

cpy 2 of 2

FEB 1 5 1974

QD
181.H₆
QH
544
C.B.F.

MERCURY IN THE ENVIRONS OF THE
NORTH SLOPE OF ALASKA

H. V. Weiss

Navy Undersea Center, San Diego, California 92132

and

K. Chew, M. Guttman, A. Host

San Diego State University, San Diego, California 92115

LIBRARY OF THE
NAVAL ARCTIC RESEARCH LABORATORY

ACKNOWLEDGMENTS

This work was supported by the office of Naval Research under grant NR 083-290.

The marine sediments were kindly provided by Peter Barnes and his colleagues of the U. S. Geological Survey, Menlo Park, California.

We thank the U. S. Coast Guard for providing the Cutter Glacier in the WEBSEC 72-73 cruises. Thanks are accorded Gary Hufford, the coordinator of these cruises, and Gregory Adam, Richard Bowman, William Gale, John Krezoski, Bruce Rutland, Alex Watt, and Dan Wolfe, Coast Guard marine science technicians who contributed importantly in sample collections.

By means of logistic support provided by the Naval Arctic Research Laboratory, Barrow, Alaska, the snows and certain river waters were gathered and we especially thank Richard Dickerson and James Aikins for their assistance in this regard.

ABSTRACT

The analysis of Greenland ice suggests that the flux of mercury from the continents to the atmosphere has increased in recent times, perhaps partly as a result of the many of man's activities that effect an alteration of terrestrial surfaces. Upon the exposure of fresh crustal matter, the natural outgassing of mercury vapor from the earth's surface could be enhanced.

Accordingly, mercury was measured in a variety of environmental materials gathered from the North Slope of Alaska to provide background data prior to the anticipated increase of activity in this environment. The materials were collected during the U. S. Coast Guard WEBSEC 72-73 cruises as well as through the facilities provided by Naval Arctic Research Laboratory in the spring of 1973.

The method of measurement depended upon radioactivation of mercury with neutrons and the subsequent quantification of characteristic gamma radiations after radiochemical purification.

Mercury concentrations in seawater at several locations in the vicinity of 151°W , 71°N averaged 20 parts per trillion. The waters from all stations east of this location showed a significantly smaller concentration. This difference may relate to penetration of Bering-Chukchi Sea water into the southern Beaufort Sea to 151°W . Marine sediments on the shelf and slope between 143°W and 153°W contained about 100 parts per billion mercury, except for those on the continental shelf between Barter Island and the Canning River, where the concentration was less than half this value. These results are consistent with sediment input from the respective rivers when their mercury content and mineralogy are considered. The mercury content of river waters was 18 ppt and in reasonable agreement with the average of snow samples (13 ppt). The burden of mercury in plankton was 37 ppb.

INTRODUCTION

Data derived from the analysis of Greenland ice suggests that the flux of mercury from the continents to the atmosphere has increased in recent times as a result of input by society (Weiss, et al., 1971). In addition to the obvious sources of mercury, it was further suggested that a fraction of the added quantity may be introduced through activities that result in alteration of terrestrial surfaces, thereby enhancing the natural outgassing of mercury vapor from the earth's crust.

With the anticipated intensification of human activity in the North Slope area, it was considered desirable to acquire baseline data. This report describes the concentration of mercury that was determined in plankton, snow, and in water and sediments from several rivers and the southern Beaufort Sea.

METHOD

Sample Collections. The plankton, and ocean sediments were collected on the US Coast Guard WEBSEC-72 Cruise during August 1972, while river sediments and river and ocean water were gathered in July - August 1973 on WEBSEC-73. By means of facilities provided by the Naval Arctic Research Laboratory (NARL), the snows were collected in mid-March 1973.

The accumulation of plankton was by standard oceanographic procedure in a vertical tow at $71^{\circ}12.0$ N, $149^{\circ}31.8$ W from a depth of 180 meters. The sample together with transfer distilled water was frozen until shortly before preparation for analysis.

Seawater samples were obtained from the southern Beaufort Sea between 146° - 151° W longitude in 8-liter Niskin bottles by standard hydrocasting procedures. Aliquots were drawn into storage containers within 15 minutes after the collection.

Samples of river water were taken from the Umiat and Gubic regions of the Colville River and from 25 miles upstream on the Sagavanirktok River. The sample was collected about 6 in. from the surface after wading into the river to a depth of 2.5 ft.

Water samples were stored in polyethylene containers that previously had been soaked for 16 hours in concentrated nitric acid. The containers were rinsed three times with sample and then nearly filled. Immediately, 10 ml of 16 N nitric acid were added and the sample was stored for analysis.

Sagavanirktok and Colville River sediments were obtained 25 miles upstream at a distance of several feet from the shoreline. The marine sediments were acquired with a grab sampler. The sediments were transferred to polyethylene storage bags with a plastic utensil, and the samples were frozen as rapidly as possible after collection.

At distances of 30 to 135 miles south of Barrow, and in 15-mile increments, the samples of snow were acquired. When these locations were reached by plane, the engine was cut. After a 10-minute wait and at a distance of about 50 meters upwind from the plane, several inches of snow were removed and discarded. The underlying deposit was transferred with a clean plastic scoop to a polyethylene bag, which was stored in a thermally insulated box during transit. Upon return to NARL, the sample was melted at indoor temperature in 3-liter polyethylene containers previously leached with nitric acid as described above and rinsed five times with double-distilled water. These containers received 30 ml of concentrated nitric acid prior to melting.

Mercury Analysis. The mercury analyses were performed by a modification of a neutron activation analysis procedure previously described (Weiss and Crozier, 1972). The changes were introduced to provide for radiochemical purity at an earlier time after the irradiation; accordingly the sensitivity was appreciably enhanced.

Sample Preparation. Mercury was isolated from snow, river, and seawater samples by coprecipitation with copper. To 1 liter of sample was added 1 mg of 99.999% copper as nitrate. Reagent-grade hydrogen sulfide gas, after passing through a millipore membrane filter, was bubbled through the solution for 30 seconds. The resultant precipitate was collected by filtration. (This, and subsequent filtrations involved passage of the solution through

millipore membrane filters of 0.45 pore size). After filtration, the walls of the sample container were washed with 10 ml of concentrated nitric acid and this wash together with the copper sulfide placed in a polyethylene irradiation vial.

About 2 to 3 grams of sediment in the frozen state and 1 gram of thawed plankton, blotted with absorbent paper, were transferred to irradiation vials and weighed. Three ml of concentrated nitric acid were added to these samples prior to irradiation. A section of frozen sediment that was in juxtaposition to the sample was chipped off and its water content was determined by drying at 110°C for 1 hour.

Comparator and Nitric Acid Blanks. The comparator consisted of 10 µg of mercury as the nitrate in 10 ml of concentrated nitric acid. The nitric acid blank comprised three irradiation vials filled with 14 ml of concentrated nitric acid.

Irradiation. Samples, comparators, and blanks were irradiated for 1 hour in a flux of 1.8×10^{12} neutrons $\text{cm}^{-2} \text{sec}^{-1}$ in a sample container that rotated at 1 rpm about the core of the Mark I TRIGA Reactor at Gulf Energy and Environment Services, San Diego, California. The irradiations occurred during the period 3 to 4 pm. The following morning, samples were processed to attain radiochemical purity.

Radiochemical Purification. Sediments and plankton were transferred to flasks that finally contained 1 ml concentrated phosphoric acid, 1 ml of mercury carrier (10 mg mercury as nitrate), 15 ml of 7 molar sulfuric acid, and 10 ml of concentrated nitric acid. The flask was attached to an apparatus described by Sjöstrand (1964) and distilled until fumes of sulfur trioxide appeared. The condensed acid was re-admitted to the flask and the distillation was repeated until sediments were white and the plankton digest was colorless.

Sediment and plankton were prepared further for radiochemical purification by addition of 25 ml of concentrated ammonium hydroxide to the digest, and the mixture was filtered. If at this stage pebbles were detected in the residual sediment, they were removed and the sample was corrected for their weight.

Ten mg of mercury carrier were added to water samples and the nitric acid blanks. The nitric acid blank was reduced in volume to about 10 ml. Water samples and blanks both received 9 ml of concentrated ammonium hydroxide and 10 mg each of potassium and sodium chloride. (These quantities of chlorides were also added prior to the succeeding precipitations.)

From this stage, with one exception noted later, all samples were treated similarly. To the filtrate were added 2.5 ml of freshly prepared stannous chloride. Mercury metal that precipitated was collected by centrifugation. The precipitate was dissolved in 5 ml aqua regia, 5 mg of copper (as nitrate) were added, and the solution was filtered. The reduction of mercury to the metal was repeated and the solid collected by filtration. The precipitate was again dissolved with 5 ml aqua regia (1 to 2 drops of concentrated phosphoric acid was added to the water samples), and the solution was neutralized with 5 ml of concentrated ammonium hydroxide. Hydrogen sulfide gas was passed through the pH-adjusted solution and the precipitate was collected by filtration. The mercuric sulfide was of sufficient purity to permit immediate measurement.

The comparator was neutralized with 9 ml of concentrated ammonium hydroxide after the addition of mercury carrier, and the mercuric sulfide was precipitated and collected for measurement.

Carrier Yield Determination. The processed mercury samples as well as mercury carrier standards (10 mg mercury) were re-irradiated for 5 seconds. Through comparison of the activity level of the samples and standards, the carrier yield was computed and the counting rate in the original irradiation was corrected for this factor.

Measurement. The radioactive measurements were made with a sodium iodide detector coupled to a 400-channel pulse-height analyzer. The counts attributable to the 77-keV radiation of ^{197}Hg were integrated by the method of Covell (1959).

RESULTS AND DISCUSSION

The mercury content of the zooplankton sample was 37 parts per billion (ppb), a value which falls within the range of 6 to 47 for zooplankton that were collected 430 km southwest of San Diego (Williams and Weiss, 1973).

The analysis of snow samples appears in Table I. Their values ranged from 3.5 to 46.2 parts per trillion (ppt), with an average of 13 ppt. This average value is substantially less than that of apparently unpolluted ice recovered from Camp Century (Weiss, et al., 1971) and the Dye-3 site (Weiss, Bertine, Koide and Goldberg, in preparation) in Greenland, where the average concentrations ranged from 50 to 60 ppt.

The mercury concentration of waters gathered 25 miles upstream on the Sagavanirktok River and the Umiat and Gubic sections of the Colville River ranged narrowly between 16.8 to 18.7 ppt. These values are not markedly different from the average concentration in snow. The disparity is attributable either to the error in average snow value derived from only eight numbers, whose range extends over an order of magnitude, or to inclusion of an incremental amount of mercury as the snows melt and pass over the terrain. The mercury content of the river waters is low as compared with the Danube and Volga Rivers, in which the concentrations measured are usually about 1 to 2 ppb (Aidin'yan and Belavskaya, 1963). On the other hand, river waters in relatively unpolluted areas usually measure between 10 to 50 ppt (Dall' Aglio, 1967).

The mercury content of Beaufort Sea water collected at various depths between 146°W and 151°W are shown in Table II. At one of these stations (151°08'W, 71°23'N) waters were analyzed in duplicate, and the error shown represents the average deviation from the mean; thus the average error is about 10%.

Marked variations of mercury concentration in the vertical are apparent. These variations do not occur as a function of depth; rather, they are random. This variability may be associated with the combining of a large fraction of the element with the particulate phase.

Of further interest is the greater average concentration of mercury in the water recovered from stations occupied at 151°W compared with all stations to the east of this longitude. The temperature data (Hufford, personal communication) indicate that Chukchi and Bering Sea water had penetrated to precisely 151°W during WEBSEC-73. The difference in mercury concentrations may, therefore, reflect varying concentrations of this element between the eastern Beaufort Sea and Chukchi-Bering Sea water masses. We contemplate the measurement of other water secured west of 151°W on WEBSEC-73 to further examine this possibility.

By way of comparison, Beaufort Sea waters contain considerably smaller quantities of mercury than Antarctic waters, where concentrations approximate 100 ppt, but are not markedly different from those collected in a transect from San Diego to an area north of the Hawaiian Islands (Williams, Robertson, Chew and Weiss, in preparation). In

fact many water masses, e.g., English Channel (Burton and Leatherland, 1971), Gulf of California (Weiss, in preparation), and the eastern tropical Pacific Ocean (Weiss, et al., 1972), are not grossly different from the Beaufort Sea in their mercury concentration.

The mercury content of sediments from the Sagavanirktok and Colville Rivers was 111.5 and 119.1 ppb, respectively. Marine sediments collected on the shelf, slope, and in the basin between 143°W to 154°W, with the exception of an area on the shelf from 143°W to 146°W, averaged 100 ppb, and no discrete pattern was evident with respect to distance from the shore (Figure I). These values are reasonably consistent with the river sediments that drain into this general area. The concentration was only 40 ppb on the shelf between the Canning River and Barter Island. Sediment was not available from the Canning River; however these lower concentrations probably reflect input from this river. That Canning River sediment is different from that derived, for example from the Colville River delta has already been established (Naidu, personal communication). The illite-to-smectite ratio in the Canning River sediment is three times greater than in the Colville. The exchange capacity of illite for a heavy metal such as mercury is considerably less than smectite; therefore the difference in mineral composition between the rivers could easily account for the differences observed in the marine sediments with respect to mercury.

In summary, the concentration of mercury in plankton, snow, river and ocean water, and sediments has been determined. These values will serve as baseline by which comparisons may be made at some future date to determine the influence of man's activities upon the concentration of this element in the North Slope environment.

REFERENCES

- WEISS, H. V., M. KOIDE and E. D. GOLDBERG. 1972. Mercury in a Greenland ice sheet; Evidence of recent input by man. *Science* 174: 692-694.
- WEISS, H. V. and T. E. CROZIER. 1972. The determination of mercury in seawater by radioactivation. *Anal. Chim. Acta.* 58: 231-233.
- SJØSTRAND, B. 1964. Simultaneous determination of mercury and arsenic in biological material by activation analysis. *Anal. Chem.* 36: 814-819.
- COVELL, D. F. 1959. Determination of gamma-ray abundance directly from the total absorption peak. *Anal. Chem.* 31: 1785-1790.
- WILLIAMS, P. M. and H. V. WEISS. 1973. Mercury in the marine environment: Concentration in seawater and in a pelagic food chain. *J. Fisheries Res. Board Canada* 30: 293-295.
- AIDIN'YAN, N. KH and G. A. BELAVSKAYA. 1963. Supergene transfer of mercury. *Trudy Inst. Geoli. Rudn. Mestorozhd. Petrog. Minearalog. i. Geokhim.* 99: 12-15.
- DALL'AGLIO, M. 1968. The abundance of mercury in 300 natural water samples from Tuscany and Latrium in Ahrens, L. H. ed. *Origin and distribution of the elements. A symposium, Paris 1967: New York Pergamon Press, p. 1065-1081.*
- BURTON, J. D. and T. M. LEATHERLAND. 1971. The noncentration of mercury in the English Channel. *Nature.* 231: 440.
- WEISS, H. V., S. YAMAMOTO, T. E. CROZIER and J. H. MATHEWSON. 1972. Mercury: Vertical Distribution at two locations in the eastern tropical Pacific Ocean. *Env. Sci. Tech.* 6: 645-645.

Table 1. Mercury in Snows South of Barrow.

Distance From Barrow, miles	Hg Concentration, ppt
30	5.2
45	3.5
60	6.4
75	46.2
90	16.7
105	8.5
120	9.8
135	6.9

Table II. The concentration of mercury in southern Beaufort Sea waters.

151° 16'W 71° 11'N		151° 04'W 71° 16'N		151° 08'W 71° 23'N		150° 10'W 70° 51'N		149° 10'W 70° 12'N		148° 10'W 70° 56'N	
Depth, m	Hg Con- centration, ng/ℓ	Depth, m	Hg Con- centration, ng/ℓ	Depth, m	Hg Con- centration, ng/ℓ	Depth, m	Hg Con- centration, ng/ℓ	Depth, m	Hg Con- centration, ng/ℓ	Depth, m	Hg Con- centration, ng/ℓ
5	(57)	5	11	1	29±2	5	14	5	15	5	11
10	19	10	17	5	19±0	10	19	10	12	10	15
15	25	15	30	10	38±6	15	12	15	9	15	10
20	22	20	20	15	19±1	20	12			20	8
		30	15	20	14±0	Mean	<u>14</u>	Mean	<u>12</u>	30	9
		40	27	30	21±0					40	13
	Mean <u>22</u>	50	15	40	15±1					Mean	<u>11</u>
	(31)	75	17	50	13±2						
		90	22	75	17±2						
				100	24±1						
			Mean <u>19</u>	100	20±4						
				200	17±3						
				300	19±2						
				400	23±2						
					Mean 21						

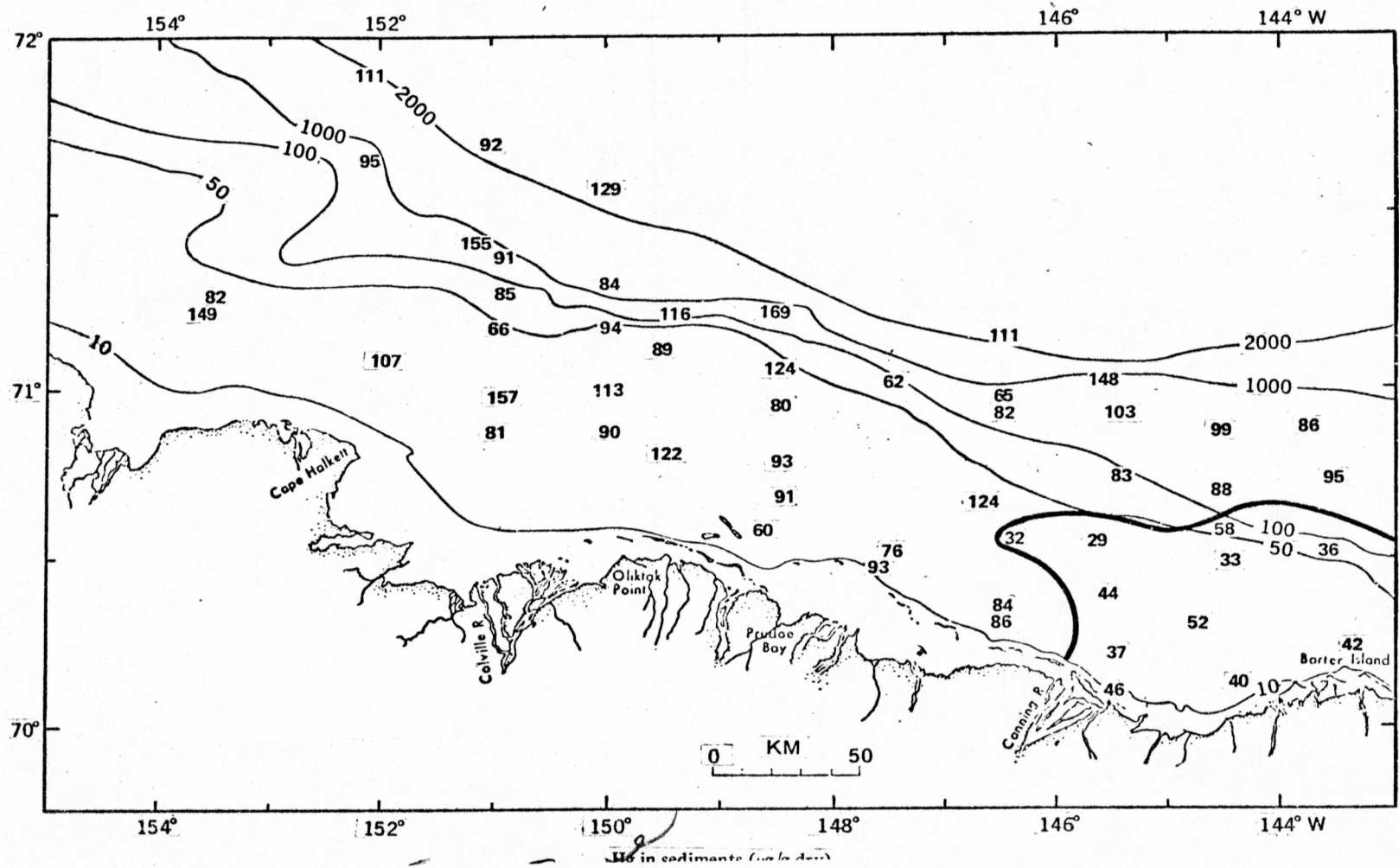


Figure I. Mercury in sediments ($\mu\text{g/g dry}$).

THE CHEMICAL COMPOSITION OF A GREENLAND GLACIER

Herbert Weiss[#], Kathe Bertine^{*}, Minoru Koide^{*} and Edward D. Goldberg^{*}

Abstract

Chemical analyses on water from dated strata of a south Greenland permanent ice sheet revealed that there is a larger amount of sulfate in samples accumulated during the past decade than in those 60 or more years older. This increase is attributed to combustion of fossil fuel. With the exception of mercury, cadmium and possibly copper, the heavy metal distributions in the glacial waters are similar to those in atmospheric dusts. Previously reported higher mercury values in recently deposited strata were not confirmed.

The world's permanent snow fields hold records both of geological events and of man's impact upon the composition of the atmosphere through their dissolved and particulate substances. These glaciers are particularly attractive for such studies inasmuch as they span nearly all of the earth's latitudes. In addition, their strata can be assigned ages through radiochemical geochronologies or through the oxygen isotopic compositions of their waters.

Some elements in glacial snows appear to have higher concentrations in recently deposited strata, phenomena ascribed to the activities of man:

[#]Naval Undersea Center, San Diego, California

^{*}Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California 92037

Cleared for Open Publication

Public Affairs Office
Naval Undersea Center

lead (Murozumi, et al., 1969); mercury, (Weiss, et al., 1971); and sulfur (Koide and Goldberg, 1971). Some of these relationships have been criticized on the basis of insufficient data (Dickson, 1972; Carr and Wilkniss, 1973). To extend the understanding of man's influence on glacial composition, newly recovered glacial materials from southern Greenland, Dye-3 (65°11'N; 43°50'W), were analyzed for sulfate, chloride, arsenic, antimony, cadmium, copper, manganese, mercury and zinc. As, Hg, Sb and Zn were initially chosen to be analyzed as consequence of the greater volatility of their compounds compared to those of other heavy metals. Their possible mobilization to the atmosphere through use by man was considered a likely possibility. Cu and Mn were selected as potential indicators of atmospheric dusts. In addition, ice recovered from Camp Century in northwest Greenland (77°10'N; 61°08'W) whose sulfate, chloride (Koide and Goldberg, 1971) and mercury (Weiss, et al., 1971) contents were determined previously, was now analyzed for copper, manganese and cadmium. To gain further understanding of an anomaly that developed in this work with respect to cadmium, the analysis of this element was extended to include freshly deposited snow from a remote area in northern Alaska between 68 and 69° north latitude.

There are some inherent difficulties in investigating the composition of glaciers. First of all, contamination of the samples can easily occur during their recovery, storage in plastic or glass containers, or chemical analysis. Methods to minimize the contamination of glacial samples were proposed by Murozumi, et al., (1969) whose values for the dominant cations and anions were substantially less than those of previous investigators. Subsequent to their studies, others (see for example, Boutron, et al., 1971 and Vostens, et al., 1970) confirmed their lower values. A second difficulty is that dissolved and particulate species occur in trace quantities within the glacial waters which requires highly sophisticated analytical equipment and techniques. For example in Greenland snow strata studied by

Murozumi, et al., (1969) the Na, Cl, Mg, Ca, K and Si concentrations were of the order of units and tens of parts per billion. Still other metals occur in the parts per trillion range.

The following results are presented with the sense that contamination with respect to all or any of the elements is possible. The extremely low values of chemical species in glaciers, coupled with the exposure to emissions from machines, men, and containers during collection and storage demand that the data be examined most critically.

Samples

Ice and snow samples were collected by C. C. Langway in the summer of 1971 in the vicinity of the Dye-3 Camp located in South Greenland. This site was established in 1959 and has been manned continuously to the present. Seasonal samples were collected from a pit excavated by diesel tracter 6 km from the Dye-3 Camp (pit 71 in Fig. 1). The walls of the pit were trimmed back 25 cm with a steel shovel and the trimmed surface was sectioned into blocks with a gas-powered chain saw. These blocks were in turn trimmed back 15 cm on each side with a polyethylene scoop. Finally, fractions of each residual block were transferred with the scoop to polypropylene sample containers and maintained in a frozen state up to the time of analysis.

Surface snows were collected from other nearby areas designated as 1, 2A, 3A and 5A in Fig. 1. Pits 0.9 m deep were dug with a steel shovel. Fifteen cm of snow were removed from a side of the pits with a polyethylene scoop and discarded. The sample derived from the cleaned surface was transferred to polyethylene or polypropylene containers.

Older samples were obtained with a thermal drilling core from a mine at the Dye-3 site. The surface of the mine was opened in 1959. The top of the core (1945-1959) contained black material and therefore was rejected.

Fresh snows were gathered from uninhabited areas in Northern Alaska 50-220 km south of the nearest community (Barrow) in March 1973. These locations were reached by plane. After a 10 minute wait and at a distance of about 50 m upwind from the plane, 5 to 10 cm of snow were removed and discarded. The underlying deposit was transferred with a clean plastic scoop to polyethylene storage containers. Samples were maintained in the solid state until preparation for analysis.

Methods

Sulfate and chloride determinations were carried out colorimetrically (Koide and Goldberg, 1971). The neutron activation analysis procedures for the heavy metals are given in Weiss and Bertine (1973). The flameless atomic absorption analyses for Cd and Zn were made using a Perkin Elmer HGA 70 and 403 equipment.

Samples derived from pit 71 were assigned seasons during sampling by their melt layers and later by oxygen isotope analyses. There remains some ambiguity in their assigned values, perhaps by one season. (Langway, personal communication).

Camp Century and Dye-3 Samples - A Comparison of Their Compositions and Fluxes

Camp Century ice has been previously investigated for its sulfur (Koide and Goldberg, 1971) selenium (Weiss et al., 1971b), lead (Murozumi et al., 1969) and mercury (Weiss, et al., 1971a) and now for Cd, Mn and Cu (Table 1).

There does not appear to be any significant difference in the ranges of these three metals between the pre-1900 and post-1940 samples, suggesting no discernible influence of man. On the other hand, Cu and Cd appear to be in higher concentrations in recently deposited snows at the Dye-3 site (see following discussion). The results for Mn, Hg and sulfate can be compared over certain time periods to those taken at Dye-3 (Table 2). Although the Camp Century concentrations for these species appear to be higher than the more southerly Dye-3 levels, the accumulation rates are essentially equivalent. The accumulation rate of ice is different at the two sites: Dye-3 with $46 \text{ g/cm}^2/\text{y}$ water equivalent and Camp Century with about $33 \text{ g/cm}^2/\text{y}$. (Langway, personal communication).

The agreements of the flux values interlock our previous investigations with this one. If contamination did occur for Mn, Hg, SO_4^{--} , Cd and Cu in both collection and analytical procedures, an unusual set of circumstances must have developed to allow the interesting agreement of the fluxes.

At Camp Century there were increased ice contents of sulfate, selenium, lead and copper during the winter season, whereas manganese and the dust levels were greater during the spring; on the other hand Cd and Hg showed no obvious seasonal patterns (this work, Koide and Goldberg, 1971; Murozumi *et al.*, 1969; and Weiss, Koide and Goldberg, 1971).

At Dye-3, where five years were sampled, only Cu showed the Winter fallout pattern. There are no distinct seasonal patterns for any of the other elements. The possibility of homogenization of the surfaces of the ice sheet through melting in the summer exists with the copper pattern surviving due to an extremely great influx of this element to the winter stratum.

Table 1. Some Trace Elements in Camp Century. Concentrations in ng/kg of water.

<u>Year of Sample</u>	<u>Mn</u>	<u>Cu</u>	<u>Cd</u>
1815.	513	445	7
1881	171	161	25
1892	208	270	7
1946	323	940	42
1952	155	250	4
1960	240	391	7
1964 (Fall)	146	469	<1
1964 (December)	272	676	7
1965 (Winter)	361	1192	2
1965 (Spring)	376	356	3
1965 (Summer)	382	376	3

Table 2: A comparison of concentrations and rates of accumulation of Hg, Cd, Cu, Mn and sulfate at Camp Century and Dye-3.

Species	Concentration (ng/kg of water)		Accumulation Rates (ng/cm ² /year)	
	Camp Century	Dye-3	Camp Century	Dye-3
SO ₄ ⁻⁻⁻	81 x 10 ³ (pre-1945)	74 x 10 ³ (pre-1920)	2.7 x 10 ³ (pre-1945)	3.4 x 10 ³ (pre-1920)
	200 x 10 ³ (post-1964)	126 x 10 ³ (post-1966)	6.6 x 10 ³ (post-1964)	5.8 x 10 ³ (post-1966)
Cd	14 (pre-1952)	11 (pre-1900)	0.5 (pre-1950)	0.5 (pre-1900)
	4 (post-1952)	640 (post-1966)	0.1 (post-1950)	29.4 (post-1966)
Cu	292 (pre-1900)	153 (1900)	9.6 (pre-1900)	7.0 (1900)
	581 (post-1945)	851 (post-1966)	19. (post-1945)	39 (post-1966)
Mn	286 (1815)	221 (1928-1971)	9.4 (1815)	10.2 (1928-1971)
Hg	60 (pre-1952)	50 (1807 - 1971)	2.0 (pre-1952)	2.2 (1807 - 1971)

Sulfate

In previous work on Greenland ice sheets, Koide and Goldberg (1971) proposed that the combustion of fossil fuels is now introducing similar amounts of sulfur into the atmosphere as are such natural processes as the oxidation of hydrogen sulfide (derived from the breakdown of organic matter) and as vulcanism. A similar result is evident in the analyses of the Dye-3 samples (Table 3). The average sulfate content in the seasonal samples, spanning the time period between 1967 and 1971, is 112 ppb by weight corrected for the sulfate introduced with sea salt. This correction was made by multiplying the chloride content by 0.15, which is the ratio of sulphate to chloride in sea water by weight, and subtracting this value from the total sulfate. The samples from the thermal drilling, excluding the uppermost 4 which may have been contaminated during the drilling process, average 65 ppb for the time period between 1807 and 1915. There is a substantially lower chloride content in the samples from the thermal drillings than in the seasonal samples, and this may represent contamination from an unknown source in the latter. If there were significant chloride contamination, the corrected sulfate concentrations would be slightly higher than those given in Table 1, unless of course, the contaminants included substantially more sulfate than would have been obtained from sea water, relative to the sea water chloride concentration.

Heavy Metals --- General

The heavy metals in glacial waters (Table 4) probably had sources either in the crustal solids of the continents in a volatilization process or in the activities of human society. Transport to the glacial sites from the continents took place through the atmosphere with a subsequent washout or fallout of the solids. If particulate transport predominates one would expect

Table 3. Chloride and Sulfate Content in the Dye-3 Seasonal and Thermal Drilling Core Samples $\mu\text{g}/\text{kg}$ of sea water.

Sample	Time of Deposition		Total Sulfate	Sulfate (Corrected for Sea Salt)	Chloride
	Year	Season			
71-1	1971	Summer	126	113	91
71-2	1971	Spring	70	60	112
71-3	1970-1971	Winter	104	94	73
71-4	1970	Fall	140	123	123
70-1	1970	Summer	159	139	141
70-2	1970	Spring	149	134	108
70-3	1969-1970	Winter	98	91	53
70-4	1969	Fall	233	210	162
69-1	1969	Summer	128	110	67
69-2	1969	Spring	79	71	58
69-3	1968-1969	Winter	161	148	96
69-4	1968	Fall	152	138	102
68-1	1968	Summer	144	131	95
68-2	1968	Spring	78	67	52
68-3	1967-1968	Winter	100	87	95
68-4	1967	Fall	91	75	112
67-1	1967	Summer	116	103	89
67-2	1967	Spring	161	147	99
67-3	1966-1967	Winter	146	129	122
67-4	1966	Fall	78	64	103
AVERAGE			126	112	98
87-97	1944*		241	214	193
265-282	1928*		44	28	112
295-305	1926*		165	146	137
362-374	1920*		101	84	119
423-428	1915		64	59	53
475-482	1910		92	83	65
527-535	1905		125	112	93
575-586	1900		86	77	66
677-686	1890		56	49	50
892-898	1869		55	45	72
991-1001	1859		47	39	59
1203-1208	1839		71	61	69
1295-1304	1829		79	70	65
1521-1535	1807		61	53	59
AVERAGE			74**	65**	65**

*Probably contaminated - top of thermal drilling core (see text).

**Excludes values for deposits 1920-1944

similarities between atmospheric dusts and glacial waters in their heavy metal distributions. Such a comparison is indicated in Table 5, where the average concentrations of heavy metals in the seasonal samples and in the 1900 sample are compared with averages of U. S. urban airs. (Such a comparison is reasonable since most dusts today are polluted.)

For antimony, manganese, arsenic, copper and zinc there is a reasonable agreement between their relative values for atmospheric particulates and glacial waters. Thus, Sb, As and Zn do not reflect selective volatilization as initially hypothesized. On the other hand, the seasonal glacial samples contained over an order of magnitude more mercury and cadmium on a relative basis. An explanation, other than contamination of the glacial samples, may relate to the forms of cadmium and mercury in the atmosphere. The air values were obtained from particulates filtered upon membranes. If the mercury and cadmium species passed through the filters, but were washed out of the atmosphere to the glaciers, this discrepancy can be explained.

Copper

Copper displays the greatest variation in concentration for the seasonal samples with a span of two orders of magnitude (Table 4). The highest concentrations occur in the fall of 1968 and the winter of 1969-1970, with values of 15.7 and 5.1 ppb, respectively. There also appears to be higher levels in the fall of 1970 and in the winter of 1966-1967 over the samples taken in adjacent seasons.

These observations suggest that the copper peaks might be related to the periods of high stratospheric fallout that occurs during the winter and fall at mid-latitudes. The origin of such copper is unknown.

We are aware of the space injection of 480 million tiny copper wires (dipoles) into space orbit at an altitude of 3650 km in May 1963. The

Table 4. Trace Metals in the Dye-3 Seasonal and Thermal Drilling Core Samples (ng/kg of water).

Sample	Time of Deposition		Sb	Hg	Mn	As	Cu	Cd	Zn
	Year	Season							
71-1	1971	Summer	12	51	329	10	162	573	1090
71-2	1971	Spring	11	49	91	19	134	450	140
71-3	1970-1971	Winter	12	38	---	16	217	293	600
71-4	1970	Fall	55	45	557	22	1020	1380	2140
70-1	1970	Summer	48	32	306	30	625	727	1170
70-2	1970	Spring	47	54	335	38	955	411	920
70-3	1969-1970	Winter	29	70	225	9	5120	457	1400
70-4	1969	Fall	91	71	784	22	841	609	1390
69-1	1969	Summer	24	73	187	13	415	1010	420
69-2	1969	Spring	17	55	73	5	244	539	620
69-3	1968-1969	Winter	25	54	152	27	2500	317	880
69-4	1968	Fall	30	43	219	15	15700	834	2270
68-1	1968	Summer	10	36	104	7	1920	745	750
68-2	1968	Spring	21	41	250	35	1480	656	670
68-3	1967-1968	Winter	42	31	228	34	1880	547	860
68-4	1967	Fall	8	31	113	21	165	511	220
67-1	1967	Summer	21	29	200	12	224	674	2870
67-2	1967	Spring	40	37	188	22	523	595	800
67-3	1966-1967	Winter	84	62	228	28	1360	709	860
67-4	1966	Fall	48	51	173	2	653	740	860
Average			34	48	250	19	851**	639	1047
87-97	1944*							2530	
265-282	1928*		11	46	242	32	427	1046	1130
295-305	1926*							3670	
362-374	1920*							730	1660
423-428	1915							25	
475-482	1910							16	
527-535	1905							86	
575-582	1900		18	78		31	153	144	960
677-686	1890							12	
782	1880			41					
991-1001	1859							30	290
1188	1840			48				16	
1203-1207	1839							5	70
1295-1308	1829							<2	
1521-1535	1807							<2	180
1572	1802			40					
Average			18	52	--	31	153	34	375

*Probably contaminated - top of thermal drilling core (see text).

**Excluding 70-3 and 69-4

Table 5. Trace Element Composition of Glacial Sample from Dye 3 and Atmospheric Dusts

<u>Element</u>	Glacial Water (ng/kg of water)		Airs (ng/m ³)
	<u>1900</u>	<u>Average for Seasonal 1966-1971</u>	<u>U.S. Urban Mean*</u>
Sb	18	34	20
Hg	78	48	3
Mn	-	250	200
As	31	19	20
Cu	153	851	200
Cd	34**	639	20
Zn	375**	1047	700

* D. E. Robertson, L. A. Rancettelli, James G. Langford and R. W. Perkins.
Unpublished data from Battelle Northwest (1972).

** Average all samples 1807-1915

orbit was nearly circular and nearly polar (Shapiro, 1966). The total weight of the copper was 20 kilograms. Each dipole was 1.78 cm in length and 0.00178 cm in diameter. Each dipole would then weigh about 50 micrograms. A reentry date of 1 January 1966 was predicted, which is about when the first peak occurred.

Shapiro suggests that the dipoles were able to radiate heat rapidly enough to avoid decomposition and most probably returned to the earth's surface in their original form. A maximum density of 5 dipoles/km² is calculated on the assumption of no disintegration. Hence, the probability of finding a single dipole in a seasonal sample area of about 100 cm² is extremely small. Thus, on the basis of the probability of accreting a single dipole in a seasonal sample area, the above explanation of the copper peaks does not appear reasonable.

Cadmium

Samples from waters deposited at Dye-3 between 1807 and 1915 had cadmium contents ranging from <2 to 144 ng/kg water with an average of 34 ng/kg. The seasonal deposits (1966-1971) contained considerably more cadmium, the average being 640 ng/kg (Table 4). For the surface samples collected from sites 1, 2A, 3A and 5A (Fig. 1) the cadmium ranged from 190 to 670 ng/kg (Table 6) in agreement with the higher values in the seasonal samples. Concordant results were obtained for samples from the same sources whether stored in polyethylene or polypropylene containers, acidified or not acidified with HNO₃ immediately after defrosting, and whether analyzed by neutron activation or atomic absorption spectrometry. Thus the incorporation of cadmium in the snows as a function of time appears not to be affected by techniques of sample storage or subsequent manipulations. Freshly deposited

surface snows were collected from a pristine area in northernmost Alaska, where there is no evident local cadmium source. Yet their cadmium concentrations ranged from 45 to 275 ng/kg (Table 7); the average value, 164 ng/kg, is considerably greater than the average for snow deposited at Dye-3 between 1807-1915.

On the other hand, the analysis for cadmium of ice recovered from Camp Century dating from 1815 to 1965 does not reveal a time-related difference and the values (<1 to 42 ng/kg) are low compared to the Dye-3 values (Table 1).

An explanation for these conflicting results may be found in the wind transport of anthropogenic cadmium to the southern, but not to the northern, site. Camp Century is 8-9° and 12° more northerly than the Alaskan and Dye-3 sites. At the southern sites, a stronger westerly wind system prevails which increases in velocities with altitude to beyond 10 kilometer. The wind velocities at Camp Century, on the average, are a factor of two less with the frequent occurrence of an easterly wind component (Mintz, 1954). The low cadmium concentrations found at Camp Century and in the Dye-3 samples (1807 - 1915) are concordant when compared with dust samples in urban air (Tables 2 and 5). Further evidence is found in the similar patterns for manganese and copper concentrations in the glacial deposits and in the urban airs.

Mercury

The mercury concentrations in the seasonal and background samples at Dye-3 are similar (Table 4). These results are contrary to those found previously (Weiss, et al., 1971a) at Camp Century where higher values were found in glacial strata deposited during the last 2 decades. The fluxes of mercury in the older strata from both sites are comparable (Table 2). The reason for the discrepancy in the recent samples is unknown.

Table 6. Cadmium Concentrations in Waters Recovered from Shallow Pits near Dye-3

<u>Site</u>	<u>Cadmium Concentration (ng/kg of water)</u>
1	390
2A	190
3A	670
5A	285

Table 7. Cadmium Concentrations in freshly deposited snows collected in March 1973 from northern Alaska

<u>Distance south of Barrow (km)</u>	<u>Cadmium Concentration (ng/kg of water)</u>
50	45
70	60
120	170
145	225
170	250
190	275
220	120

References

- Bertine, K. K. and Edward D. Goldberg. Fossil fuel combustion and the major sedimentary cycle. Science 173, 233-235 (1971).
- Boutron, C., M. Echevin and C. Lorius. Chemistry of Polar snows. Estimation of rates of deposition in Antarctica. Geochim. Cosmochim. Acta 26, 1029-1041 (1972).
- Carr, Roderick A. and Peter E. Wilkniss. Mercury in the Greenland ice sheet: further data. Science 181, 843-844 (1973).
- Dansgaard, W., S. J. Johnsen, J. Møller, and C. C. Langway, Jr. One thousand centuries of climatic record from Camp Century on the Greenland Ice Sheet. Science 166, 377-381 (1969).
- Dickson, Edward M. Mercury and lead in the Greenland Ice sheet: a reexamination of the data. Science 177, 536-538 (1972).
- Koide, M. and Edward D. Goldberg. Atmospheric sulfur and fossil fuel combustion. J. Geophysical Res. 76, 7689-7696 (1971).
- Mintz, Yale. The observed zonal circulation of the atmosphere. Bull. Am. Met. Soc. 35, 208-214 (1954).
- Murozumi, M., T. J. Chow and C. Patterson. Chemical concentrations of pollutant lead aerosols, terrestrial dusts and sea salts in Greenland and Antarctic snow strata. Geochim. Cosmochim. Acta 33, 1247-1294 (1969).
- Shapiro, I. I. Last of the west ford dipoles. Science 154, 1445-1448 (1966).
- Vosters, M., F. Hanappe and P. Buat-Meand. Determination of Cl, Na, Mg, Ka and Ca in firn sample 66-A-z from New Byrd Station, Antarctica --- Comparison with work of Murozumi, Chow and Patterson. Geochim. Cosmochim. Acta 34, 399-401 (1970).
- Weiss, H. V., M. Koide and E. D. Goldberg. Mercury in a Greenland ice sheet: evidence of recent input by man. Science 174, 692-694 (1971a).

Weiss, H. V., K. K. Bertine. Simultaneous determination of arsenic, antimony, cadmium, copper, manganese and mercury in glacial ice by neutron activation. Anal. Chem. Acta 65, 253-259 (1973).

Weiss, H. V., M. Koide and E. D. Goldberg. Selenium and sulfur in a Greenland Ice Sheet: Relation to fossil fuel combustion, Science 172, 261-263 (1971b).

Acknowledgements

We thank Dr. C. C. Langway of the US Army Cold Regions Research and Engineering, Hanover, N. H. for his encouragement on this project and for the Greenland Dye-3 ice samples and C. C. Patterson who supplied the Camp Century samples. The Naval Arctic Research Laboratory, Barrow, Alaska provided support in the collection of Alaska snow materials. E. Nelson performed many of the chemical analyses.

This work was supported in part by the National Science Foundation under grant GV-36955; and the Office of Naval Research under grant NR 083-290.

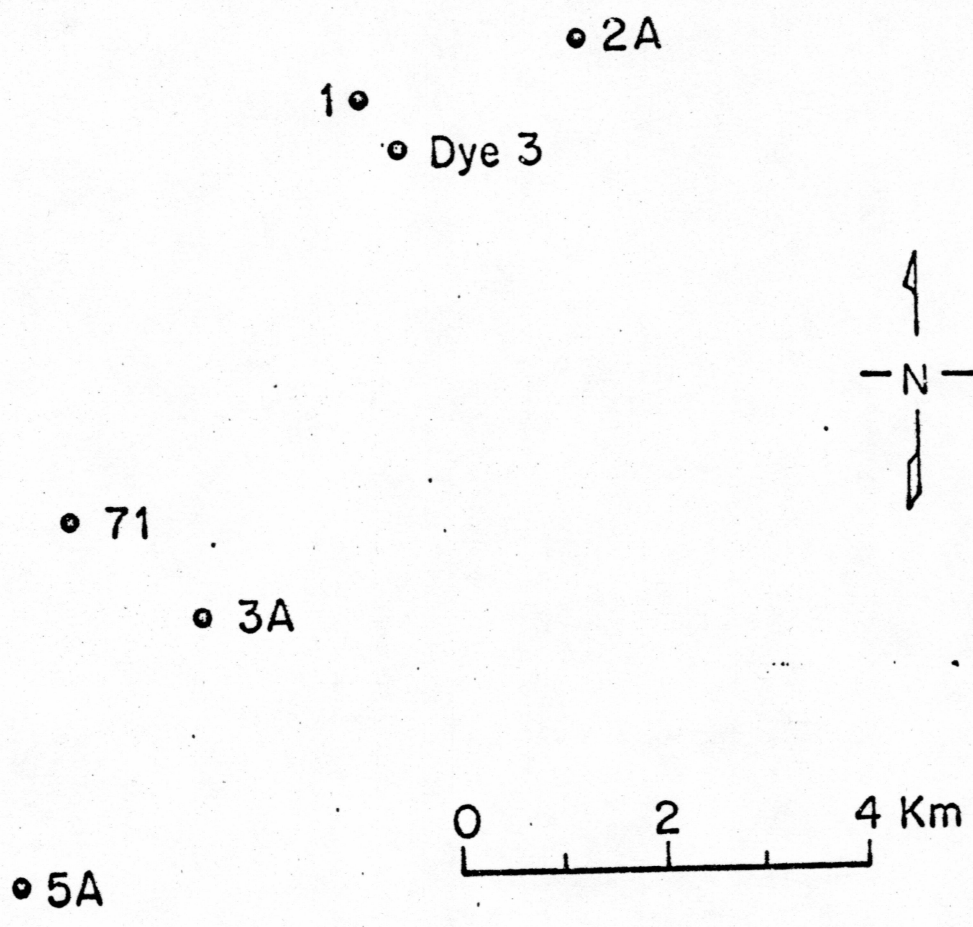


Figure 1 Dye 3 sample locations