Trace Metals in Human and Animal Hair from the 15th Century Graves at Qilakitsoq Compared with Recent Samples

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Hansen, J. C., Toribara, T. Y. & Muhs, A. G. 1989. Trace Metals in Human and Animal Hair from the 15th Century Graves at Qilakitsoq Compared with Recent Samples. Meddr. Grønland, Man & Soc. 12: 161–167. Copenhagen 1990-01-26.

Samples from eight Qilakitsoq mummies were analysed by X-ray fluorescence spectrometry, providing a multielement longitudinal analysis along a single strand of hair to obtain concentration profiles. Comparison of the profiles could indicate whether all mummies had died at the same time. No characteristic profiles were found and consequently the question was not answered.

Atomic absorption spectrometry was used to analyse six mummy hair samples, and 22 present day hair samples. In addition nine animal hair samples from the graves and ten present day seal hair samples were analysed.

Quantitative measurements of metals have shown an increase with time for the toxic metals mercury and lead, while cadmium and copper were unchanged, and zinc showed a slight increase. Definite decreases were found for bromine, iron and selenium.

The increase of exposure to toxic metals is assumed to be due to an increase in pollution of the northern hemisphere, while the decrease in essential micronutrients is due to the change in eating habits towards more imported food in the Greenlandic diet.

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Trace metal concentrations in human and animal hair reflect the environment in which the individual has lived. Thus analysis of essential elements can provide information on dietary status, and determination of non-essential elements can give information on exposure level to toxic pollutants.

Hair as an index medium for determining trace metals has aroused increasing interest because hair concentrates most elements, especially heavy metals, to a higher degree than do other tissues or body fluids. Hair samples are easily obtained, transported, stored and, because of its resistance to biological degradation, hair allows comparisons over a wide time range. Such a comparison over a period of 500 years has been possible with the mummies from Qilakitsoq, from which hair samples have been taken, and with animal hair samples collected from the fur wrappings of the bodies.

In the following the results of these investigations are reported and a comparison is made between concentrations found in the older and in more recent hair samples from the district where the graves were found.

The objective of the study was, in the first place, to compare concentrations of toxic elements over a span of time, and secondly to attempt to obtain indices of contemporaneity for the mummies through longitudinal sectional analysis along single hair strands and comparisons between concentration profiles.

Material and methods

Samples were collected at the Danish National Museum, which also provided recent samples of seal hair. The recent human samples originate from a heavy metal survey carried out in 1979 in West Greenland (Hansen 1981).

Two different analytical procedures were used.

1) *Atomic absorption spectrometry.* These analyses were carried out at the Institute of Hygiene, University of Aarhus, Denmark. The analytical procedures are described in detail elsewhere (Hansen 1981; Hansen *et al.* 1983a, 1983b).

By this method six human and nine animal samples

Table 1. Intercomparison: IAEA Powdered Human Hair HH-1

	IAEA			Own results		
	x̄	SD	Range of accepted lab. averages	N	x̄	SD
Cd	0.26	0.13	0.02 - 0.54	5	0.36	0.03
Cu	10.23	3.17	1.89 - 19.05	5	8.93	0.20
Hg	1.70	0.24	1.20 - 2.30	5	2.13	0.05
Pb	2.73	1.40	0.00 - 5.50	5	3.58	0.35

from the graves and 22 human and 10 animal recent samples were analysed. The following elements were determined by this method: mercury, cadmium, lead, copper and selenium.

As reference material IAEA powdered human hair HH–1 was used. The results are compared in Table 1.

2) *Non-destructive X-ray fluorescence spectrometry.* This method, described in detail elsewhere (Toribara *et al.* 1982), provides automatic longitudinal scanning for some 16 elements in consecutive hair segments. The mass (in µg/mm) is determined simultaneously at each point and the absolute concentrations are computed in mg/kg for the elements. The method is non-destructive and results including mass show much reproducible detail. The millimetre by millimetre longitudinal analysis allows recapitulation for previous metal exposure for months or years depending upon the length of the hair strand. This type of analysis was carried out at the Environmental Health Sciences Center, Division of Toxicology, Department of Radiation Biology and Biophysics, The University of Rochester Medical Center.

Only human samples were analysed, eight human (six adults and two children) fifteenth century samples and two recent samples. The following elements were determined: calcium, manganese, iron, copper, zinc, bromine, mercury and lead, as these elements occur in measurable concentrations with reasonable counting times.

A comparison between the two methods for elements determined by both is given in Table 2.

Table 2. Comparison of mean concentrations in identical samples obtained by X-ray and AAS.

Method / Element	15th cent. (N:6)		20th cent. (N:2)	
	X-ray	AAS	X-ray	AAS
Hg	3.2	3.1	14.3	19.9
Pb	n.d.	0.7	44.0	56.9
Cu	8.1	8.8	11.0	16.3

Whether or not hair samples should be washed prior to analysis to remove external contamination is a matter of discussion. Some ions as Na, K, Ca, Mg, Br, Mn, Fe, Cu, Zn and Cd are shown to be removed by washing (Kopito & Shwachman 1975; Salmela *et al.* 1981). Elements which may also be added to hair from solutions similar in composition to sweat are: Zn, Cu, Ag, Fe(3), Cr(4) at pH 5.5, Se(2), Cl, Br, and I at pH 3.5 (Bate & Dyer 1965). Mercury may easily be added to hair, but once incorporated it is almost impossible to remove without altering the hair considerably (Toribara *et al.* 1984).

The samples in this study were not washed before analysis with x-ray spectrometry, while samples analysed by atomic absorption were washed according to the procedure described by Petering *et al.* (1971). The problem, however, may not be that important as good agreement of results was obtained by the two methods (cf. Table 2).

One other precaution concerns the interpretation of the hair level, even after ascertaining that the history show that nothing has occured which would lead one to believe that the concentration has changed, as is the case with the samples here described. A general assumption would be that the hair concentration would be directly proportional to the concentration of the fluid in contact with the root of the hair. This has been shown to the case for methyl mercury (Amin-Zaki *et al.* 1976), while Klevay (1970) could not show such a correlation for zinc. Lead, mercury, copper and probably zinc data provide the most reliable basis for conclusions, while the data on other elements should be interpreted with some caution.

Interpretation of analytical results

Accurate analythical methods measure the actual amount present in the sample. However, the amount present in the hair sample may not be the quantity which was incorporated into the hair at the time of its formation. Once the hair has emerged the concentration of an element at any part of the hair should not change unless external exposure to treatment such as washing, bleaching or exposure to rain or dust from the atmosphere induces it.

Results

Fig. 1 shows concentration profiles of eight elements in hair from one of the mummies compared with those from a recent Greenlander. In all fifteenth century samples no characteristic profiles with peak values were found, so it has not been possible to get indices of whether or not they died at the same time.

Fig. 2 shows an energy spectrum from a one millimetre segment of a single strand of hair taken from a mummified body. The peak corresponding to zinc indicates that the concentration of this metal is slightly lower than those found in normal modern samples. The peaks corresponding to bromine and iron indicate that levels of these elements are definitely elevated compared to modern samples.

Calculated mean values and mass from mummies (six

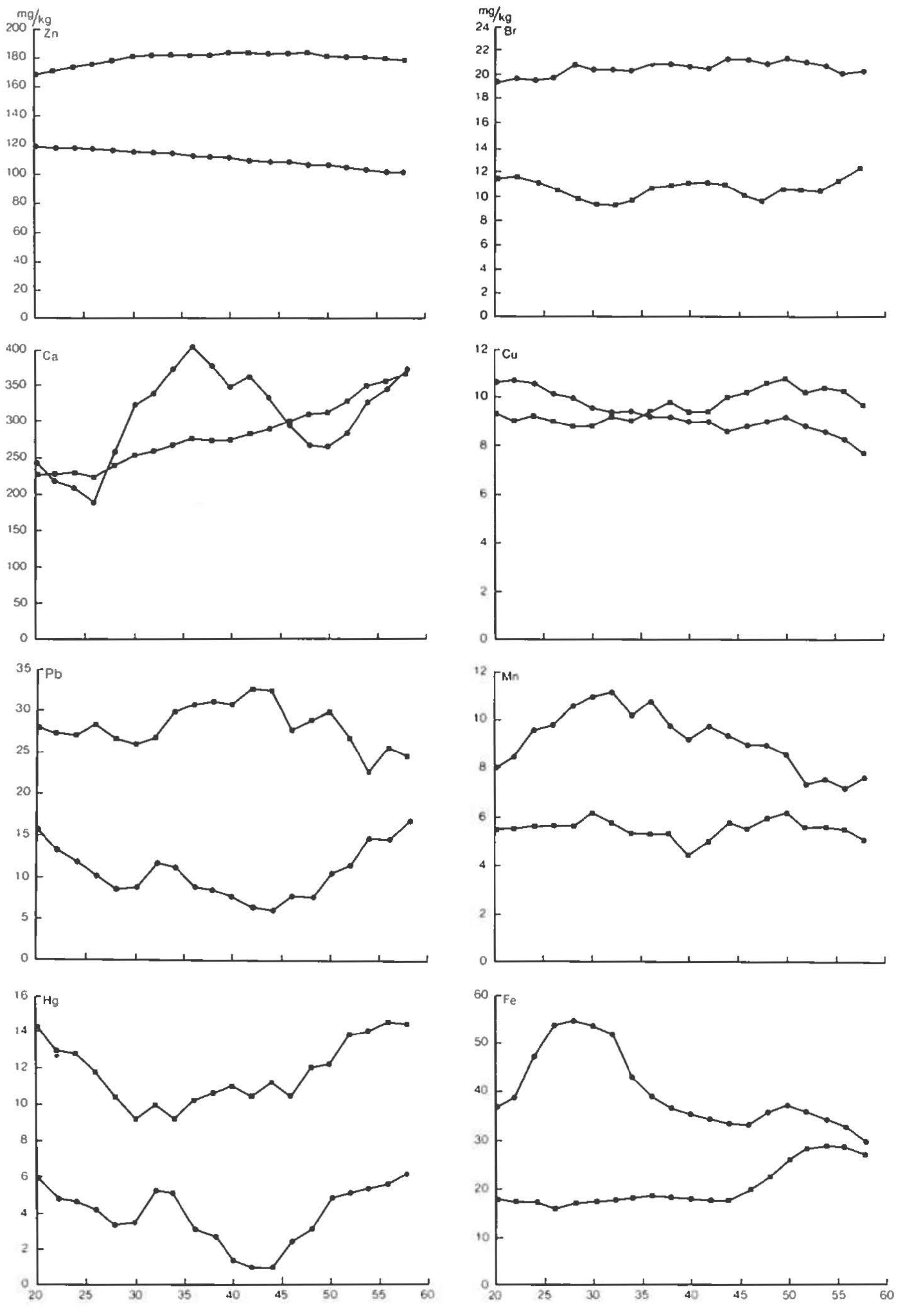

Fig. 1. Longitudinal analysis of a single strand of hair ■-■ Sample from a present-day Greenlander ●-● Sample from a mummified body.

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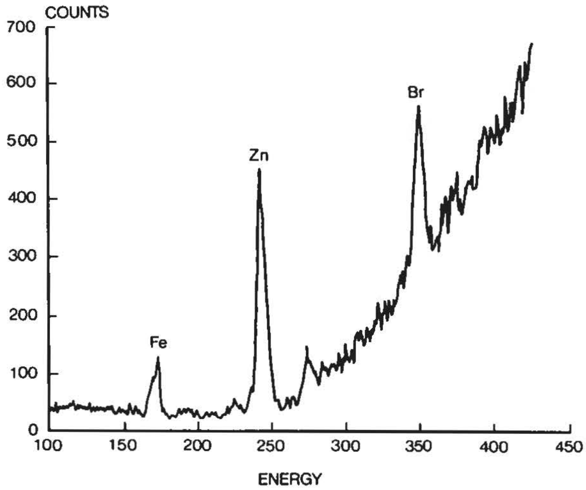


Fig. 2. The energy spectrum from a one millimetre segment of a single strand of hair taken from a mummified body.

adults and two children) and from two recent samples are shown in Table 3. The table also includes for comparison the results of analysis of twenty recent Quebec Inuit samples (Toribara *et al.* 1982). It is seen that children's hair has weights (μg/mm) different from the other groups. For this reason, the results for children's hair have been separated, as the concentrations due to the different hair weight are not necessarily comparable with the concentrations in adults.

No significant difference in hair weight is found between ancient and recent adults, which indicate that no substantial loss has taken place with time.

The results of the atomic absorption analysis are presented in Table 4 and Fig. 3, which, on a logarithmic scale, indicates mean concentrations and the 95% confidence interval.

The figure shows parallel results for mercury and lead concentrations in human and animal samples. Human hair contains more than animal hair reflecting the fact that humans are at a higher level in the food chain.

Table 3. Trace elements concentrations in human hair samples obtained by X-ray fluorescence. Mean and 1 x SD (in brackets) indicated.

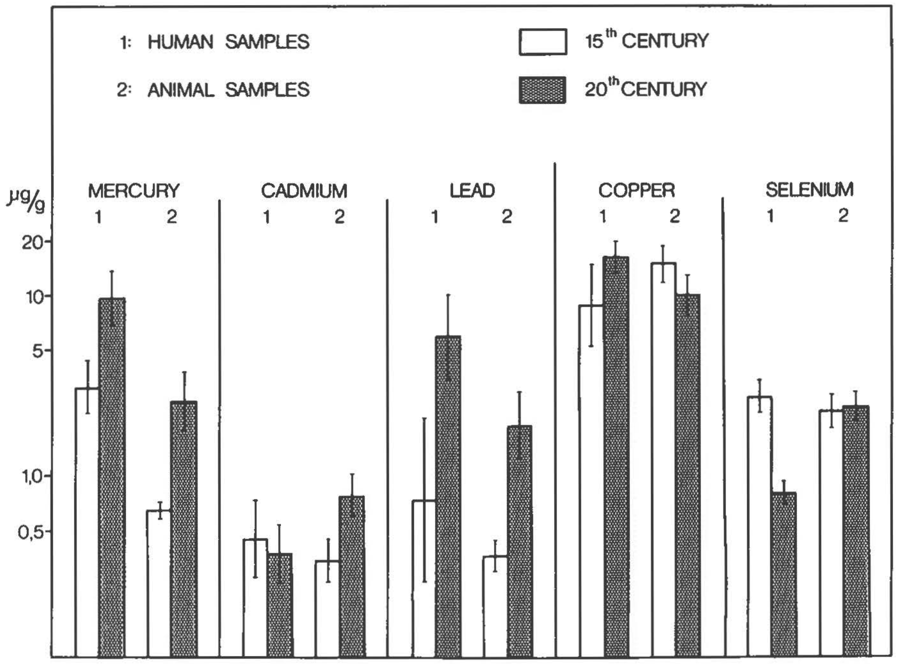
	N	Hair Weight μg/mm	Ca	Pb	Hg	Br	Zn	Cu	Fe
			mg/kg						
15th century samples, Adults	6	5.70 (0.97)	203 (123)	n.d.	3.2 (3.4)	32.9 (10.6)	110 (32)	8.1 (2.4)	123 (94)
15th century samples, Children	2	2.4	1458	24.0	10.0	–	153	18.0	120
Quebec Inuit	20	6.48 (2.55)	224 (103)	8.9 (9.9)	9.93 (14.0)	4.3 (4.5)	171 (43)	14.3 (4.8)	16.9 (7.7)
Recent Greenlandic samples	2	6.20	212	44.0	14.25	17.0	149	11.0	17.5

n.d.: non-detectable concentrations
– : not analysed

Table 4. Trace element concentrations in human and animal hair samples, obtained by atomic absorptionspectrometry. Means and 95% confidence intervals (in brackets) are indicated. Units mg/kg.

Element	Human samples 15th century No.	Mean	Human samples 20th century No.	Mean	Animal samples 15th century No.	Mean	Animal samples 20th century No.	Mean
Hg	6	3.1 (2.3–4.2)	22	9.8 (6.8–13.5)	9	0.6 (0.5–0.7)	10	2.6 (1.8–3.7)
Cd	6	0.5 (0.3–4.2)	22	0.4 (0.3–0.5)	9	0.3 (0.3–0.5)	10	0.8 (0.6–1.0)
Pb	6	0.7 (0.3–2.1)	22	6.0 (3.5–10.3)	9	0.4 (0.3–0.4)	10	1.9 (1.2–1.8)
Cu	6	8.8 (5.3–14.6)	18	16.5 (13.6–19.5)	9	15.1 (12.0–14.6)	8	10.0 (7.7–12.9)
Se	5	2.8 (2.3–3.5)	10	0.8 (0.7–0.9)	9	2.3 (1.9–2.9)	8	2.4 (2.0–3.0)

Fig. 3. Element concentrations in human and animal samples from the 15th and 20th centuries determined by atomic absorption spectrometry. Mean and 95% confidence interval indicated (log scale).



As the two methods have given an identical pattern of information, each element will be commented upon separately in the following, without reference to method.

Discussion of individual elements

Toxic elements

Mercury concentrations in human hair and blood samples from arctic areas have been shown to be much higher than those from industrialized countries. A close relationship between the amount of marine food eaten and blood and hair mercury concentrations has been demonstrated (Hansen 1981; Hansen *el al.* 1983a,b).

The results reported here have shown that mercury has increased significantly with time in human as well as animal hair by factors of 3.2 and 4.3 respectively. The higher factor in animals may be due to the fact that people in the fifteenth century exclusively depended on marine food, while present-day Greenlanders, even those who eat traditional food, will eat supplementary imported food. The increased mercury concentrations cannot be proven to be due to man-made pollution, as variations in natural environmental mercury concentrations have been demonstrated (Petit 1977).

The increase is, however, likely to be a result of man's use of mercury, which has been increasing during historical time. The human hair concentration in ancient samples, compared with present-day Danish mercury hair concentrations is high. In a Danish survey carried out in 1980 a mean of 0.6 µg/g was found (Bach 1980). So even if the exposure in Greenland has increased, it must be realized that in areas with dominantly marine food sources a relatively high mercury exposure is natural.

Cadmium, like mercury, is an environmental pollutant causing great concern. Daily intake in Greenland today through food especially seal liver, exceeds the WHO tolerable weekly (Johansen 1982). The results have shown, however, that in human samples no difference can be observed between old and new samples and that both are within what is regarded as a normal concentration level. This is in agreement with the results from the West Greenland survey 1979 (Hansen 1981), in which it was found that dietary cadmium from marine food was not reflected in hair.

A moderate increase in cadmium is found in animal hair (cf. Table 4), which may mean that seals today are more exposed to cadmium than in earlier times, as industrial use of this element started only in this century.

That no increase is observed in humans may be due to the fact that cadmium is bound in seal liver in a chemical form that is not easily absorbed in the human gastrointestinal tract.

Lead is the toxic element that has been shown to increase most with time in human as well animal samples with factors of 8.3 and 4.1 respectively. Lead has thus increased most in humans, probably because, unlike mercury and cadmium, lead is not likely to be taken up via marine food. Only small concentrations of lead have been found in traditional Greenlandic food (Johansen 1982). The human lead sources in Greenland remain unidentified, however.

Contrary to the results reported here, Toribara *et al.* (1984) demonstrated higher hair lead values in old frozen Barrow bodies than in present day Canadian Inuit. Lead concentrations found in four hair samples taken in 1884 in East Greenland were also a little higher than those found in the same district today (Hansen, unpublished data).

The increase in lead concentrations reported here could support the idea of increasing lead pollution of the northern hemisphere in the historical era, as suggested by Settle and Patterson (1980).

Essential micronutrients

Among the essential elements analysed, copper and calcium showed no time-related differences. This conforms with reports on ancient and recent samples from Canada (Toribara *et al.* 1984). Also in agreement with this study, zinc concentrations tend to be lower in old samples than in recent ones (cf. Table 3). This change is explained by the fact that populations living primarily on fish, especially of the white type, risk zinc deficiency, while varied food, as eaten today is more likely to provide sufficient zinc. If, however, marine mammals are part of the diet, zinc supplements should be sufficient, as these are rich in zinc (Johansen 1982). Thus the difference may not be significant and is probably due to the fact that hair zinc concentrations are influenced by external factors.

Selenium concentrations in modern an ancient animal hair are not different (Table 4 and Fig. 3), indicating that this element, homeostatically regulated in the mammalian body, has not changed in the marine environment during the last 500 years. The decreased concentration in modern human samples compared with old ones can be interpreted as being due to a change in eating habits. People of the fifteenth century presumably depended on marine food alone, which is rich in selenium, while at the present time the diet is mixed with imported (Danish) food items containing lower selenium levels.

Another possible explanation is that the increased mercury intake will bind more selenium because of chemical interaction *in vivo*, with formation of biologically inert complexes leading to a lower uptake in hair. The decline in hair selenium concentrations is, however, most likely an expression of a change in eating habits, as the same decline is observed for iron (cf. Table 3), which is high in the traditional Eskimo diet and low in imported food. In further support of this theory, there is less bromine in modern samples, as this element presumably originates from marine food.

Conclusion

Analysis of hair samples from eight fifteenth-century mummies found in Qilakitsoq has not provided an answer to the question of contemporaneity of the eight bodies. However, comparisons of analytical data on present-day samples from the same district with data from these ancient samples have contributed to our knowledge of the development of heavy metal pollution during the last 500 years. Significant increases in mercury concentrations have been found in both human and animal samples. A relatively high mercury exposure is natural in arctic areas, and related to transport of mercury through the food chains. Lead has also increased significantly with time, while cadmium shows a low and, in general, unchanged concentration level. Unchanged concentrations were also found for cadmium and copper, while zinc showed a minor increase.

Selenium, bromine and iron in human samples were found to be definitely elevated compared with modern samples. This phenomenon is thought to be a reflection of changing eating habits, as ancient Eskimos were totally dependent on local, i.e. marine food, while modern Greenlanders to an increasing degree eat imported food.

The data show that levels of exposure to certain toxic metals such as mercury and lead have significantly increased and that the supply of some essential micronutrients such as selenium and iron has decreased with time. This development is caused partly by increasing pollution and partly by the ongoing change in the cultural pattern in Greenland away from the traditional Eskimo way of life towards the culture of the industrialized societies. These changes, in the long run, may lead to increased health hazards from the environment.

The investigation of the elements in hair has contributed to a better understanding of present-day heavy metal exposure in Greenland.

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