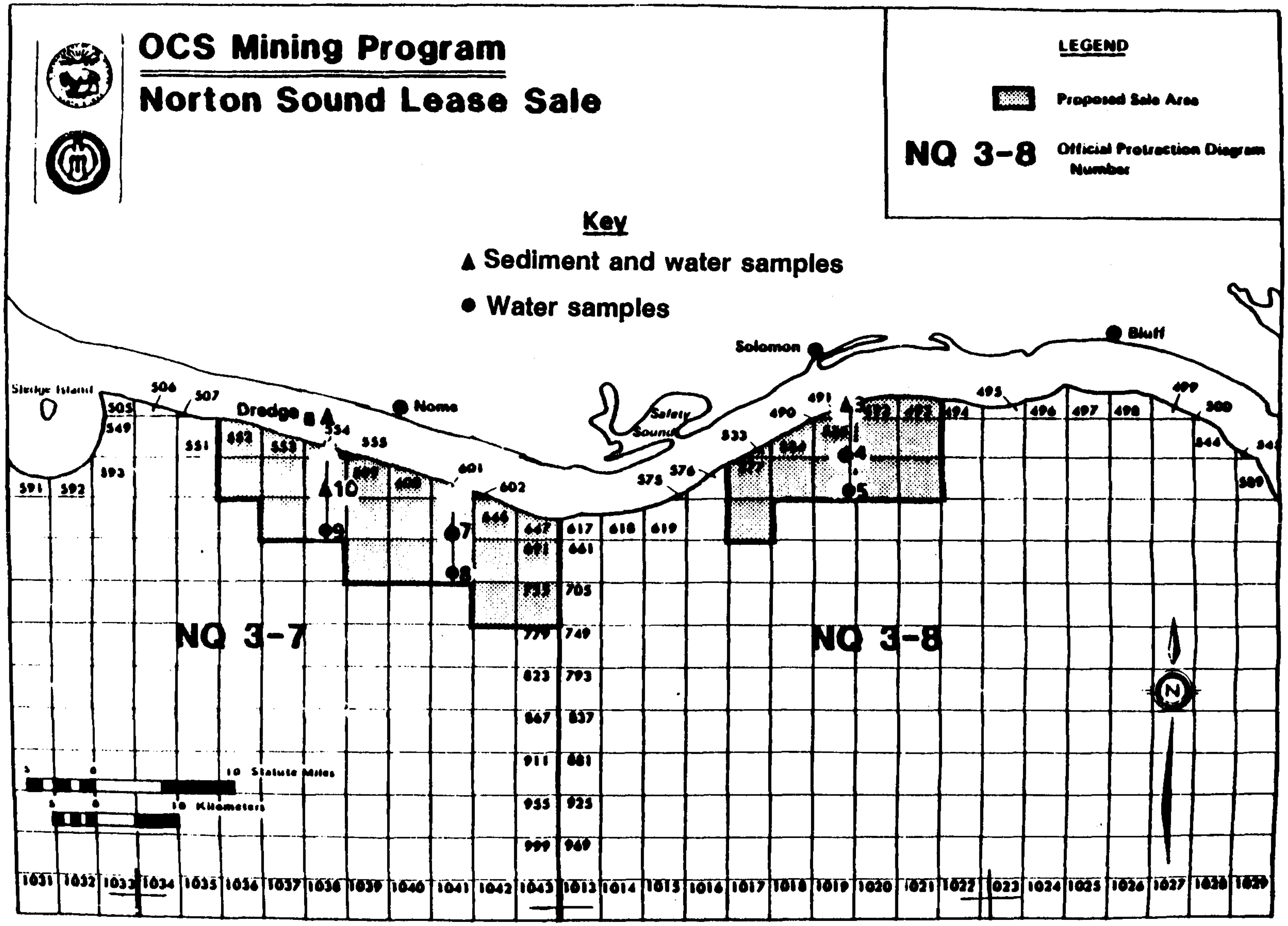

FIGURE 1. Locations of Samples Collected from the Proposed Federal Lease Sale Area and from the State Lease Area (After MMS, 1988). Each of the station locations has a prefix MMS.

TABLE 1. Location of Stations for Collection of Seawater or Sediment

Station No.	Date(s)	Latitude (N)	Longitude (W)
		Seawater	
Dredge	6/19/89 6/20/89 9/6/89	Gold dredge site, coordinates not available for water samples. See Figure 1 for approximate locations.	
4	6/20/89	64°28.2'	164°18.0'
5	6/20/89	64°24.2'	164°18.0'
7	6/20/89	64°22.5'	165°16.2'
8	6/20/89	64°14.4'	165°16.0'
9	6/19/89 6/20/89 9/6/89	64°22.1'	165°34.0'
10	6/19/89 6/20/89 9/6/89	64°24.6'	165°32.0'
		Sediments	
Dredge	9/15/89	64°30.5'	165°34.0'
3	10/88	64°31.1'	164°18.2'
10	10/88	64°24.6'	165°32.0'

ANALYTICAL METHODS

Analytical methods were designed to be sufficiently sensitive to detect the ambient concentration of metals in seawater, sediments, and hair samples. The methods used to preconcentrate or digest the water and sediment samples would allow quantification of both dissolved metals and metals sorbed or bound to sediments and organic matter.

SEAWATER

Seawater samples were analyzed for total metals. Mercury was analyzed by cold-vapor atomic fluorescence (CVAF) with a gold-amalgamation preconcentration step (Bloom and Crecelius 1983). Arsenic was analyzed by hydride generation with a cryogenic preconcentration step, similarly to the methods used by Andreae (1977). Cadmium, copper, lead, and nickel were analyzed using Zeeman (Perkin-Elmer, Norwalk, Connecticut) graphite furnace AA (ZGFAA) after preconcentration with an organic complexer (Bloom and Crecelius 1984). Zinc was analyzed by direct-injection ZGFAA. The technique was not sensitive enough to detect Zn in some seawater samples.

Several seawater samples were also analyzed for metals after digestion by the EPA digestion technique for total recoverable metals (Method 3005, EPA 1986), designed for solubilizing metals in waste water. The digestion method involves adding acid and evaporating off approximately 80% of the water, diluting the digestate back to the original volume, and analyzing the digestate by either flame, furnace, hydride, or CVAF. A disadvantage of using this technique for seawater is that the digestion procedures present opportunities for sample contamination from the acid, the dilution water, and the digestion vessel.

SEDIMENT

Sediment samples were analyzed for total metals by a combination of energy-dispersive x-ray fluorescence (Nielson and Sanders 1983) for As, Cr, Cu, Ni, Pb, and Zn and by CVAF for Cd and Hg, after the complete dissolution of the sediment by a mixture of nitric, perchloric, and hydro-fluoric acids at elevated temperature and pressure (Freitas et al. 1989).

HAIR

Hair samples were analyzed for Hg and As. Between 0.01 and 0.3 g of hair were collected in the form of 10 to 20 full strands (6- to 18-in. long) from each participant and placed in a preweighed, numbered, 23-mL glass vial with a Teflon lid. All vials and lids had been boiled for 24 h in concentrated nitric acid, and samplers wore gloves to avoid contaminating samples. To make it easier to place samples in vials, long hair was snipped into short sections.

Upon receipt by PNL, all vials were weighed and sample weights were recorded. The five heaviest samples were split into thirds to allow for sample repetitions and archiving of a small subset of samples for other uses, such as interlaboratory calibration. Three certified reference materials (dogfish liver, dogfish muscle, and human hair [NIES-1]) were treated identically to the hair samples.

Digestion of the samples was accomplished by refluxing samples with 5 mL concentrated nitric acid at 250°F for 6 h with a glass marble on top of the vial. Samples were allowed to cool and were then brought to a volume of 22.77 mL with tap water shown to be low in Hg. The samples were digested in groups of 20 to 30 over 2 weeks.

For the analysis of Hg, 100 μL of each sample was analyzed by CVAF using the method of Bloom and Crecelius (1983). Five of the sample digestates were analyzed twice to ascertain instrumental precision. Five of the samples were digested twice and the results of the analysis of each digestate were compared to determine the precision of the entire analytical procedure. The three standard reference materials were analyzed exactly as the samples to determine accuracy. Reagent blanks were analyzed for each group of digestates, and the value found was subtracted from the Hg value reported for each sample. The reagent blank was remarkably consistent.

Arsenic in the same hair digestate was quantified by ZGFAA using Pd as a matrix modifier. The detection limit varied over a range of about 0.1 to 1.0 µg/g dry weight of hair because of the differences in weight of samples digested.

QUALITY CONTROL

In order to provide documentation as to the quality of the chemical data, the following quality control samples were analyzed: (1) certified reference seawater, (2) certified reference hair, and (3) intercomparison samples with another laboratory.

SEAWATER

Quality control results for seawater (Table 2) include procedural blanks and our results for the analysis of reference coastal seawater (CASS-1) certified for six trace metals. Our results agree with the certified value, indicating that our results are accurate. Because no certified water sample for mercury in seawater is available, three water samples were sent to and analyzed by Dr. Gary Gill at the University of California at Santa Cruz. The results of this interlaboratory comparison (Table 3) showed excellent agreement for Hg concentrations typical of coastal seawater. These results are convincing evidence that mercury concentrations in Norton Sound are similar to those found in other nonpolluted coastal areas.

TABLE 2. Quality Control Data for Trace Metals in Seawater from Norton Sound

	Concentration, µg/L						
Sample	As	Cd	Cu	Hg	Ni	Pb	Zn
Procedural Blank 1	0.19	0.002	< 0.01	< 0.0001	0.015	0.016	1.00
Procedural Blank 2	0.13	0.002	< 0.01	< 0.0001	< 0.013	0.023	1.17
Procedural Blank 3	0.16	0.002	< 0.01	< 0.0001	< 0.013	< 0.003	1.08
CASS-1 Seawater Reference							
PNL Results	1.12	0.030	0.28	-	0.270	0.233	0.931
Certified Value	1.04	0.026	0.29	None	0.290	0.251	0.980
Certified Limits	± 0.07	± 0.005	± 0.03	-	± 0.031	± 0.027	± 0.099

- = Data not available.

TABLE 3. Interlaboratory Comparison for Total Mercury in Seawater Collected from Norton Sound in June 1989

Station	Sample	Date	Concentration, μg/L	
			PNL	Gary Gill - UCSC
100 m Down-Current	Mid-depth	6-19	0.0024	0.0037
9	S-1	6-19	0.0010	0.0007
10	S-3	6-20	0.0017	0.0012

HAIR

The hair standard NIES-1 is certified for Hg but not As. This standard was analyzed several times for Hg and a mean concentration of 4.22 μg/g, compared with the certified value of 4.42 μg/g, was determined. Two marine tissue standards also analyzed for Hg agreed well. The As concentration of the NIES-1 hair standard was below detection.

Three of the five samples digested twice to ascertain reproducibility were sent to Dr. Stephen LaPierre at the Laboratoire de Sante Publique du Quebec for interlaboratory calibration of our Hg method. Dr. LaPierre analyzed our digestate by his method (modified Mago's) in addition to digesting dry samples by a strong-base/cysteine method. Agreement between Dr. LaPierre's results for his digestate and our digestate was within 17%. Agreement between Dr. LaPierre's analysis of our digestate and our analysis of our digestate was within 18%.

RESULTS AND DISCUSSION

METALS IN SEAWATER

Tables 4 and 5 present the concentrations of seven metals in surface (S) and bottom (B) water from six stations in Norton Sound for samples collected in June and September, respectively. At each station, two or three field-replicate samples were taken. The concentrations of all seven metals are typical of nonpolluted coastal water whereas the concentrations of Cu and Ni, which range from 0.67 to 1.6 µg/L and 0.65 to 2.5 µg/L, respectively, are slightly higher than expected. Usually, these concentrations are on the order of 0.5 µg/L. Copper and Pb concentrations are consistently higher in the bottom than in the surface water, but the other five metals do not show any trends. There do not appear to be any differences between stations.

Tables 6 and 7 present concentrations of metals in water samples collected up-current and down-current of the BIMA. There is no indication of Hg contamination during dredging operations. The water-quality survey conducted by Western Gold Exploration and Mining Company during the summer of 1989 supports this. The down-current bottom-water samples, which contain high suspended-solids concentrations, have significantly elevated concentrations of As, Cd, Cu, Ni, Pb, and Zn. These high concentrations are to be expected, because the suspended solids in the acidified seawater samples contribute crustal metals, which are presumably not bioavailable when bound to the suspended solids (Campbell et al. 1988). When these samples were filtered in the field (0.4 µm), the concentrations of dissolved metals were similar to those at the up-current station (Table 7).

Concentrations of metals in Snake River water samples are similar to concentrations in Norton Sound seawater (Table 8). This indicates that the river does not have a significant influence on the concentration of metals in offshore water or in seawater at the gold-dredging site.

TABLE 4. Concentrations of Trace Metals in Seawater Collected in June 1989 from Regional Stations in Norton Sound near Nome, Alaska

			Concentration, μg/L						
Station	Date	Sample	As	Cd	Cu	Hg	Ni	Pb	Zn
4	6/20/89	S-1	0.77	0.07	0.79	0.0007	1.8	0.07	< 0.65
4	6/20/89	S-2	0.82	0.07	0.76	0.0016	2.1	0.03	< 0.65
4	6/20/89	B-1	0.95	0.07	1.2	0.0011	2.5	0.14	1.0
4	6/20/89	B-2	1.0	0.07	1.1	0.0012	1.7	0.15	< 0.65
5	6/20/89	S-1	0.81	0.06	0.76	0.0012	1.9	0.01	< 0.65
5	6/20/89	S-2	0.74	0.06	0.77	0.0008	1.7	0.04	< 0.65
5	6/20/89	B-1	0.77	0.07	1.2	0.0012	1.3	0.13	< 0.65
5	6/20/89	B-2	0.86	0.07	1.2	0.0012	1.6	0.14	0.83
7	6/20/89	S-1	0.81	0.07	0.67	0.0011	0.82	0.03	< 0.65
7	6/20/89	S-2	0.57	0.07	1.0	0.0017	1.6	0.02	< 0.65
7	6/20/89	B-1	0.95	0.07	1.3	0.0019	1.5	0.26	1.1
7	6/20/89	B-2	0.68	0.07	1.2	0.0014	1.6	0.20	< 0.65
8	6/20/89	S-1	0.58	0.07	0.91	0.0010	1.2	0.06	< 0.65
8	6/20/89	S-2	0.43	0.07	0.82	0.0019	0.84	0.05	< 0.65
8	6/20/89	B-1	0.92	0.07	1.4	0.0020	1.6	0.36	0.93
8	6/20/89	B-2	0.80	0.06	1.5	0.0021	1.7	0.39	1.9
9	6/19/89	S-1	0.62	0.05	1.6	0.0009	1.6	0.22	1.8
9	6/19/89	S-2	0.74	0.06	1.6	0.0008	1.4	0.07	< 0.65
9	6/19/89	B-1	0.98	0.05	1.3	0.0015	2.2	0.26	3.6
9	6/19/89	B-2	0.89	0.06	1.2	0.0012	1.7	0.21	< 0.65
10	6/19/89	S-1	0.50	0.06	0.97	0.0008	0.65	0.04	0.64
10	6/19/89	S-2	0.85	0.06	1.0	0.0006	0.97	0.03	0.73
10	6/20/89	S-3	0.84	0.05	1.1	0.0008	1.3	0.06	1.1
10	6/19/89	B-1	0.69	0.06	1.1	0.0013	1.7	0.21	< 0.65
10	6/19/89	B-2	0.88	0.06	1.1	0.0012	1.8	0.20	< 0.65
10	6/20/89	B-3	0.90	0.07	1.2	0.0015	1.9	0.19	0.83

TABLE 5. Concentrations of Trace Metals in Seawater Collected on September 6, 1989, from Regional Stations in Norton Sound near Nome, Alaska

		Concentration, µg/L						
Station	**Sample**	**As**	**Cd**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
9	S-1	1.31	0.06	0.76	0.0006	4.0	0.10	0.87
9	S-2	0.76	0.06	1.3	0.0004	2.6	0.02	0.87
9	B-1	1.21	0.06	0.71	0.0009	2.6	0.20	<0.55
9	B-2	1.16	0.05	0.63	0.0008	1.0	0.09	0.87
10	S-1	0.73	0.06	1.3	0.0004	1.1	0.02	1.1
10	S-2	0.77	0.06	1.4	0.0003	1.8	<0.01	0.60
10	B-1	1.10	0.06	0.74	0.0007	1.8	0.12	<0.56
10	B-2	1.11	0.06	0.74	0.0007	0.8	0.08	0.73

TABLE 6. Concentrations of Trace Metals in Seawater Collected in June 1989 Near the BIMA Gold Dredge in Norton Sound, Alaska

Station	Sample	Date	Concentration, μg/L As	Cd	Cu	Hg	Ni	Pb	Zn
2000 m Up-Current	Surface	6/19/89	0.87	0.07	1.2	0.0009	1.7	0.14	< 0.65
2000 m Up-Current	Mid	6/19/89	2.07	0.07	1.4	0.0014	3.2	0.24	1.7
2000 m Up-Current	Bottom	6/19/89	1.8	0.07	1.5	0.0027	1.7	0.41	1.5
100 m Down-Current	Surface	6/19/89	2.57	0.07	1.6	0.0010	2.9	0.34	1.8
100 m Down-Current	Mid	6/19/89	5.05	0.11	11	0.0011	24	2.9	11
100 m Down-Current	Bottom	6/19/89	5.0	0.14	33	0.0014	24	4.2	13
2000 m Up-Current	Surface	6/21/89	1.5	0.07	1.6	0.0004	1.8	0.24	< 0.65
2000 m Up-Current	Mid	6/21/89	1.9	0.07	1.1	0.0007	2.0	0.22	< 0.65
2000 m Up-Current	Bottom	6/21/89	1.4	0.07	1.4	0.0007	1.8	0.23	< 0.65
100 m Down-Current	Surface	6/21/89	1.7	0.07	1.3	0.0015	2.6	0.23	< 0.65
100 m Down-Current	Mid	6/21/89	2.5	0.08	1.7	0.0006	2.6	0.55	2.0
100 m Down-Current	Bottom	6/21/89	9.2	0.13	21	0.0009	21	3.4	9.8

TABLE 7. Concentrations of Trace Metals in Seawater Collected on September 6, 1989, Near the BIMA Gold Dredge in Norton Sound, Alaska

Station	Sample	As	Cd	Cu	Hg	Ni	Pb	Zn
		Concentration, µg/L						
		Filtered						
100 m Down-Current	Surface	1.00	0.06	2.4	0.0008	2.3	0.03	1.1
100 m Down-Current	Mid	0.90	0.02	1.7	0.0009	4.6	0.06	0.69
100 m Down-Current	Bottom	0.78	0.03	0.50	0.0007	4.9	0.01	< 0.55
2000 m Up-Current	Bottom	0.93	0.06	1.1	0.0005	1.3	<0.01	< 0.55
		Unfiltered						
100 m Down-Current	Surface	1.47	0.07	1.5	0.0009	2.3	0.18	1.5
100 m Down-Current	Mid	14.08	0.23	51	0.0030	66	13	29
100 m Down-Current	Bottom	23.18	0.11	51	0.0030	68	13	28
2000 m Up-Current	Surface	1.12	0.07	1.4	0.0002	2.4	0.07	< 0.55
2000 m Up-Current	Mid	1.17	0.06	1.4	0.0008	2.4	0.06	< 0.55
2000 m Up-Current	Bottom	1.30	0.07	1.5	0.0008	2.4	0.14	0.92

TABLE 8. Concentrations of Trace Metals in the Snake River Water near Nome, Alaska, on June 20, 1989

	Concentration, μg/L						
Station	As	Cd	Cu	Hg	Ni	Pb	Zn
1	3.70	0.02	1.0	0.004	1.5	0.36	3.42
2	4.08	0.03	1.1	0.004	1.8	0.42	2.28

TOTAL RECOVERABLE DIGESTION OF SEAWATER

The EPA Method 3005 Total Recoverable Metals digestion procedure was applied to eight seawater samples, which were also analyzed by the chemical oceanographic methods previously described. Table 9 presents the results for total recoverable metals along with the approximate concentrations of metals in seawater samples from Stations 9 and 10 analyzed by chemical oceanographic methods. The data in Tables 4 and 6 include the individual results for these eight seawater samples analyzed by chemical oceanographic methods without the Method 3005 digestion.

After the seawater was digested by Method 3005, the five metals Cd, Cu, Ni, Pb, and Zn were analyzed by direct injection into the ZGFAA without a preconcentration step. Arsenic was analyzed by hydride generation with a preconcentration step, and Hg was analyzed by CVAF with a preconcentration step. The results for Cd, Cu, Ni, and Pb, shown in Table 9, are largely below detection, because of matrix interferences. Arsenic and Hg were detected in all eight samples. The As concentrations were similar to those in nondigested samples except for the 100-m down-current mid-sample, which contained approximately an order of magnitude higher concentration after digestion. Mercury concentrations were an order of magnitude higher after digestion, a result, we believe, of sample contamination during the digestion procedure, not of mercury release from particulate matter, since both our and Gary Gill's analyses for total mercury did not exceed 0.0037 μg/L.

TABLE 9. Concentrations of Trace Metals by Total Recoverable Digestion, EPA Method 3005, in Seawater Collected in June 1989 Near the BIMA Gold Dredge in Norton Sound, Alaska, and Approximate Concentrations from Stations 9 and 10 from Chemical Oceanographic Methods

			Concentration, µg/L						
Station	Sample	Date	As	Cd	Cu	Hg	Ni	Pb	Zn
2000 m Up-Current	Mid	6/19/89	2.57	0.70	< 4.5	0.021	< 12	< 1.2	24
100 m Down-Current	Surface	6/19/89	3.45	< 0.68	< 4.5	0.019	< 12	< 1.2	8.3
100 m Down-Current	Mid	6/19/89	41.25	< 0.68	10.8	0.031	< 12	3.7	36
9	S-1	6/19/89	1.11	< 0.68	< 4.5	0.020	< 12	< 1.2	4.8
9	B-1	6/19/89	1.95	< 0.68	< 4.5	0.037	< 12	< 1.2	9.2
10	S-1	6/19/89	0.77	< 0.68	< 4.5	0.020	< 12	< 1.2	6.2
10	S-2	6/19/89	0.98	< 0.68	< 4.5	0.022	< 12	< 1.2	< 4.6
10	S-3	6/20/89	1.05	0.73	< 4.5	0.019	< 12	< 1.2	5.3

Analysis by Chemical Oceanographic Methods (from Tables 4 and 6)

			Concentration, µg/L						
Station	Sample	Date	As	Cd	Cu	Hg	Ni	Pb	Zn
9 and 10	5 Samples	6/19/89	0.7	0.056	1.20	0.0009	1.7	0.1	< 0.65

The detection limits for Cd, Cu, Ni, and Pb could be lowered at least an order of magnitude if after the Method 3005 digestion the metals were preconcentrated with a complexing agent, as was done with the seawater samples that were not digested. However, the major disadvantage of the Method 3005 digestion was that significant contamination of the seawater occurred during the digestion even though care was taken to use clean Teflon digestion containers and high-purity acid, and even though the samples were protected from airborne contamination.

We do not believe that this comparison demonstrates that Method 3005 released from seawater metals not detected by other methods that did not include a digestion step, with the exception of As in samples with high suspended solids. In an ongoing study, PNL is comparing several digestion methods for the analysis of metals in seawater. Results are expected to be available by the end of 1990.

SEDIMENT ELUTRIATE TEST

Three sediment samples were subjected to a sediment elutriate test to simulate the release of metals to seawater when sediments are suspended as the result of dredging. The elutriate test consisted of mixing 4 parts seawater with 1 part wet sediment (by volume) in a beaker for 30 minutes. After the mixture settled for an hour, the overlying water was filtered (0.4 μm) and the concentrations of dissolved metal were determined. The concentrations of As^{+3}, As^{+5}, Cu, Hg, Ni, and H^+ (pH) were determined on three elutriates and on the receiving water used to conduct the elutriate test. The results in Table 10 show that the pH was reduced slightly and that some metals were released by some sediment samples while other metals were removed. Copper was removed from the seawater by all samples. Nickel was removed by two sediments and was released by the BIMA sample. Mercury increased slightly in all elutriates, and As increased with the majority being present as As^{+3}, or the arsenite form.

TABLE 10. Concentrations of Trace Metals in Norton Sound Sediment Elutriates (Filtered)

		Concentration, µg/L				
Station	pH	As^{+3}	As^{+5}	Cu	Hg	Ni
Sta 3	7.6	4.1	1.2	0.34	0.00044	1.2
Sta 10	7.6	3.4	1.2	0.48	0.00037	0.8
BIMA Site (9-15-89)	7.6	10.9	7.1	0.56	0.00026	18.8
Norton Sound Receiving Water	7.8	0.1	0.6	1.17	0.00019	2.0

The elutriate tests indicate that dredging activities may release As and Ni to seawater. Because the sediment samples from Stations 3 and 10 were stored frozen for a year, these tests may not be representative. The sediment sample from the BIMA site was stored for several weeks at 4°C before the test was conducted, which could also influence the results. When future elutriate tests are conducted, the holding time should be minimized to reduce possible storage effects.

Table 11 shows the concentrations of metals in the sediment samples used in the elutriate tests. Except for the relatively high concentration of As in the BIMA sample, the concentrations of other metals are relatively uniform within these sediment samples and are typical of sandy or silty sediments in Norton Sound (Bronson 1988).

TABLE 11. Concentrations of Trace Metals in Norton Sound Sediments

	Concentration, µg/g dry weight							
Station	As	Cd	Cu	Cr	Hg	Pb	Ni	Zn
Sta 3	12	0.20	32	81	0.065	11	37	98
Sta 10	13	0.16	23	74	0.033	12	28	80
BIMA Site (9-15-89)	67	0.18	20	73	0.016	11	35	80

MERCURY AND ARSENIC IN HAIR SAMPLES

Concentrations of mercury and arsenic were determined in 200 hair samples collected during September and October 1989 from Nome women of childbearing age. The results of these analyses are presented in Table 12. Mercury concentrations range from 0.02 to 8.0, with an approximate mean of 1 ppm. Only 12 samples exceeded 3 ppm. Arsenic concentrations were usually below the limit of detection, which varied greatly depending upon the quantity of hair digested. The concentrations of arsenic that were detected ranged from 0.03 to 0.80 ppm, with a mean of 0.26 ppm. Arsenic was detected in 42 of the 200 samples. There does not appear to be a correlation between Hg and As in hair.

The results from the hair analyses indicate that these women ingest relatively small amounts of Hg and As. Because the total length of hair sampled (6 to 18 in.) was analyzed, and because hair samples represented approximately 1 to 3 years of growth, the results indicate an average exposure from ingestion rather than reflecting seasonal extremes that may occur. The level of concern for Hg in hair of pregnant women is 10 ppm without a safety factor. The relatively low Hg concentrations for these women may be because their diet includes few meals of fish or marine mammals or it may reflect that the species that are ingested in Nome contain lower concentrations of Hg than species from other Arctic regions. The limited mercury data for fish and marine mammals caught near Nome indicate low mercury levels in these animals (Bronson 1988; ENSR 1990).

The level of concern for arsenic in human hair is about 1 ppm. Arsenic content of human hair has served as an indicator in incidents of suspected poisoning. Based on analyses of 1,000 human hair samples, the median concentrations for females is 0.37 ppm (Smith 1964). Values greater than about 2 to 3 ppm indicate possible poisoning, although higher concentrations have been recorded in occupational surveys (National Research Council 1977). Published data for arsenic in hair related to consumption of marine organisms are not readily available. The arsenic concentrations for the Nome hair samples indicate no arsenic contamination in the food or water of these women. Five hair samples contained undetectable As at detection limits in the range of 1.02 to 1.18 ppm As. The detection limit exceeded 1 ppm because of the small sample size of hair. Presumably the As concentrations in these five hair samples are also below 1 ppm.

The mercury data for the Nome hair samples are significantly lower than data reported by Galster (1976) for Hg in Alaskan Eskimo mothers and infants. Galster's results for hair of mothers in the Yukon-Kuskokwin Delta average 4.3 ppm Hg. Analysis of the diet of women from the Delta indicated that most of their Hg intake was from seal oil and fish.

TABLE 12. Hair Samples Collected at Nome for the Norton Sound Project

Sample	Sample Wt, g	Perm/ Color(a)	Concentration, μg/g	
			As	Hg
1	0.2232	c	< 0.08	0.87
2	0.1216	p	< 0.14	0.74
3	0.1632	p	< 0.11	0.60
4	0.0482		< 0.36	0.20
5	0.1228	p	0.32	0.17
6	0.3225	p	0.06	0.81
7	0.1872	p	< 0.09	0.75
8	0.1716	p	< 0.10	0.32
9	0.2344	p	0.09	1.96
10	0.1185	p	0.17	0.62
11	0.1669	p	< 0.10	1.74
12	0.2292	p	< 0.08	1.56
13	0.2494	pc	< 0.07	1.48
14	0.1140		< 0.15	1.02
15	0.1492	p	0.13	1.06
16	0.1549		< 0.11	1.02
17	0.1596	p	< 0.11	0.28
18	0.1301		< 0.13	0.51
19	0.1673	p	< 0.10	1.23
20	0.1717	p	< 0.10	2.15
21	0.2392		< 0.07	0.48
22	0.2418		0.16	1.35
23	0.1187	p	< 0.15	0.73
24	0.2317	p	0.09	0.50
25	0.1287	p	0.23	2.51
26	0.1749		0.34	0.39
27	0.1651	p	< 0.10	0.59
28	0.0879		< 0.20	0.79
29	0.1395		0.21	1.12
30	0.1020		< 0.17	0.57
31	0.0747		0.24	3.46
32	0.2017	p	< 0.23	0.58
33	0.1947	p	< 0.09	1.32
34	0.0389		< 0.44	0.86
35	0.1436		< 0.12	1.60
36	0.1723	p	< 0.10	1.25
37	0.0988	p	< 0.17	0.59
38	0.1600		< 0.11	0.89
39	0.0344		< 0.50	0.47
40	0.1058		< 0.16	0.51
41	0.1155		< 0.15	0.38
42	0.0408		< 0.42	0.98
43	0.1878		< 0.09	0.47
44	0.1175	p	0.17	0.42

TABLE 12. (contd)

Sample	Sample Wt, g	Perm/ Color(a)	Concentration, μg/g	
			As	Hg
45	0.0661	p	< 0.26	0.52
46	0.2005	p	0.10	0.74
47	0.1167	p	0.17	0.55
48	0.0710	p	< 0.24	0.35
49	0.1527		< 0.11	1.87
50	0.1854	p	0.11	0.39
51	0.2034		< 0.32	0.92
52	0.0331		< 0.32	0.87
53	0.0663	pc	< 0.32	0.43
54	0.0431	p	< 0.32	0.52
55	0.0473	p	< 0.32	0.23
56	0.1925	p	< 0.32	1.16
57	0.0932		< 0.32	1.06
58	0.0403	pc	< 0.32	0.41
59	0.0846	p	< 0.32	0.39
60	0.1718		< 0.32	0.27
61	0.0305	p	< 0.32	0.90
62	0.0861	p	< 0.32	0.61
63	0.0345		< 0.32	1.72
64	0.0569	p	< 0.32	0.65
65	0.1229	p	< 0.32	0.34
66	0.1544	p	< 0.32	1.38
67	0.0323		< 0.32	0.49
68	0.0487	p	< 0.32	0.84
69	0.0481	p	< 0.32	0.37
70	0.2317	p	< 0.32	1.12
71	0.1354		< 0.32	0.26
72	0.2304	pc	< 0.32	0.36
73	0.0391	p	< 0.32	0.53
74	0.0481	p	< 0.32	1.11
75	0.1116	p	< 0.32	0.73
76	0.0852	p	< 0.20	0.53
77	0.0975		< 0.18	0.29
78	0.0705		< 0.24	0.96
79	0.0976	p	< 0.18	0.33
80	0.0407		< 0.42	0.44
81	0.1989	p	< 0.09	0.29
82	0.2412	p	< 0.07	0.55
83	0.0894	p	0.33	0.30
84	0.0202	p	0.07	3.82
85	0.0432	p	0.08	3.70
86	0.0914	p	< 0.19	0.91
87	0.1288	p	< 0.13	1.17
88	0.1672		0.12	0.50
89	0.0449		0.44	0.52

TABLE 12. (contd)

Sample	Sample Wt, g	Perm/Color[(a)]	Concentration, μg/g	
			As	Hg
90	0.1279	p	0.23	0.79
91	0.1173	p	< 0.15	0.90
92	0.1083	p	< 0.16	0.26
93	0.1290	p	0.15	0.54
94	0.1780	p	0.22	0.92
95	0.0454	p	< 0.38	0.21
96	0.1342	p	< 0.13	0.46
97	0.1848	p	< 0.09	1.58
98	0.0285		< 0.60	0.42
99	0.1356	p	< 0.13	2.15
100	0.1343	p	< 0.13	0.47
101	0.0609	p	< 0.28	0.33
102	0.0917	p	< 0.19	0.96
103	0.0193	pc	< 0.89	0.34
104	0.0245	pc	< 0.70	0.50
105	0.0512		< 0.34	1.67
106	0.0634	pc	< 0.27	0.27
107	0.0251	p	< 0.68	0.25
108	0.0437		< 0.39	0.66
109	0.0384		< 0.45	0.34
110	0.0403		0.49	0.83
111	0.0575		< 0.30	0.21
112	0.0528		< 0.33	0.22
113	0.0460		< 0.37	0.33
114	0.1770		< 0.10	0.86
115	0.0199		< 0.86	0.70
116	0.0478	p	< 0.36	0.37
117	0.0344		0.18	6.22
118	0.0995		0.03	2.95
119	0.0644		< 0.27	0.31
120	0.1162		< 0.15	0.65
121	0.0318	p	< 0.54	0.42
122	0.0773		0.39	0.88
123	0.0473		0.42	0.50
124	0.0374	p	0.80	1.01
125	0.0186	p	< 0.92	1.16
126	0.0171		< 1.00	0.08
127	0.0218		< 0.79	0.82
128	0.0535	p	0.07	8.02
129	0.0461	p	< 0.14	4.53
130	0.0447		< 0.38	1.41
131	0.0181		< 0.95	0.35
132	0.0386		< 0.44	0.31
133	0.0193		< 0.89	1.43

TABLE 12. (contd)

Sample	Sample Wt g	Perm/Color[(a)]	Concentration, µg/g As	Concentration, µg/g Hg	Mean[(b)]
134	0.1875		< 0.09	1.13	
135	0.0316		< 0.54	0.30	
136	0.0148		< 1.16	1.09	
137	0.0169	p	< 1.02	0.90	
138	0.0361	p	< 0.48	0.23	
139	0.0427	pc	< 0.40	0.50	
140	0.0358	p	< 0.48	0.29	
141	0.0154		< 1.11	0.40	
142	0.0434		< 0.40	0.19	
143	0.0168		< 1.02	0.94	
144	0.0240		< 0.72	0.66	
145	0.0771	p	< 0.22	0.80	
146	0.0147	p	0.24	3.16	
147	0.0243	p	< 0.71	0.37	
148	0.0405	p	< 0.42	0.55	
149	0.0391		< 0.44	0.99	
150	0.0145	p	< 1.18	0.85	
151	0.0698	p	< 0.25	0.49	
151 DUP	0.0698	p	-	0.43	0.463
152	0.0582	p	0.03	3.76	
152 DUP	0.0582	p	-	3.74	3.748
153	0.0289	p	< 0.59	1.77	
153 DUP	0.0289	p	-	1.73	1.745
154	0.0633	pc	< 0.27	0.41	
154 DUP	0.0633	pc	-	0.37	0.387
155	0.0302	p	< 0.57	0.23	
155 DUP	0.0302	p	-	0.17	0.204
156	0.1356	p	< 0.13	0.44	
156 DUP	0.1356	p	-	0.44	0.437
157	0.0405		< 0.42	0.69	
157 DUP	0.0405		-	0.59	0.635
158	0.0909	p	0.55	1.57	
158 DUP	0.0909	p	-	1.60	1.584
159	0.0308	p	< 0.56	0.07	
160	0.2341	p	< 0.07	1.51	
161	0.0384	p	< 0.45	0.75	
162	0.0443		< 0.39	0.28	
163	0.0610		< 0.28	0.73	
164	0.0205	p	< 0.84	0.83	
165	0.0327		< 0.53	0.37	
166	0.0557	p	< 0.31	0.39	
167	0.0368	p	< 0.47	0.75	
168	0.0444	p	< 0.14	3.80	
169	0.1501	p	< 0.11	0.02	

TABLE 12. (contd)

Sample	Sample Wt, g	Perm/ Color[(a)]	Concentration, µg/g	
			As	Hg
170	0.0324		0.27	3.01
171	0.0184		< 0.93	0.47
172	0.0406	p	< 0.42	1.39
173	0.0424	p	< 0.41	1.51
174	0.0631		0.31	1.53
175	0.0867		0.23	0.60
176	0.0355	p	0.15	3.46
177	0.0468	p	0.42	1.75
178	0.0552	p	0.54	0.09
179	0.0701	p	0.10	4.06
180	0.0902		0.71	2.66
181	0.0663	p	0.60	0.59
182	0.1442		< 0.12	1.10
183	0.1514	pc	< 0.26	1.19
184	0.1031		< 0.17	1.00
185	0.0714	p	< 0.24	0.70
186	0.0416	p	< 0.41	0.39
187	0.0786	p	< 0.22	1.12
188	0.0587	p	< 0.29	0.43
189	0.0581	p	< 0.30	0.69
190	0.0917	p	< 0.19	0.50
191	0.0419	p	< 0.41	0.26
192	0.1121	p	< 0.15	1.57
193	0.0547		< 0.31	0.53
194	0.0398	p	< 0.43	2.05
195	0.0459	p	< 0.37	0.13
196	0.0372		< 0.46	0.56
197	0.0555	p	< 0.31	0.20
198	0.0453	p	< 0.38	0.56
199	0.1600	p	< 0.11	0.14
200	0.0605	p	< 0.28	0.43

TABLE 12. (contd)

Sample	Sample Wt, g	Concentration, µg/g			
		As	Hg	Hg Mean	Hg % Dev.(c)
105.2	0.0378	-	1.16		
105.2 DUP	0.0378	-	1.67	1.414	18.2
114.2	0.1400	-	1.03		
114.2 DUP	0.1400	-	0.86	0.944	8.5
152.2	0.0367	-	1.06		
152.2 DUP	0.0367	-	0.99	1.025	3.5
160.2	0.0964	-	2.06		
160.2 DUP	0.0964	-	1.51	1.785	15.6
167.2	0.0251	-	0.80		
167.2 DUP	0.0251	-	0.75	0.774	3.2
					9.803

Sample	Concentration, µg/g		
	As	Hg	St. Dev.
DOLT-1	-	0.284	-
Certified	-	0.225	
DORM-1	-	0.817	-
Certified	-	0.798	
NIES-1	< 0.15	4.219	0.412
Certified	None	4.42	

(a) Hair had been permed (p) or colored (c).
(b) Same digestate analyzed twice for Hg.
(c) Same sample digested twice.
- = Data not available.

REFERENCES

Andreae, M. O. 1977. "Determination of Arsenic Species in Natural Waters." Anal. Chem. 49:820.

Bloom, N. S., and E. A. Crecelius. 1983. "Determination of Mercury in Seawater at Sub-nanogram per Liter Levels." Mar. Chem. 14:49-59.

Bloom, N. S., and E. A. Crecelius. 1984. "Determination of Silver in Sea Water by Coprecipitation with Cobalt Pyrrolidinedithicarbamate and Zeeman Graphite-Furnace Atomic Absorption Spectrometry." Anal. Chim. Acta. 156:139-145.

Bronson, M. T. 1988. Trace Contaminants in Surface Sediment of the Northern Bering Sea: A Statistical Review. Laboratory for the Study of Information Science, University of Rhode Island, Kingston, Rhode Island.

Campbell, P.G.C., A. G. Lewis, P. M. Chapman, A. A. Crowder, W. K. Fletcher, B. Imber, S. N. Luoma, P. M. Stokes, and M. Winfrey. 1988. Biologically Available Metals in Sediments. Publication No. NRCC 27694, National Research Council of Canada, Ottawa, Canada.

ENSR Consulting and Engineering. 1990. Nome Offshore Placer Project Final Annual Report 1989. Document No. 7235-007, Western Gold Exploration and Mining Company, Limited Partnership, Nome, Alaska.

EPA. 1986. Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. 3rd ed. SW-846, U.S. Environmental Protection Agency, Washington, D.C.

Freitas, S., P. D. Boehm, R. Hillman, E. Crecelius, H. Costa, R. C. Tuckfield, C. Peven, J. Clayton, A. Uhler, G. Durell, H. Trulli, and N. Young. 1989. Phase 3 Final Report on National Status and Trends Mussel Watch Program. U.S. Department of Commerce, National Oceanic and Atmospheric Administration Ocean Assessments Division.

Galster, W. A. 1976. "Mercury in Alaskan Eskimo Mothers and Infants." Environmental Health Perspectives 15:135-140.

MMS. 1988. Draft Environmental Impact Statement. I-1 to V-3. U.S. Department Interior, Minerals Management Service, Alaska OCS Region, Anchorage, Alaska.

National Research Council. 1977. Arsenic. National Academy of Sciences, Washington, D.C.

Nielson, K. K. and Sanders, R. W. 1983. "Multielement Analysis of Unweighed Biological and Geological Samples Using Backscatter and Fundamental Parameters." Adv. X-Ray Anal. 26:385-390.

Smith, H. 1964. "The Interpretation of the Arsenic Content of Human Hair." _Forensic Sci. Soc. J._ 4:192-199.