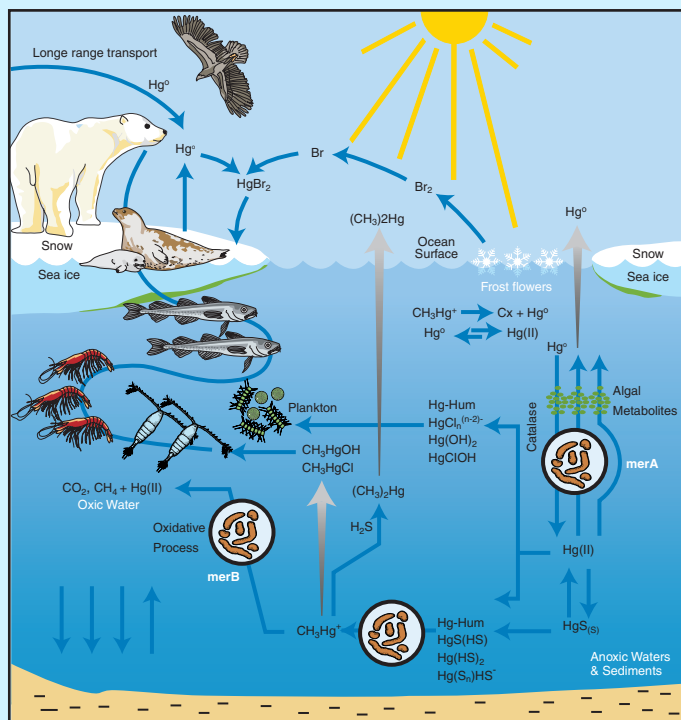




Fate of mercury in the Arctic (FOMA)

NERI Technical Report No. 511





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2004

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Data sheet

Title: Fate of mercury in the Arctic (FOMA)

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Abstract: This report is the final reporting of the project FONA, funded by the Danish Environmental Protection Agency with means from the MIKA/DANCEA funds for Environmental Support to the Arctic Region. The aim of the project is to study the inter-compartment mercury transport chain in the arctic area. From atmospheric deposition of mercury on sea surfaces to uptake in marine organisms, bio-accumulation, and finally mercury levels in mammals. The studies in the project are focused on the behaviour of mercury during the spring period where special phenomena lead to an enhanced deposition of mercury in the Arctic environment, at a time where the marine ecosystem is particularly active. The studies also include a comprehensive time trend study of mercury in top carnivore species. Each of these studies contributes towards establishing the knowledge necessary to develop a general model for transport and uptake of mercury in the Arctic. The report focus on the surface exchange of mercury, the uptake of abiotic mercury into the biological system, and the bio-accumulation in the first steps of the food web, and the resulting distribution and time trend of mercury in selected animals feeding on various trophic levels.

Keywords: Mercury, atmosphere, bioaccumulation, toodweb, trends, arctic

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Preface

This report is the final reporting of the project FOMA, funded by the Danish Environmental Protection Agency with means from the MIKA/DANCEA funds for Environmental Support to the Arctic Region. The aim of the project is to study the inter-compartment mercury transport chain in the arctic area. From atmospheric deposition of mercury on sea surfaces to uptake in marine organisms, bioaccumulation, and finally mercury levels in mammals.

The project was planned and carried out in co-operation between three departments at NERI: Dep. of Arctic Environment, Dep. of Atmospheric Environment, and Dep. of Marine Ecology. The University of Southern Denmark and the University of Copenhagen also took part in the project.

Chapters 2,4, and 5 are short descriptions of - and conclusions from the three subprojects. Each subproject also present it's own report. Chapter 3 is a short presentation of and conclusions from another project carried out at NERI, which is relevant and related to the main project and to the understanding of the fate of mercury in the Arctic. The authors of the chapters are the people participating in the subprojects. The authors of this report are the principal investigators of the subprojects and the persons responsible for the final conclusions in this report.

The studies in the project are focused on the behaviour of mercury during the spring period where special phenomena lead to an enhanced deposition of mercury in the Arctic environment, at a time where the marine ecosystem is particularly active. The studies also include a comprehensive time trend study of mercury in top carnivore species. Each of these studies contributes towards establishing the knowledge necessary to develop a general model for transport and uptake of mercury in the Arctic - the ultimate goal.

Sammenfatning

Kviksølv bioakkumulerer i de arktiske fødekæder. Derfor finder man de højeste kviksølvniveauer i rovdyr øverst i fødekæden som for eksempel sæler, tandhvaler, isbjørne og mennesker. Fødeindtaget er den største kviksølvkilde for både mennesker og dyr, men processerne fra kilde til individ er på nuværende tidspunkt utilstrækkeligt beskrevet. Det drejer sig om processer over: emission, atmosfærisk transport, atmosfærisk deposition, transport til havvand (- reemission – transport til havvand) optag i plankton samt transport til højere trofiske niveauer.

En beskrivelse af denne transport kræver bidrag fra en række forskellige fagdiscipliner. Derfor har 3 DMU afdelinger (afd. Atmosfærisk Miljø, Afd. for Marine Økologi og Afd. for Arktisk Miljø) bidraget til projektet hvor både fysisk/kemiske og traditionelle biologiske, discipliner er anvendt.

De første fluxmålinger i verden af atmosfærisk kviksølv er udført i forbindelse med projektet. Fluxmålingerne viser, at AMDEs (Atmospheric Mercury depletion Episodes) fører til mere end en fordobling af kviksølv belastningen til det arktiske miljø. Dette sker gennem omdannelsen af GEM (Gaseous Elemental Mercury) til RGM (Reactive Gaseous Mercury) efterfulgt af deposition af RGM til sne. Disse resultater er anvendt til at lave en ny parameterisering for fjernelsesprocesserne af atmosfærisk kviksølv til Danish Eulerian Hemispheric Model (DEHM). Ligeledes er resultaterne anvendt til at validere modellen. Nord for polar cirklen er en deponering på ca. 200 tons/år kviksølv til overfladen blevet estimeret.

I uforstyrrede marine sedimentkerner er kviksølv koncentrationen og dermed sedimentationshastigheden højere i dag i forhold til for 50 til 100 år siden. Denne forøgelse kan tolkes som menneskeskabt bidrag. Derfor viser resultaterne i dette studie af marine sedimenter fra Grønland, at ca. 50% af kviksølv fluxen til Grønland er af menneskeskabt oprindelse.

I havet omkring Grønland viser de første forsøg, at 80% af den totale mængde kviksølv er opløst eller forbundet med partikler $<0.45 \mu\text{m}$. Da kviksølv bioakkumuleres er kviksølv koncentrationen klart afhængig af det trofiske niveau i fødekæden. Mens der kun er en svag kobling mellem transportvejene af kviksølv og kulstof i de lave trofiske niveauer, forekommer der signifikant højere kviksølv niveauer på højere trofiske niveauer som krabber, fisk, fugle og sæler. Kviksølvkoncentrationen i isbjørnes hår er i perioden 1999-2001 8.3 gange højere i Østgrønland end basis niveauet fra det 1300 A.D. i Vestgrønland. Siden 1960 er kviksølv koncentrationen isbjørnes tænder og hår faldet betydeligt i Østgrønland mens dette er usikkert for Nordvestgrønland grundet manglende prøver fra de seneste 20 år.

Ud af 12 analyser af udviklingstendenser på 3 rovfuglearter viste 11 analyser en stigende tendens, hvoraf kun 4 grupper var signifikante (immature jagtfalke – alle vandrefalke– immature og voksne

havørne). Stigningen på disse grupper var mellem 0.008 og 0.05 mg/(kg tørvægt år).

Den samlede arbejdsindsats, som indtil nu har været brugt til at forstå sammenhængen mellem transport, deposition og bioakkumulering i det arktiske miljø viser vanskeligheden ved at etablere en sådan model. På den anden side vil en fortsat indsats forhåbentlig medføre, at fremtidige udviklingstendenser af effekten på mennesker og udvalgte arter kan forudsiges.

På nuværende tidspunkt er denne sammenhæng ikke etableret. Vi har behov for at gennemføre fælles feltkampagner for at studere forbindelsen mellem atmosfærisk input under AMDEs, optag i den pelagiske fødekæde og transporten til højere trofiske niveauer.

Der er stadig store usikkerheder på inter-kompartiment fluxene og fremtidige aktiviteter skal organiseres som fælles kampagner med et mere holistisk fremgangsmåde med fokus på perioder og områder med AMDEs.

Baseret på den opnåede viden bør en model udvikles, der kan forklare observerede niveauer og inter-kompartiment transport. Endelig bør der laves beregninger, der viser modellens og systemet følsomhed overfor ændringer i emissioner, klima og fødekæden.

Summary

Mercury compounds are bio-accumulated. As a consequence the highest levels of mercury are measured in top predators like seals, toothed whales, polar bears, and also humans. The main mercury source for humans is the diet but the processes that links emission with effects through the transport chain: emission – atmospheric transport – atmospheric deposition – transport to seawater (– reemission – transport to seawater) – uptake in plankton – transfer to higher trophic levels are at present insufficiently known.

The complexity of the problem stresses the need of contributions from many disciplines. Therefore 3 departments of NERI (ATMI, MAR and AM) are contributing to the work and traditional biological, chemical and physical disciplines are presented.

The first measurements ever of atmospheric mercury fluxes have been carried out within the present project. The flux measurements in the campaigns have demonstrated that AMDEs (Atmospheric Mercury depletion Episodes) more than doubles the input of mercury to the Arctic environment through the transformation of GEM (Gaseous elemental Mercury) to RGM (Reactive Gaseous Mercury) and the deposition of RGM to the snow. These findings have been used to establish a new parameterisation of the removal of atmospheric mercury for Danish Eulerian Hemispheric Model (DEHM) and to validate the model. As a first estimate about 200 tons/year is deposited to the surface north of polar circle.

In undisturbed sediment cores the mercury concentration and the mercury sedimentation are generally higher in present day sediments than in sediments formed 50 and 100 years ago. This can be interpreted as anthropogenic input. Thus this study of marine sediments from Greenland supports the conclusion from other studies that approximately half of the mercury flux in the Arctic is anthropogenic,

Preliminary results in seawater indicate that 80% of total mercury is found in dissolved form or associated with particles < 0.45 µm. Mercury content is clearly dependent on trophic position in the food web. Significant increase in mercury content is found in predators such as crabs, fish, birds and seals. The coupling between transport pathways of carbon and mercury is weak at lower trophic levels.

A substantial decrease of Hg concentrations in teeth and hair of polar bears since 1960 was found. Hg concentrations in hair of polar bears sampled in East Greenland during 1999-2001 was 8.3 times higher than baseline levels in West Greenland obtained from 1300 AD. Of 12 trend analyses performed on three birds of prey, 11 analyses showed increasing trend, however, only 4 groups from West Greenland were found to be significant (immature gyrfalcon – all peregrines, and immature and adult White-tailed eagle). The increase of these time series ranged between 0.008 mg/kg dw per year to 0.05 mg/kg dw per year.

The present joint effort aiming at understanding the link between transport, deposition and bioaccumulation in the Arctic environment shows that such a model is not easily established. However, continued effort on developing such a model may fulfil the goal of predicting future trends and effects on humans and exposed target species.

However, at present this connection is not established. We need to carry out joint field campaigns to study the connection between the atmospheric input during AMDEs, the pelagic food chain and the transfer to higher trophic levels.

Large uncertainties on the inter-compartment fluxes still exist and future activities should be organised as joint campaigns having a more holistic approach with focus on periods and target areas with AMDEs.

Based on the obtained knowledge a model has to be developed that can explain the observed levels and inter compartment transport patterns. Finally scenario calculations have to be performed to demonstrate the sensitivity of the model and the system towards changes in climate, emissions and the food web.

1 Introduction

- Toxicity of mercury* All mercury compounds are toxic (WHO, 2000) and in particular organic mercury compounds. For example methylmercury is readily taken up and it has a negative effect on the central nervous system in humans and animals on higher trophic levels. A Cohort study on the Faeroe Islands demonstrate that levels of methyl mercury previously considered to be low has a negative effect on the intellectual development of children (Grandjean et al., 1998).
- Hg application and emission* Mercury has been widely used in mining noble metals because it forms alloys with them. Furthermore, mercury was used in the chloro-alkali industry (Hylander and Meili, 2003). The emission from industrial use of mercury reached its maximum in the 1950's (Hylander and Meili, 2003). Finally, a large amount of mercury is emitted from coal burning and today this is the dominant source in Europe, North America and Asia (Pacyna and Pacyna, 2002). As a consequence the emission of mercury to the environment has been extremely variable during the last 100 years. West Europe and North America were previously the main emitters of mercury but now the emission is moving eastwards e.g. to China due to increased coal combustion (Pacyna and Pacyna 2002).
- Hg in the Arctic* In the Arctic the human exposure is closely connected to the intake of fish, seabirds, seals and whales (Johansen et al. 2004), which are major ingredients in the traditional food, compared to e.g. Europe or North America (AMAP 2003, Riget et al. 2000). The ambient concentrations in the atmosphere, waters etc. are too low to be of direct concern (Pirrone et al. 2002, position paper for DG- ENV, Commission of EU but rather is the transport media where mercury can be transported to the Arctic from the sources at mid latitudes.
- Historical levels of Hg* From peat cores it is deduced that the ambient level of present time mercury is three times higher than in pre-industrial times and that it reached a level 30 times higher than pre-industrial levels in the 1950s (Shotyk et al. 2003). Asmund and Nielsen (2000) have shown that the mercury content in sediments from Greenland has doubled during the last 100 years. The mercury content in hair of children in Greenland (living in an area just north of Disco Island) has been compared with the mercury content in mummies of humans from the 15th century. The level has increased from 3.1 ppm at that time to 9.8 ppm in 1985 (Hansen et al. 1989, Hansen and Asmund, 2003). Time trend data of mercury in Greenland biotic soft tissue from the last 30 years does not yet show a consistent trend (Riget and Dietz, 2000; Riget et al., 2004).
- Transport pattern* Mercury compounds are bio-accumulated. As a consequence the highest levels of mercury compounds are found in top predators like seals, toothed whales, polar bears, and also humans (AMAP, report 2003). The main mercury source for humans in general is the diet but the processes that link emission – atmospheric transport – atmospheric deposition – transport to seawater (– reemission – transport to sea water) – uptake in plankton – transfer to higher trophic levels are at present insufficiently known (see front page figure).

Atmospheric processes

Mercury is photo-oxidised in the atmosphere. The lifetime outside the Arctic is itself of large dispute and estimates vary between about 1 year (Lin and Pehkonen, 1998, Schroeder and Lin, 2000) and about 15 days using the results of the latest study of the rate constant of Hg° with O_3 (Pal and Ariya, 2004). The products of the reaction(s) are deposited fast either by dry or wet deposition but once deposited it can be reduced and re-emitted to the atmosphere, the so called "hopping" or distillation process. In 1998 Schroeder et al. (1998) presented for the first time observations of Atmospheric Mercury Depletion Episodes (AMDEs), where GEM was depleted within few hours. Due to the long range transport of mercury and the AMDEs the Arctic is a receptor area for deposition of atmospheric mercury although there are not any local sources (Skov et al. 2004). Since the first observations of AMDEs it has been a highly prioritised scientific challenge to investigate the significance of this phenomenon (e.g. Schroeder et al. 2003 and references in there). Despite this interest, it is still not possible to make a quantitative description of transport pattern of mercury in the Arctic environment. As a consequence, effects of remediating strategies cannot be determined by scenario calculations of possible future emission restrictions and the connection between changing emission areas and Arctic receptor points is also unknown. Furthermore, the lack of a quantitative understanding also makes it impossible to predict the effect of global climate change on the flow of mercury from emission to its final destiny. For example occurrence of seasonal ice in the Arctic is necessary for depletion of mercury during spring (Lindberg et al. 2002, Skov et al. 2004). Thus the retreating ice coverage observed in the Arctic is expected to lead to changes in the number of mercury depletion episodes and their geographical distribution. Furthermore global change may lead to a change of habitats in the Arctic and North Atlantic Oceans. This in turn may change the diversity of algae and bacteria that may lead to a changed conversion rate of abiotic mercury into biotic mercury.

Bio-uptake of Hg

The AMDEs occur simultaneously with the stratification of the water column and the onset of phytoplankton bloom when sea ice breaks up and dramatically increases the light available for primary production. Thus, the timing of the mercury release to the water column may be tightly linked to an efficient assimilation to the primary producers as the production season initiates. Large copepod of the genus *Calanus* play a central role in the trophic pathway in high latitude ecosystems as grazer on the phytoplankton and as food for marine fish and birds. In the late winter the *Calanus* populations emerge to the surface layer prior to the spring bloom ready to harvest the developing bloom. During their feeding in the pelagic zone the *Calanus* produces large faecal pellets, by packing the smaller ingested phytoplankton to pellet, and as a consequence sedimentation is accelerated up to 100 - 150 m day⁻¹. About midsummer the copepods return to their wintering depths above the bottom, thereby dramatically changing the trophic pathways in the pelagic and the coupling to the benthos (Barkay et al., 2003).

Bioavailable mercury

According to the current knowledge about bacterial conversion of ionic mercury two different processes (reduction or methylation) can occur depending on environmental conditions and the type of bacte-

ria present (*Barkay et al., 2003*). The fate of the mercury in the Arctic marine ecosystem therefore depends on which of these processes dominates and where they take place.

The bioavailable Hg(II) in the water column will be reduced to elemental mercury, which will return to the atmosphere, but a lot of Hg(II) might be bound to organic material such as phytoplankton and therefore not available to bacterial transformation. During the spring bloom the sedimenting phytoplankton, marine snow and faecal material will bring the Hg(II) to the sediment. Sulphate reducing bacteria commonly present in marine sediments can under anaerobic conditions methylate Hg(II) to methyl mercury compounds, which become bio-accumulated through the benthic-based food chains.

Hg bio-accumulation

As stated above mercury is accumulated in the food chain. Marine mammals in the Arctic (e.g. seals and whales) are important food resources for the local people and a connection between their intake of traditional food and their level of mercury in soft tissue, blood and hair is well established. However, there is a lack of knowledge of the factors controlling bio-accumulation up through the marine food chain in Greenland. It is necessary to know these factors in order to describe the mercury accumulation through the food chain and predict the effects.

Joint report

Results in this report describe the inter-compartment mercury transport chain in the environment that leads from atmospheric deposition of mercury on sea surfaces to uptake in marine organisms, bio-accumulation and the resulting levels in mammals. The aim of this work is to fill some of the gaps needed to establish a model for the transport and uptake of Hg. The report focuses on the surface exchange of mercury, the uptake of abiotic mercury into the biological system and the bioaccumulation in the first steps of the food web and the resulting distribution and time trend of mercury in selected animals feeding on various trophic levels.

Interdisciplinary work

The complexity of the problem makes it obvious that contributions from many professional areas are needed. Therefore 3 departments of NERI (Depart. of Atmospheric Environment, Dept. of Marine Ecology and Dept. Arctic Environment) are contributing to the work by combining traditional biological, chemical and physical disciplines.

Subproject reports

Within the specific areas more comprehensive reports are under preparation where the findings in each subproject are explained in detail.

2 The fate of atmospheric mercury in the Arctic and the load of it to the Arctic environment

Skov, H. Christensen, J. Wählén, P. Goodsite, M.E. Larsen, M.R.B. and Brooks, S.

2.1 Background

Ubiquitous pollutant

As explained above mercury is a ubiquitous pollutant. In the Northern Hemisphere it is found in background areas at concentrations close to 1.5 ng/m^3 throughout the year.

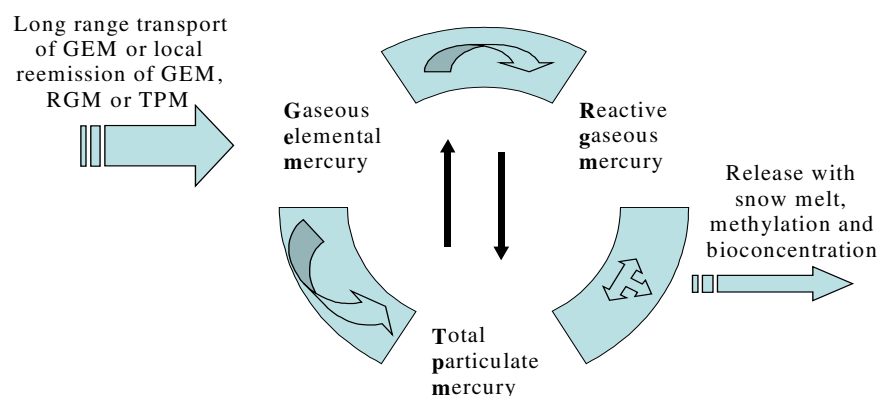


Figure 2.1 A simple scheme of the processes of atmospheric mercury in the Arctic during AMDE

AMDE

GEM is fast converted to reactive gaseous mercury (RGM) during atmospheric mercury depletion episodes (AMDE) that occur in the Arctic Spring (Schroeder *et al.* 1998). RGM is either deposited to the surface leading to a mercury accumulation in the Arctic or alternatively transformed into fine particulate mercury, FPM, see Figure 2.1.

The aim of the atmospheric part

The aim of the atmospheric part of FOMA is to determine the quantity of mercury deposition and the quantity of RGM transformation to FPM. The processes are finally parameterised and used in the Danish Eulerian Hemispheric Model.

Field campaigns

In 2001 flux measurements of RGM were carried out for the first time (based on basic funding and funding from SNF and others). The work was a co-operative study between National Oceanic and Atmospheric Administration (NOAA), Oak Ridge National Laboratory (ORNL) and Environmental Protection Agency (EPA), USA. The project was continued in field campaigns in 2002, 2003 and 2004 at

Barrow, Alaska where the Danish activities in 2003 were fully financed by DANCEA and partly financed for 2004 season. Furthermore, a campaign partly financed by DANCEA was performed at Station Nord in 2002.

In the present chapter focus is on flux measurements and their application for the determination of the input flux of mercury to the Arctic. For a reliable description a long series of other parameters were measured. They are described in a report only dealing with atmospheric part of FOMA (*Skov et al. 2004a*). Furthermore, work was carried out to develop the needed new methods for making a reliable description of the atmospheric processes. They are all described in *Skov et al. (2004a)*.

2.2 Experimental section

Scope and co-operation

From 2001 to 2004 campaigns were carried out at Station Nord, Northeast Greenland and Barrow, North Slope, Alaska in co-operation between NERI, NOAA and ORNL. Furthermore, EPA was participating in the first year and NILU and meteorological Service Canada (MSC), Canada in the last year. Finally, Domaine Universitaire, Grenoble, France participated at Station Nord in 2002. The study was extended to include students both from the University of Copenhagen and from the University of Southern Denmark. All the campaigns were in general carried out from mid March to mid April where AMDEs were observed to be most active.

The Barrow campaigns

In Barrow continuous measurements were carried out of GEM, RGM, FPM and Particle size distributions using commercially available instruments (see FOMA, subproject Atmosphere Report, *Skov et al. 2004b*). Furthermore, RGM, GEM and ozone fluxes were measured.

REA

RGM fluxes were measured by relaxed eddy accumulation, REA, where a sonic anemometer measures the vertical wind speed and through the connection to a fast shifting valve system air samples can be sampled in upward air and in downward air. The difference in the concentrations in the two channels is proportional to the flux, F as expressed in equation 2.1.

$$F = \beta \sigma_w (C_{\text{up}} - C_{\text{down}}) \quad (2.1)$$

Uncertainty

where β is an empirical constant, σ_w is the standard deviation of the vertical wind velocity and C_{up} and C_{down} are respectively the concentrations in the upward and downward wind. GEM fluxes were measured by the gradient method at about 20 m and 1 m above the ground in 2004 (*Brooks et al. 2004, report*). Finally, gradient measurements of RGM were carried out in 2004 for supporting the REA results.

Details of the different analytical techniques are described in *Skov et al. 2004b*. Here is only listed the estimated uncertainties of the methods based on reproducibility experiments and best estimates, see Table 2.1.

Table 2.1 The uncertainty of the measurements of the various species at Barrow, Alaska. For all the mercury species the uncertainty is estimated from reproducibility experiments

	Ozone monitor	Tekran GEM	Tekran RGM	Tekran FPM	RGM Flux	GEM Gradient
Unit	ppbv	ng/m ³	pg/m ³	pg/m ³	pg Hg m ⁻² min ⁻¹	pg Hg m ⁻² min ⁻¹
Range	0-50	at 0.5	0-1000	0-50	-22 to 30	-10 to 20
std dev	6%	20%	20%	40%	33%	33%

No RGM flux data were obtained from Station Nord in 2002 because of either lack of wind or too low RGM concentrations. Furthermore there is not any REA-data from Barrow in 2004 because of technical problems due to extreme weather conditions. Temperature varied between -4°C and -40°C so that the instrument broke down.

2.3 Results and discussion

REA flux of RGM

Figure 2.2. Shows the results of the RGM flux measurements using equation 2.1 and results in the spring campaigns in 2001 to 2003 and the calculated deposition velocities (V_d), equation 2.2.

$$V_d = F/C_{\text{average}} \quad (2.2)$$

where C_{average} is the average concentration.

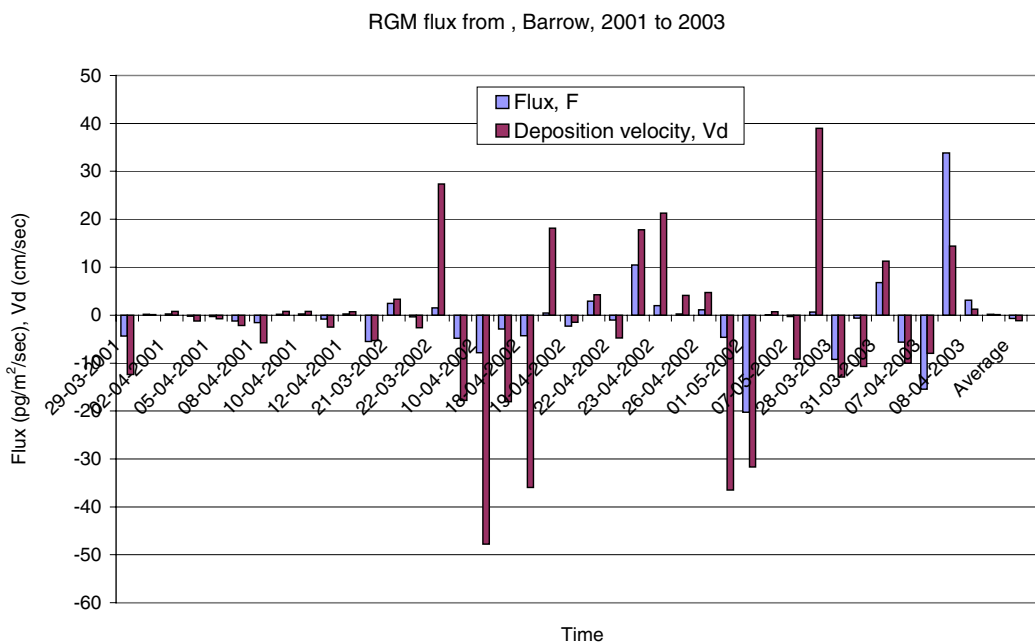


Figure 2.2 The measured flux at Point Barrow Alaska and the corresponding deposition velocities.

The flux measurements were carried out during atmospheric mercury depletion episodes where large concentrations of RGM are built up (up to 1000 pg/m^3), see Skov *et al.* (2004a).

Reliability of flux measurements

There are periods with both emissions (positive flux values) and depositions (negative flux values). Only depositions were expected due to the observed short lifetime of RGM. So an obvious question is; whether the measured fluxes are real or due to measurement artefacts. This central question is discussed profoundly in Skov *et al.* (2004a). The conclusion of the flux measurements is that the measurements are correct. But there is an extra contribution from a fast oxidation of GEM to RGM near the snow surface during AMDE that sometimes gives an extra contribution in the up channel. Thus an additional contribution to C_{up} has to be included so that equation 2.1 is expressed as;

$$F = \beta\sigma_w(C_{\text{up}} - C_{\text{down}}) = \beta\sigma_w(C_x - C_{\text{chem}} - C_{\text{down}}) \quad (2.3),$$

where C_x is C_{up} plus a contribution from the chemical formation near or on the snow surface.

Surface reactions

Unfortunately we can only measure C_x and not C_{chem} . Therefore it is only possible to give an upper limit for the deposition (of the negative fluxes) based on the average of a whole campaign. The average fluxes are listed in Table 2.2 for the three years 2001, 2002 and 2003 together with average value of all the measurements. Furthermore is shown the values without positive flux values.

Table 2.2 The average flux, concentration and deposition velocity of RGM at Barrow Alaska in the three campaigns in Spring. The results in parenthesis are calculated without positive flux values.

Year	Average F pg/m ² /sec	Average C pg/m ³	V _d cm/sec
2001	-0.67 (-1.42)	43.56 (34.07)	-1.54 (-4.16)
2002	-1.54 (-4.92)	29.74 (39.93)	-5.17 (-12.31)
2003	1.63 (-7.73)	145.93 (81.84)	1.16 (-9.45)
Average*	-0.67 (-4.45)	56.78 (46.24)	-1.17 (-9.63)

*Average is the average of all measured fluxes and concentrations and not only the three values listed here. V_d is calculated from the average flux and concentration.

Lower limit

The obtained average F values have to be considered as upper limits also the ones where positive values have been excluded. Thus the same is valid for the deposition velocity V_d also shown in Table 2.2.

Deposition resistance

The deposition velocity is an important feature but it can not be used directly in physical chemical transport models because the deposition velocity depends strongly on the meteorological conditions. Instead the resistance R is used;

$$R = -1/V_d \quad (2.4)$$

The resistance is composed of different resistances

- the aerodynamic resistance R_a dependent on meteorology
- the laminar resistance R_b dependent on meteorology and the properties of the compound
- the surface resistance R_c dependent only on the properties of the compound

R is expressed in equation 2.4:

$$R = R_a + R_b + R_c \quad (2.5)$$

The fundamental assumption for the resistance description is that the flux is the same over all resistances.

R_b is to a good approximation 0 for a snow surface and R_a can be calculated from meteorological data available from the sonic.

$$R_a = U/(U^*)^2 \quad (2.6)$$

where U is the wind speed and -(U*)² is the vertical momentum (Asman et al. 1994). R_a is calculated to be 106 sec/m in 2003 and R is calculated from equation 2.4. to be 10.4 sec/m. It is clear from equation 2.5 that there is a discrepancy between the R and R_a value as R_c cannot be negative.

The very low R is explained by the fast reaction between Br and Hg near the surface so that the aerodynamic resistance, which leads to a breakdown of the assumption of constant flow over the resistances.

The very small R value indicates that the surface resistance must be small as well. Therefore R_c is to a first assumption assumed to be 0 in model calculations of the deposition of RGM.

Load of atmospheric mercury to the Arctic

This result is implemented in the first model calculations of the load of atmospheric mercury to the Arctic, using the Danish Eulerian Hemispheric Model, DEHM, see Figure 2.3. (AMAP 2003, Skov et al. 2004, Christensen et al. 2004). The total amount of mercury deposited north of the polar circle is calculated to be 208 tonnes/year.

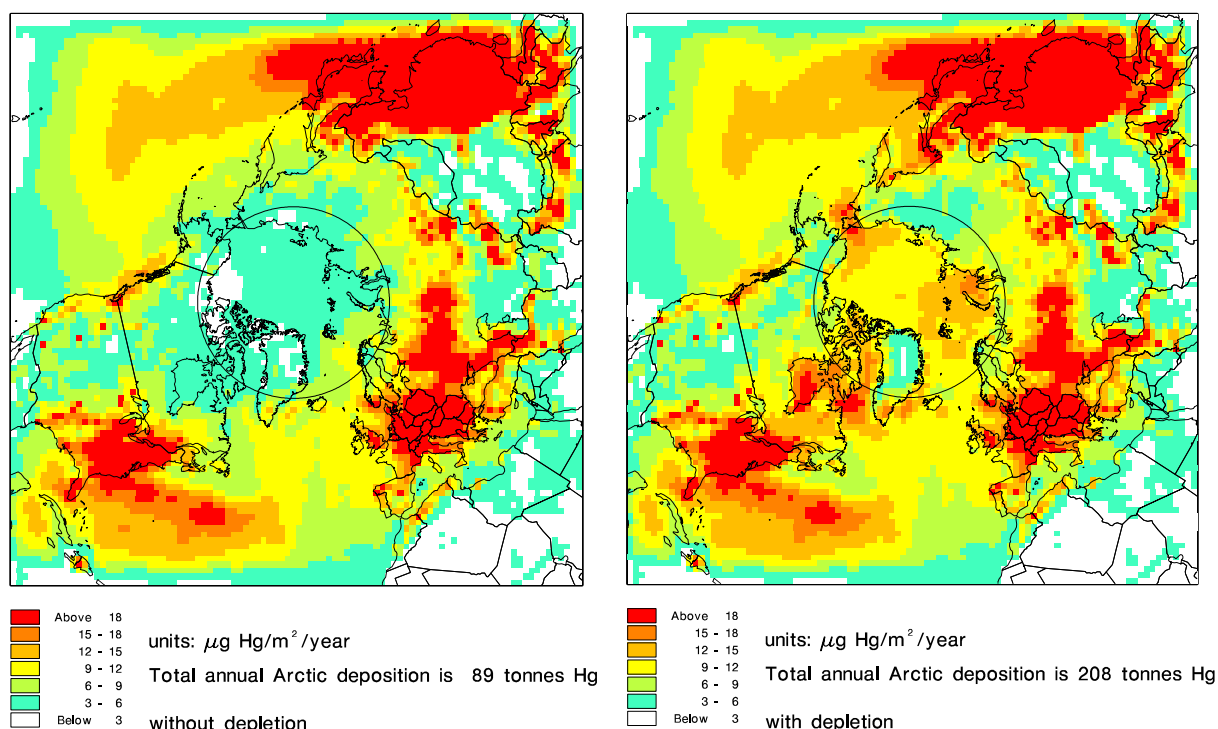


Figure 2.3 The total annual average deposition of mercury without Arctic mercury depletion (left) and with (right) in $\mu\text{g Hg/m}^2/\text{year}$ for the years 1999 and 2000. The total annual deposition north of the polar circle is indicated as well

Re-emission

A significant amount is re-emitted. In 2004 NOAA measured the re-emission of GEM. The first analysis of the re-emission indicates that about 50% of the deposited mercury are re-emitted, see Figure 2.4.

Geographical distribution?

On the other hand the surface reactions at the Barrow site indicate that bromine species are deposited to the surface and re-emitted leading to near surface oxidation of GEM. These processes can thus lead to GEM depletion inland downwind of marine areas. In fact enhanced mercury depletion has been observed more than 40 km inland from North coast of Alaska (Douglas and Sturm, 2004). This process is not taken into account in the present version of DEHM.

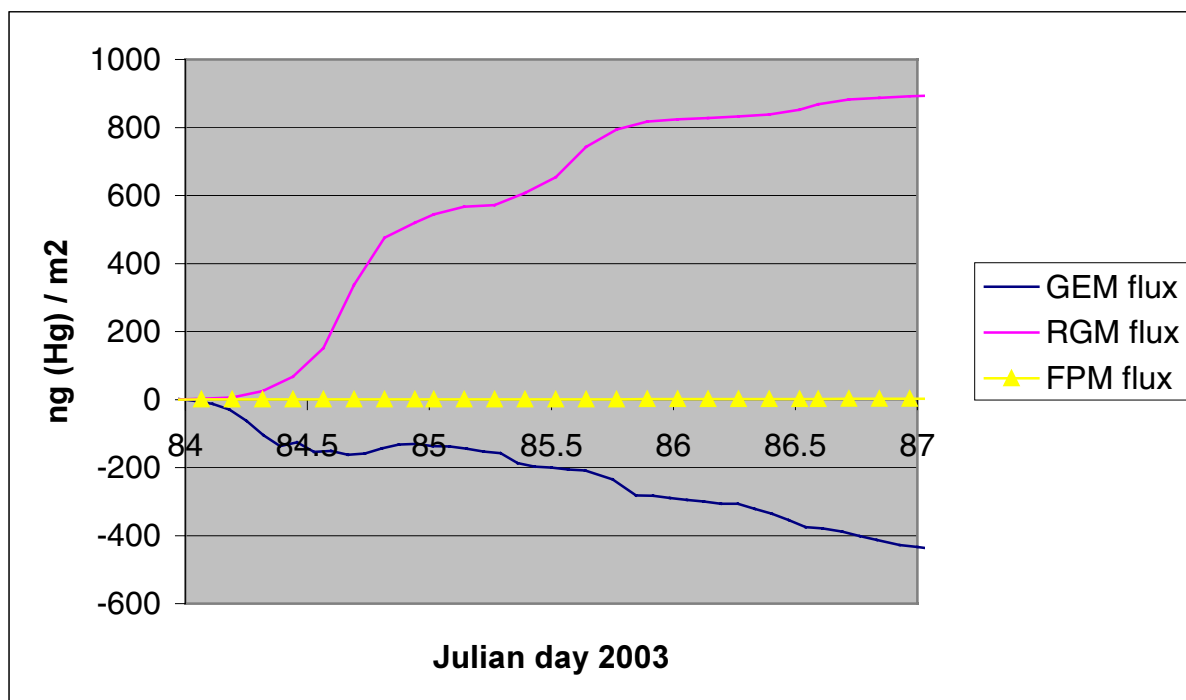


Figure 2.4 The fluxes of RGM, GEM, and FPM for Julian day 84 to 86 (April 1-3). Positive fluxes are depositions and negative fluxes are emissions. GEM flux is by gradient method, whereas RGM and FPM are estimated from the determined V_d for RGM and for particles together with inversion height and atmospheric turbulence (Brooks et al. 2004)

Extrapolation with models

It is difficult to incorporate the result in Figure 2.4 and the discussion above into models because the underlying processes are only poorly understood. We do not know if the re-emission has a seasonal variation. At Alert, Canada GEM, RGM and FPM have also been measured and FPM is found to be much higher there than RGM. This is contrary to what is normally observed at Barrow, Alaska. We do not have any explanation of this discrepancy though the joint campaign in 2004 at Barrow showed that it is not due to measurement errors but it is real values. Furthermore the mechanisms of conversion of GEM to RGM and the fate of RGM is not even qualitatively understood. Clearly the description in Figure 2.2 is too simple.

Mass balance

Finally large quantities of mercury are transported horizontally with blowing snow and this makes it impossible to make an estimate of a mass balance of the deposition. But during the three-day period shown in Figure 2.4 a daily increase of mercury in snow of about 17 ng/litre was observed. This is at least in good qualitative agreement with the observed input flux of atmospheric mercury.

2.4 Conclusion

The first measurements ever of atmospheric mercury fluxes have been carried out. The flux measurements in the campaigns have demonstrated that AMDEs more than doubles the input of mercury to the Arctic environment through the transformation of GEM to RGM and the deposition of RGM to the snow. These findings have been used to make a new parameterisation of the removal of atmospheric mercury for DEHM and to validate the model.

Thus, for the first time the load of atmospheric mercury to the Arctic has been estimated using atmospheric transport models (*AMAP 2003, Skov et 2004*). About 208 tons/year is deposited north of the Polar circle. The measurement of re-emission indicate and discussion of the geographical extension of AMDE show that the estimate is encumbered with a very large uncertainty.

3 Mercury in dated Greenland marine sediments

Asmund, G. and Nielsen, S.P.

3.1 Background

The observations in peat, ice cores etc. indicate an increase of the mercury load on the Arctic marine environment due to anthropogenic activities. If this holds, an increase of the mercury content in marine sediments may be expected. Therefore marine sediment were included in the Arctic Monitoring and Assessment Programme to study the time trends of mercury and to establish a background level and the extent to which the present mercury is of anthropogenic origin (Asmund and Nielsen, 2004). The study presented in this chapter is not a part of FOMA but it is closely related to the other mercury studies and furthermore also funded by DANCEA. Therefore we have decided to include this chapter on the marine sediments.

3.2 Sample collection

Sediment samples from Greenland have been collected by a gravity stainless steel core sampler HAPS with an internal diameter of 13.4 cm in the period 1985 to 1994. The cores were cut into 1 cm slices.

3.3 Analyses

Lead-210 analysis

Most of the sediment samples were analysed for Pb-210 indirectly by determination of their content of Po-210, which is in equilibrium with Pb-210. The samples were analysed for Po-210 by radiochemical procedures followed by alpha spectrometry. Analyses of Pb-210 were made for a few samples by gamma spectrometry.

Mercury and other trace elements

Loring and Asmund (1995) have reported results for several trace elements including manganese in these samples. Mercury was determined by cold flameless AAS and the flow injection method (Perkin Elmer FIMS).

Greenland Cores with diagenesis

For three cores the manganese concentrations were found to be very different in the 3 slices analysed, (see table 3). One other core was also suspected to exhibit diagenesis due to a strange profile and colour changes in the sediment. The results of these cores will not be used to draw conclusions about the time trend of mercury fluxes.

3.4 Discussion

Regression of mercury versus depth

The mercury concentrations were treated by linear regression after logarithmic transformation of the mercury concentration, according to the model:

$$\text{Ln}(\text{Hg-concentration}) = a (\text{depth}) + b \quad (3.1)$$

Increasing flux of mercury

The regression was restricted to the part of the sediment layers that were younger than 100 years (relevant for 7 of the cores) and was evaluated at a significance level of 5%. Of the 16 cores not suspected of diagenesis, 9 showed a significant decrease of mercury concentration with depth. Six cores showed a non-significant decrease with depth, and one showed a non-significant increase of mercury concentration with depth. There is thus strong evidence that the mercury flux to Greenland marine sediments have increased during this century.

Quantification of the increase

In order to quantify the change in mercury deposition, an average value m is calculated for the coefficient a in equation 3.1 obtained for all those cores that are not suspected for diagenesis. As the different estimates of m have varying uncertainties, the average is calculated after weighting the m -value with $1/s^2$ (s =standard deviation of m).

The result of this calculation gives:

$$m = -0.0071 \text{ year}^{-1}$$

with a calculated standard deviation of 0.00094

The calculation of the standard deviation of m assumes that all m -values are estimates of one true value with methods of different accuracy. This assumption might not be correct, so the uncertainty of the calculated m might be much larger. With the above value of m , the relative concentration of mercury in Greenland marine sediments can be calculated for the last 100 years:

Year	Relative mercury concentration
1990	100%
1965	83.7%
1940	70.1%
1915	58.6%
1890	49.1%

From this calculation it is seen that the best estimate of the increase of the mercury concentration (and therefore also mercury flux to the sediments) is a doubling during the last 100 years. It is therefore quite reasonable to assume, in line with *Lockhart et al. (1996)*, that half of the mercury found today in marine surface sediments in Greenland is of anthropogenic origin. *Nriagu (1989)* also found that approximately half of the atmospheric mercury is of anthropogenic origin. The mean

value of m would not have changed significantly if the four cores suspected for diagenesis were included.

3.5 Conclusion.

In undisturbed sediment cores the mercury concentration and the mercury sedimentation are generally higher in present day sediments than in sediments formed 50 and 100 years ago. This can be TAKEN? as an indication of anthropogenic input. Thus these results from the sediments can probably explain the high concentrations of mercury in animals and humans in the Arctic, but only partly. The results indicate that the anthropogenic fraction is a significant part of the mercury in the marine sediments; at least half of it is believed to be of anthropogenic origin. Thus this study of marine sediments from Greenland supports the conclusion from other studies that approximately half of the present mercury flux in the Arctic is anthropogenic.

4 The uptake of abiotic mercury in the biological system and bioaccumulation in the first steps of the food chain

Sejr, M.K. Rysgaard, S. Rigaard-Petersen, N. and Nielsen, T.G.

4.1 Background

Efficient mercury assimilation?

When sea ice melts in the spring the precipitated mercury leaks out from the sea ice compartment to the underlying water column as described in the Chapter 1. The timing of this occurs at the same time as the stratification of the water column. This stratification together with the increased light availability also triggers the spring phytoplankton bloom. Thus, the timing of the mercury release to the pelagic environment may be tightly linked to an efficient assimilation to the primary producers as the productive season is initiated.

Copepods

Large copepods of the genus *Calanus* play a central role in the trophic pathway in high latitude ecosystems as grazers on the phytoplankton and as food for marine fish and birds. In the late winter the *Calanus* populations emerge to the surface layer prior to the spring bloom to be ready to harvest the developing bloom. During their feeding in the pelagic zone the *Calanus* produces large faecal pellets, by packing the smaller ingested phytoplankton to pellets, which cause acceleration of the sedimentation with a rate up to 100 - 150 m d⁻¹. About mid-summer the copepods return to their wintering depths above the bottom, thereby changing the trophic pathways in the pelagic and the coupling to the benthos dramatically.

Spring bloom

A strong pulse following the spring blooms often characterizes the input of organic matter to the sediment surface. Several studies have documented high standing stocks of benthic fauna in the Arctic region. An efficient transfer of organic matter produced in the water column to the sea floor through a close pelagic-benthic coupling together with low metabolism of benthic fauna are part of the reason why high benthic biomass can be maintained. When *Calanus* are present in the productive part of the water column they accelerate the vertical flux through their production of fecal pellets. The fast sinking energy rich pellets can contribute with up to 50 % of the vertical flux.

Rapid mercury transfer

Despite permanently low temperatures, near-shore Arctic benthic communities mineralize organic matter as efficiently and as rapidly as communities at lower latitudes and are therefore expected to transfer mercury rapidly to higher trophic levels by benthic consumers (e.g. eider, bearded seals and walrus).

Transport through lower trophic levels

This chapter focuses on the transport of mercury through the lower trophic levels of the marine food web. The fate of mercury through the marine food web is hypothesised to be very dependent on how

mercury enters the pelagic food web, two main entrances are hypothesised

1) Phytoplankton • *Calanus* • Fish larvae

•

Calanus pellets

•

2) Phytoplankton • Benthos • Eiders, seals & walrus

In deep waters the benthos is fuelled by sedimentation of phytoplankton from the upper part of the water column. Faecal pellets from zooplankton that have a much higher sinking rate than phytoplankton can however enhance this pathway.

Objective

The objective of the present project was to:

Study the entry and fate of mercury via 1) the pelagic vs. 2) the benthic food web with special emphasis on the role of copepod faecal pellets in accelerating the transfer through the benthos based food web.

An elucidation of the seasonal mercury pulse through the lower trophic levels believed to appear from the AMDE.

4.2 Methods

Two intensive field campaigns were conducted one in the spring April/May in connection with the break up of the sea ice and one at the end of the productive season in August-September 2003. The two campaigns covered sampling for about two weeks of water column structure, biomass and primary production of phytoplankton, bacteria, micro and mesozooplankton and benthos on a 50 m deep station in the Disko Bay, West Greenland. These measurements form the background description of the food web structure. To investigate the pools and fate of the mercury, the mercury concentrations were measured in water, phytoplankton, copepods, fresh faecal pellets and benthos.

4.3 Results and discussion

Two campaigns

The conducted field campaigns of the present project covered the two situations that we aimed at. First a spring bloom (April-May) situation with relatively cold mixed water and very high phytoplankton biomass (15-20 $\mu\text{g Chl } a \text{ l}^{-1}$) was studied and then a late summer situation (August-September) campaign with warm water and low plankton biomass (1-3 $\mu\text{g Chl } a \text{ l}^{-1}$) was carried out. Despite a significant difference in the structure and composition of the pelagic food web, no seasonal difference in the mercury content of water, copepods or sediment traps content were measured. So despite the perfect

timing of the field campaigns of present investigation, no signal of the AMDE was detectable in the measured pelagic or benthic parameters. Therefore the results from both campaigns are depicted together in Figure 4.1 to 4.3. One explanation for the missing spring peak in mercury could be the fact the ice cover was very reduced in 2003, consequently the spring bloom could have started and the mercury from the AMDE sedimented one month prior to our investigation. It is well established that fresh sea ice is needed in order to have AMDE (Skov et al. 2004, Lindberg et al. 2002).

Major part as dissolved mercury

A general observation was that the major part of the total mercury (80%) was found in dissolved form or associated with particles < 0.45 µm. So a weak coupling was observed between the trophic pathways of carbon and mercury in the Arctic pelagic food web. Thus, the hypothesis about the importance of copepod faecal pellets in the vertical mercury flux could not be verified. In general the preliminary calculations show that a very low proportion of total mercury is bound in the biota this indicates a limited amount of bio-available mercury.

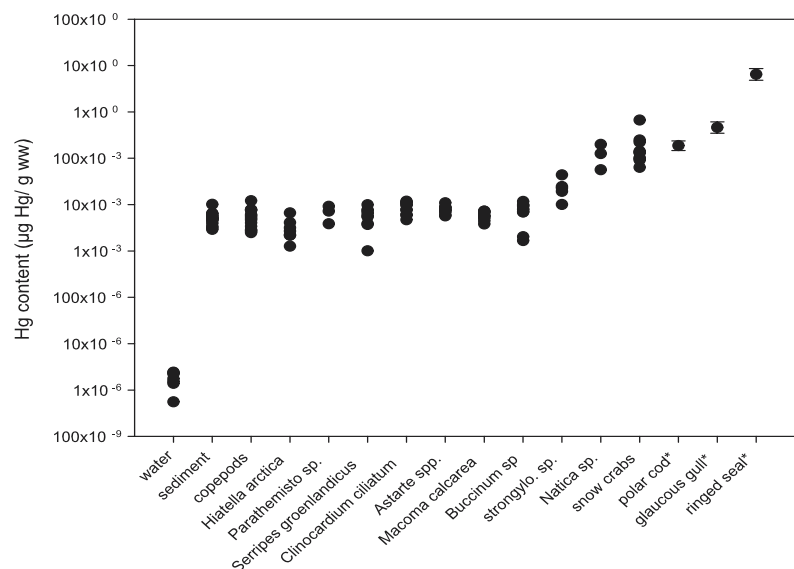


Figure 4.1 Concentration of Mercury in water and sediment and selected key spp. from the Disko bay area. Significant increase in Mercury content is found in predators such as crabs, fish and seals.

Bio-accumulation

On the other hand our results demonstrated a clear bio-accumulation in the lower trophic levels, the mercury content is clearly dependent on trophic position within the food web, see Figur 4.1. Significant higher mercury contents were measured in predators such as crabs, fish, birds and seals. In addition a significant correlation between mercury content and size/age was observed in benthic invertebrates indicating accumulation through time, see Figur 4.2 and Figure 4.3.

Mercury in snow crabs

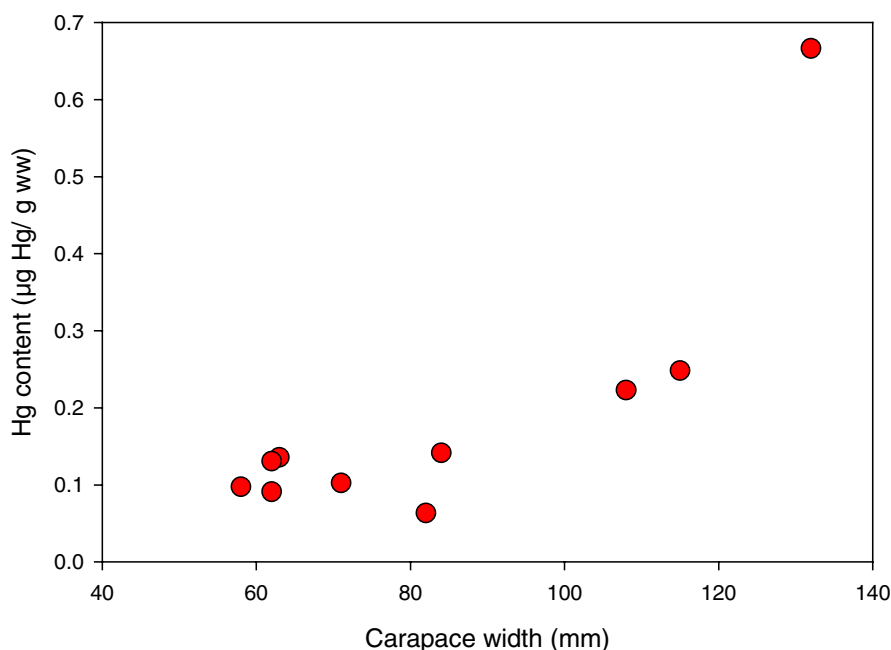


Figure 4.2 Concentration of Mercury Hg in different age classes bivalve *Clinocardium cordatum*

Mercury fluxes

Based on analysis of the unsupported ^{210}Pb content and the ^{137}Cs concentration in intact undisturbed sediment cores from the location it could be estimated that a total of $2.5 \pm 1.8 \text{ kg m}^{-2} \text{ yr}^{-1}$ dry sediment is accumulated per year. This corresponds to a rise in the sea floor of $3.8 \pm 2.8 \text{ mm yr}^{-1}$. Combining accumulation data with the mercury measurements in the sediment material it could be derived that a total of $22 \pm 6 \text{ µg Hg m}^{-2} \text{ yr}^{-1}$ is permanently buried in the sediment. From the atmosphere $12 \text{ µg Hg m}^{-2} \text{ year}^{-1}$ is deposited to the Disko Bay. These two numbers are very close and the difference could possibly be explained by the fact that the sediment may receive material from a larger area (i.e. also coastal runoff). On the other hand the accumulation seems to be small in comparison with the high vertical export ($3.8 \pm 2.3 \text{ µg Hg m}^{-2} \text{ d}^{-1}$) from the water column during spring bloom conditions. This indicates that Hg is either taken up in benthic animals or released again to the overlying water due to bacterial recycling of organic components. Given the density and Hg concentration in bivalves (Figure 4.2), the annual accumulation of Hg can be estimated to about $2 \text{ µg Hg m}^{-2} \text{ yr}^{-1}$. Thus, a significant fraction of the vertical Hg flux during spring ends up in benthic animals. The number is preliminary, as we need to include the entire benthic community. In addition, we have preliminary evidence that bacterial activity in the sediment may significantly influence the fate of sedimented Hg. Despite the highly seasonal variation in both atmospheric deposition of Hg and its timing with peak biological activity, Hg seems to be present in much less variable concentrations in both water column and sediment. However, the low variation can most probably be explained by the lack of sea ice in April/May 2003, which means that AMDE could not be detected that year in the Disko Bay. Finally, our study suggests that microorganisms ($< 0.45 \text{ µm}$) may play a much

higher role in Hg transformations to bioavailable forms of Hg than previously believed.

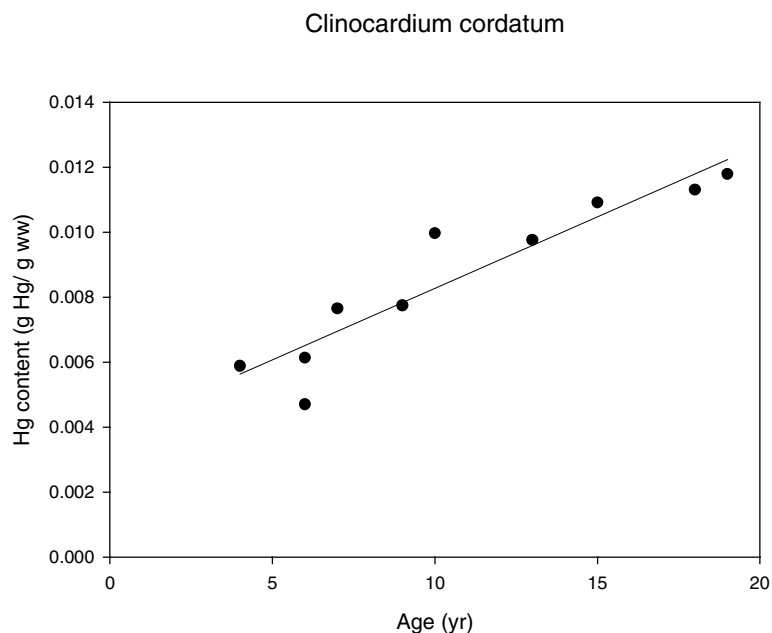


Figure 4.3 Concentration of mercury in different size classes of the commercially important snow crab (*Chionoecetes opilio*).

4.4 Conclusion

- Preliminary results indicate that 80% of total mercury is found in dissolved form or associated with particles $< 0.45 \mu\text{m}$
- *Calanus* fecal pellets did not seem to control the vertical flux of total mercury in Disko Bay.
- No seasonal trend in mercury content of water, copepods or sediment traps was found in agreement with the lack of ice cover.
- Significant correlation between Mercury content and size/age was found in benthic invertebrates indicating accumulation through time.
- Mercury content is clearly dependent on trophic position within the food web. Significant increase in mercury content is found in predators such as crabs, fish, birds and seals.
- The vertical transport of mercury during spring is estimated to $3.8 \pm 2.3 \mu\text{g Hg m}^{-2} \text{d}^{-1}$.
- From Hg profiles in the sediment it is estimated that a total of $22 \pm 6 \mu\text{g Hg m}^{-2} \text{yr}^{-1}$ is permanently buried in the sediment.
- Preliminary calculations show that a very low proportion of total mercury is bound in the biota indicating that the bioavailability is limited.
- The coupling between transport pathways of carbon and mercury is weak at lower trophic levels.

5 The temporal and geographical mercury patterns in polar bears and birds of prey

Dietz, R. Riget, F. Olsen, M.T. Sonne, C. Born, E. Grandjean, P. Kirkegaard, M. Asmund, G. Baagøe, H. Boertman, D. Falk, K. Fjeldsaa, J. Egevang, C. Wille, F. and Møller, S.

5.1 Introduction

Mercury increase

Mercury levels continue to increase in some arctic animals in some areas (Braune *et al.* in press) and may already negatively affect the reproduction in peregrine falcons (*Falco peregrinus*), while impacts are suspected in fish, birds, and marine mammals as well (Derome & Fairbrother in press). Current mercury emissions have decreased in Europe and North America, but these declines have been offset by increases in East Asia. Further reductions in global emissions will require global action. Of particular concern are the rising emissions of mercury from Asia and the discovery of mercury depletion events in the Arctic. Recent increases in mercury levels in some Arctic animals indicate that the risk posed by mercury to Arctic ecosystems and people may be increasing (Braune *et al.* in press).

Long time trends

Aside from a few data sets comparing metals in moose (*Alces alces*), caribou/reindeer (*Rangifer tarandus*), Arctic char (*Salvelinus alpinus*) and pike (*Esox lucius*) over a period of no more than thirty years, there are no long-term trend data sets for heavy metals in soft tissue of Arctic biota. For Greenland the data have been summarised by Riget and Dietz (2000) and Riget *et al.* (2004) and the need for longer time series have been documented by power analysis (Riget *et al.*, 2000; Bignert *et al.*, 2004). However, data spanning several centuries exist on Hg in human teeth from Norway (Eide *et al.* 1993; Twinnereim *et al.* 1997) and also on Hg in human hair from Greenland (Hansen *et al.* 1991) and from Canada (Wheatley and Wheatley 1988), that all document an increase in present Hg loads compared to historic levels. Similar findings has been documented from the marine biota where e.g. Outridge *et al.*, (1997, 2002) compared Hg levels in the teeth of recently collected beluga (*Delphinapterus leucas*) and walrus (*Odobenus rosmarus*) to archaeological samples.

Present chapter

In this chapter we present summary data on Hg concentrations in polar bear (*Ursus maritimus*) teeth and hair from 1830 to 2001 and from birds of prey (Gyr Falcon (*Falco rusticolus*), Peregrine Falcon (*Falco peregrinus*) and White-tailed eagle (*Haliaeetus albicilla*) (Dietz *et al.* in prep a, b). The purpose is to determine long-term trends in concentrations of this heavy metal in Arctic top carnivores.

The objectives of the present study were to:

- Deduce the long-term trends in mercury concentrations in top carnivore species (polar bear teeth and hair and in birds) from Greenland and compare those with other data-series from the Arctic .

5.2 Polar bears

5.2.1 Material and methods

5.2.1.1 Teeth

Sample composition

Teeth were extracted from a total of 356 polar bears: West Greenland (n=89), East Greenland (n=261) and Svalbard (n=6) polar bear skulls. The majority of the skulls had been sampled by expeditions (n=280) from 1830 to 1987 and had been stored at the Zoological Museum in Copenhagen, Denmark. In addition, 76 skulls, sampled during 1999-2001 by subsistence hunters living in East Greenland were analysed.

Preparation

The skulls from 1999-2001 were macerated and boiled so muscles and tendons could be removed gently prior to H₂O₂ oxidation for 24 to 48 hours. A similar procedure was presumably used on the older skulls as well but this we do not know with certainty. The upper third of the teeth including the enamel (crown) was cut off by a Proxon tool[®] (diamond-cutting blade) and used for the Hg analysis. The lower two third were used for age determination (see section 4.2).

5.2.1.2 Hair

Sample preparation

A total of 523 hair samples from the period 1300 AC to 2001 were available for analysis: 394 from East Greenland, 98 from Northwest Greenland and 31 from Svalbard (*Born et al. 1991*). Historic samples (n=37) taken from traditional Inuit clothing and other Inuit artefacts, held at the National Museum of Copenhagen. From The Zoological Museum in Copenhagen another 15 samples were obtained from polar bear skin. The last source was the Greenland National Museum and Archives in Nuuk, where 4 polar bear hair samples were obtained from traditional Inuit clothing of which 2 dated back to year 1300.

Preparation

A hair sample was collected from the skin and stored in a polyethylene plastic bag until analysis. Before the hair samples were diluted they were rinsed in a detergent to clean the sample for possible external contamination.

5.2.2 Results and discussion

5.2.2.1 Polar bears

Mercury in teeth

In general, the mercury concentration in polar bear teeth showed a weak (Slope 0.008; P=0.099; DF=97; Tested by linear regression) increase from approximately 1830 to 1950-1960 on East Greenland, which was followed by a quite substantial significant decrease (-0.125; P<0.0001; DF=155; see also Figure 5.1). For West Greenland an even weaker increase (Slope 0.004; P=0.095; DF=30) before 1960 was observed, likewise followed by a significant decrease (-0.090;

$P < 0.0001$; $DF = 55$). Based on the means in 10 years intervals from 1960 to 2000 a 234 fold decrease was observed in the mean levels from 1.38 to 0.0059 mg/kg in the teeth of East Greenland polar bears. Because of the lack of samples from West Greenland in the last 30 years it is unknown whether a similar pronounced decrease had occurred there.

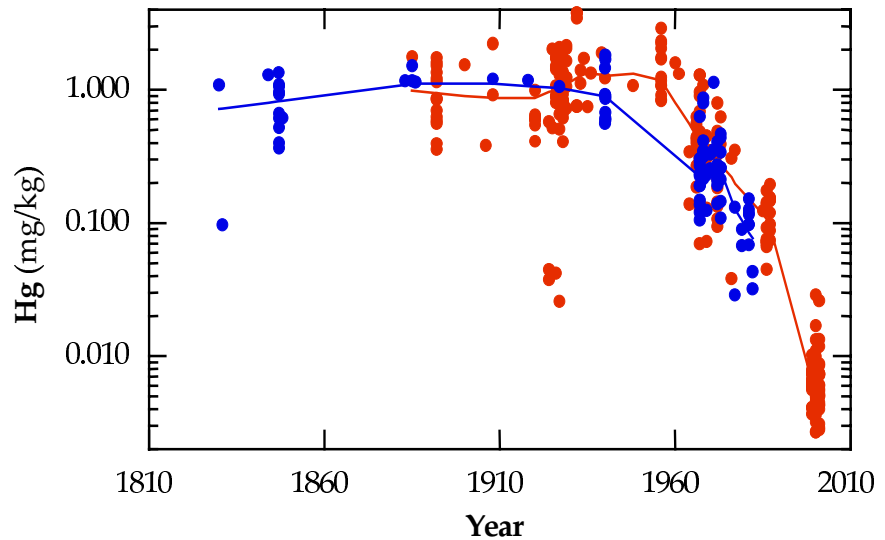


Figure 5.1 Mercury in polar bear teeth from 1835 to 2001 ($n = 345$) depicted on a logarithmic y-axis. Signatures are separated into East (red) and West (blue) Greenland. Lines are calculated using LOWEST smoother with a smoothing span of 30%.

The mercury concentration in hair from East Greenland polar bears showed a weak decrease during 1850-1950, see Figure 5.2. After 1950 the decrease became steeper with a minor increase around 1990. The Hg concentration in hair of West Greenland polar bears showed a steeper decrease from 1890 to 1950, after which period an increase was seen. Due to the limited samples available from East Greenland during 1950-70 (and from West Greenland only two samples were available for the period 1955-84) the period of peak concentrations could not be determined. Two samples excavated at Nullit in Northwest Greenland and dated from 1300 AC had a mean of 0.52 mg/kg and may be considered as a baseline level. The highest mean level (37.1 mg/kg) obtained in the period 1905-1914 from East Greenland was 8.6 times higher than that seen in the period 1999-2001 (4.31 mg/kg) and 71.3 times higher than the assumed baseline level. The Hg concentration (7.89 mg/kg) in the latest samples collected in West Greenland (1985-94) were 15.2 times higher than the baseline concentration.

Mercury in hair

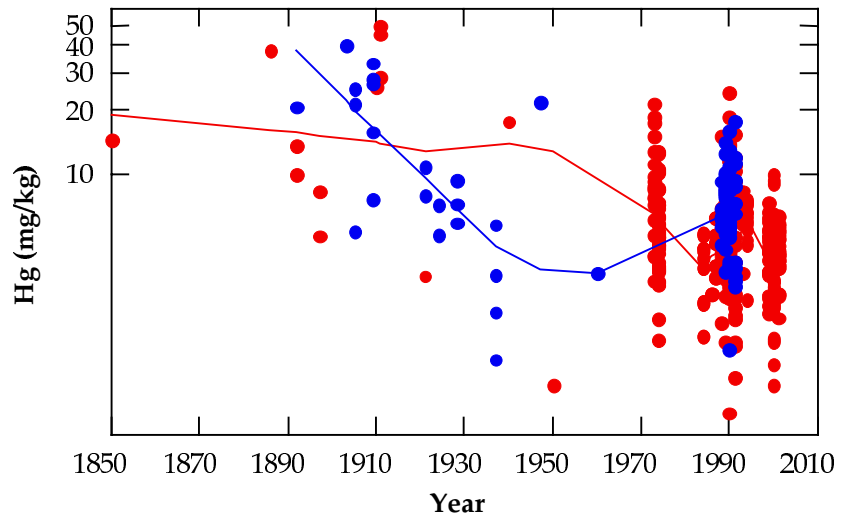


Figure 5.2 Mercury in polar bear hair from 1850 to 2001 (n=424) depicted on a logarithmic y-axis. Signatures are separated into East (red) and West (blue) Greenland. Lines are calculated using LOWEST smoother with a smoothing span of 30%.

Trends in teeth and hair

The long-term trends in Hg concentrations observed in teeth and hair of polar bear are rather different. While the Hg concentrations in teeth from East Greenland show a weak increase up to about 1960, the Hg concentrations in hair show a weak decrease. After 1960, the Hg concentrations in teeth from East Greenland show a substantial decrease (about 234 times), while the decrease in Hg concentrations in hair are much lesser (about 8 times). The reasons for this difference in time trends in teeth and hair are unknown. Especially we are not able to explain the substantial decrease in Hg concentrations in teeth, which appear to have happened since 1960 (See *Dietz et al in prep a* for further details).

5.3 Birds of prey

5.3.1 Introduction

As outlined in section 5.1 a severe lack of temporal trend data has been identified from most areas and trophic levels. A recent study (Dietz et al. in prep b) aims at determining the long-term (150 years) temporal trends of mercury (Hg) in feathers of Greenland gyrfalcon (*Falco rusticolus*), Peregrine (*Falco peregrinus*) and White-tailed eagle (*Haliaeetus albicilla*) from Greenland and compare those with other time-series data from the Arctic. A summary of this study is presented here.

5.3.2 Material and methods

5.3.2.1 Feathers

The tip of the fifth primary was collected from three species of birds of prey. However, for gyrfalcon females the fourth primary was chosen, as the timing of the moulting of this feather is believed to take place simultaneously with the fifth primary of the male and the other species.

5.3.2.2 Gyrfalcon

Feathers from a total of 539 gyrfalcons were analysed representing birds from Northwest Greenland (n=2), central West Greenland (n=247), Southwest Greenland (n=103), Northeast Greenland (n=39), Southeast Greenland (n=24) and Greenland birds with uncertain sampling locations (n=47). Beside these Greenland birds, gyrfalcons were available from Iceland (n=52), Faroe Island (n=2) and Scandinavia (n=23). The majority of the birds were study skins from the Zoological Museum (ZM) (n=518) collected from 1834 to 1998. Some recent specimens were stored in freezer in Zoological Museum (year: 1991-1996; n=8) and Greenland Institute of Natural Resources (GINR) (year: 1998-2002; n=11). In addition two recently collected shed feathers (1984, 1998 and 2003) were obtained from Knud Falk and Peter Åstrup.

5.3.2.3 Peregrine Falcon

Feathers from a total of 286 peregrines were analysed representing birds from Northwest Greenland (n=2), central West Greenland (n=74), Southwest Greenland (n=51), Southeast Greenland (n=2) and Greenland birds with uncertain sampling locations (n=10). Beside these Greenland birds, peregrines were available North America (n=5), Faroe Island, Scandinavia (n=14), Denmark (n=114), Europe (n=4), Siberia (n=3), South America (n=2) and the Middleeast (n=2). The majority of the birds were study skins from the ZM (n=265) collected from 1840 to 2000. Some recent specimens were obtained from the freezers of ZM (year: 1994; n=1) and GINR (year: 1998-2001; n=3). In addition, 17 shed feathers from adult breeders were collected between 1981 and 2003 during visits to nest sites in a study area in South Greenland (Falk et al. 1986).

5.3.2.4 White tailed eagle

Feathers from a total of 166 white tailed eagles were analysed representing birds from central West Greenland (n=87), Southwest Greenland (n=34) and Greenland birds with uncertain sampling locations (n=11). Beside these Greenland birds, white tailed eagles were available from North America (n=3), Iceland (n=3), and Denmark (n=20). The majority of the birds were study skins from the Zoological Museum (n=119) collected from 1862 to 1982. Some recent specimens were stored in freezer in ZM (year: 1987-1996; n=22) and GINR (year: 1985-2003; n=7) and NERI (year: 1997-2000; n=10). In addition some recently collected shed feathers (year: 1980-2003; n=8) were obtained from various persons (Knud Falk, Frank Wille).

5.3.3 Results and discussion

A significant ($P=0.02$; $n=193$; ANOVA) species related difference in mean log transformed Hg concentrations of adult birds were found (Figure 5.3). The adult Greenland White tailed eagles were significantly higher than both the adult gyrfalcons and the adult peregrines from Greenland. However, no significant difference could be detected between the adult Greenland gyrfalcons and peregrines. No significant differences ($p=0.89$; $n=51$) could be detected among the immature birds. A significant ($p<0.0001$; $n=449$) species related difference in mean log transformed concentrations of the juvenile birds as well (decreasing order: juvenile white tailed eagle – juvenile peregrine – juvenile gyrfalcon). The juvenile gyrfalcon had significantly lower Hg concentrations than the two other species, between which no significant difference was found.

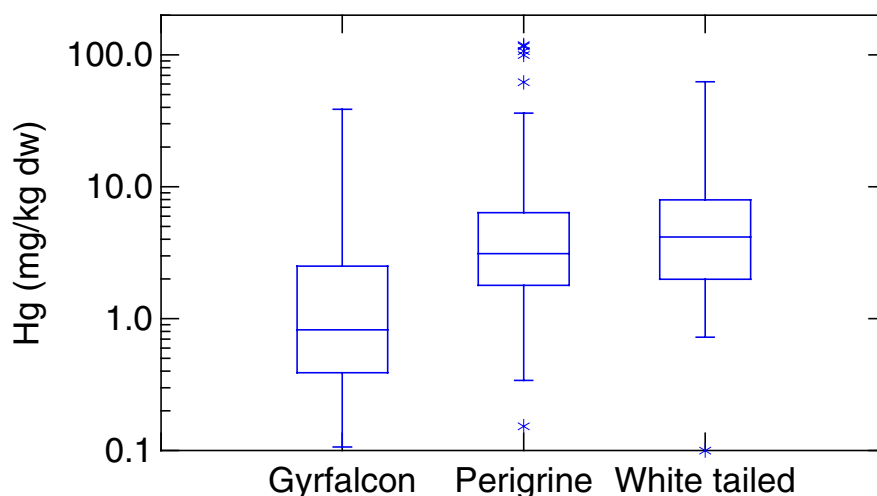


Figure 5.3 Distribution of the relative Hg concentrations (mg/kg dw) in the 5th primary of gyrfalcons, peregrines and white tailed eagles from Greenland. The box plot lines indicate median levels. The box covers 50% of the values and the whiskers shows the range of values that falls within 1.5 x spread of the box hinges

Age accumulation

For all three species Hg concentrations were found to be significantly lower in juvenile birds than in older birds. In case of peregrine, the adult females had significantly higher Hg concentrations than the adult males. Adult females gyrfalcon had also higher Hg concentrations than the adult males, however the difference was not significant at the 5% level.

Geographical trend

A regional comparison (not taking temporal trends into account) of the juvenile gyrfalcons gave significant ($P=0.0499$) higher concentration of Hg in the West Greenland gyrfalcons compared to the East Coast. No significant difference ($P=0.92$) could be detected between juvenile gyrfalcons from West Greenland and Iceland. A regional comparison was carried out between peregrine from Southwest and central West Greenland (see Figure 5.4). Of the three comparisons (juveniles, adult females and adult males) all three showed highest concentrations in Southwest Greenland. However, the difference was only significant in case of the juveniles ($p=0.02$, t-test; $N=48/11$). Also a comparison between peregrines from Greenland and Denmark was

performed. The Hg concentrations in juvenile peregrine, adult male and female were higher in Greenland than in Denmark but not significantly so. Significantly higher Hg concentrations in juvenile white tailed eagles from Denmark compared to Greenland were found ($p=0.004$; $n=54$).

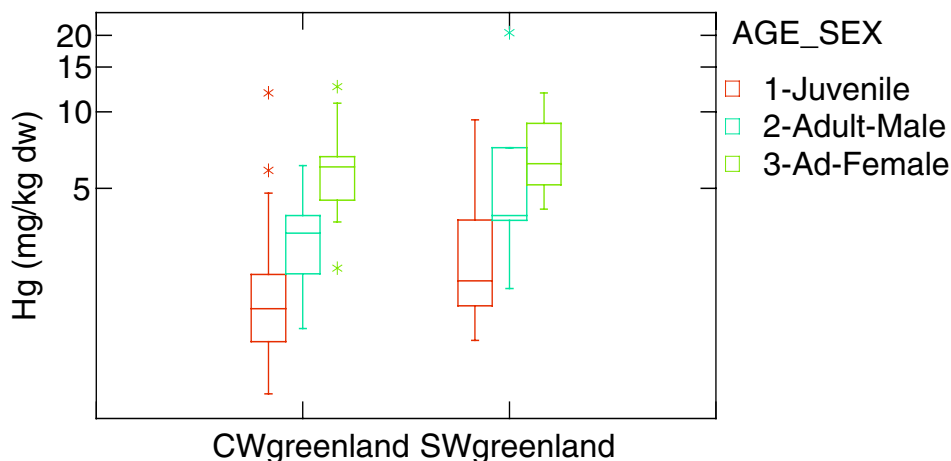


Figure 5.4 Distribution of the relative Hg concentrations (mg/kg dw) in the 5th primary of the groups: juvenile, adult male and female peregrine from central West and Southwest Greenland. The box plot signatures are explained in Figure 5.3.

Temporal trend

The temporal trends differed in the three species of birds of prey. In juvenile gyrfalcon from West Greenland dating back to 1851 no clear trend appeared although the slope of the linear regression was positive (Table 5.1; n.s.: not significant). The only decreasing trend (n.s.) in mercury concentrations was found for adult gyrfalcon back to 1883, although it was not significant. However, only few data were available from the period 1925-1990 making this analysis very uncertain. Comparing Hg concentrations in adult gyrfalcon in the period before 1925 with the period after 1990 showed a significant decrease by a factor of app. 3.5. In both juvenile and adult peregrine from West Greenland dating back to 1879 and 1845, respectively, the Hg concentrations showed an increasing trend, although not found significantly so (Table 5.1; Figure 5.5). Again data from the period 1925-1980 were few and therefore no confirm conclusion should be made. However, comparing Hg concentrations in adult peregrine before 1930 with after 1980 showed a significant increase by a factor 1.6. In juvenile, immature and adult white tailed eagles from West Greenland dating back to 1884, 1884 and 1869, respectively the Hg concentrations again showed an increasing trend (n.s.), as was the case for peregrines. The same lack of data from a longer period in the last century was evident. However, comparing Hg concentrations in adult white tailed eagle before 1940 with after 1979 showed a significant increase by a factor 2.2.

Table 5.1 Summary of the performed linear regressions to detect possible temporal trends of Hg in Gyrfalcons, Perigrine and White tailed eagles from Greenland.

Species	Region	Age group	Not taken into account	Slope	P	N
Gyrfalcon	Greenland	All ages	Region, age and sex	0.00059	0.8200399	
	West Greenland	All ages	Age and sex	0.00260	0.3600337	
	East Greenland	All ages	Age and sex	0.00086	0.9200	62
	West Greenland	Juvenile	Sex	0.00220	0.4600242	
	West Greenland	Immature	Sex	0.04900	0.0180	12
	West Greenland	Adult	Sex	-0.00770	0.1400	74
Perigrine	West Greenland	All	Age and Sex	0.00780	<0.0001	110
	West Greenland	Juvenile	Sex	0.00450	0.0620	64
	West Greenland	Adult	Sex	0.00370	0.0560	44
White tailed eagle	West Greenland	Juvenile	Region and Sex	0.00160	0.6200	40
	West Greenland	Immature	Region and Sex	0.00900	0.0290	34
	West Greenland	Adult	Region and Sex	0.00880	0.0015	48

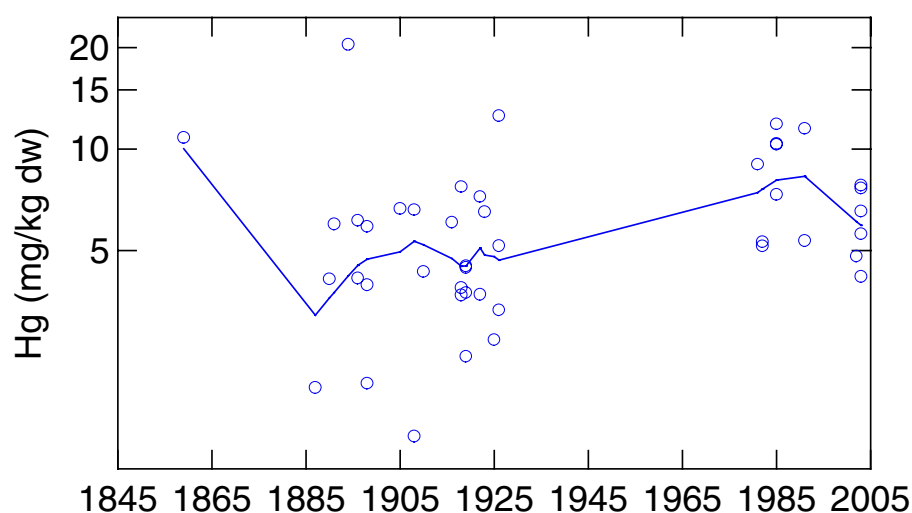


Figure 5.5 An example of the mercury in adult peregrine feather from West Greenland in 1859 to 2003. Lines are calculated using LOWEST smoother with a smoothing span of 30%.

5.4 Conclusion

- A substantial decrease of Hg concentrations in teeth of polar bears since 1960 was found. The decreasing trend in polar bear teeth was most obvious for East Greenland (234 times). The recent 22 years trend in Northwest Greenland was obscured by a lack of samples.
- Hg concentrations in hair of polar bears showed a decrease especially during the last 30 years in East Greenland. However, the decrease (1.5% per year) was much lesser than the decrease found in polar bear teeth. Concentrations in Northwest Greenland bears may be increasing.

- Hg concentrations in hair of polar bears sampled in East Greenland during 1999-2001 was 8.3 times higher than baseline levels in West Greenland obtained from 1300 AD. However, the level was 71.3 times lower than the maximum level in the period 1905-14.
- Mercury concentrations in feathers of gyrfalcon, peregrine and white-tailed eagle were significantly lower in juvenile than in older birds.
- Regional comparisons revealed small differences in Hg concentrations in feather between regions.
- Of 12 trend analyses performed, 11 analyses showed increasing trend, however, only 4 were found to be significant (gyrfalcon, West Greenland, immature – peregrine, West Greenland, all birds – White-tailed eagle, West Greenland, immature – White-tailed eagle, West Greenland, adult). The increase of these time series ranged between 0.008 mg/kg dw per year to 0.05 mg/kg dw per year.

6 Overall conclusion

Atmospheric flux

The first flux measurements of RGM in the atmosphere are presented together with flux measurements of GEM. The results are applied in a new parameterisation of DEHM and the load of atmospheric mercury to the Arctic is estimated. About 200 tons/year is deposited to the surface north of polar circle?

Mercury in marine sediments

Studies of marine sediments indicate that the mercury concentration has doubled since pre-industrial times.

Pelagic food web

A clear bio-magnification of mercury was detected through the food web. However, the mercury concentration in plankton could not be correlated with the timing of the depletion of mercury from the atmosphere. A very small proportion of the total mercury was bound in the biota.

Temporal trends at high trophic levels

The temporal trend and geographical variation of the mercury content in polar bears and birds of prey were investigated. A substantial decrease of the content of mercury in the teeth of polar bears was observed. This trend was most obvious for polar bears from East Greenland. A lack of samples from the last 22 years in Northwest Greenland makes conclusions from this period inconclusive. The time trend of mercury in hair of polar bears was less pronounced. The hair samples showed an increase until 1950 after which a decrease was detected in East Greenland. In Northwest Greenland an increase was detected in hair samples from the 1990's as found in the last half of the 20'th century for most birds of prey comparisons from West Greenland.

In general the Hg concentrations of birds of prey covered a broad range even though they were divided into age groups. This may reflect differences in the individual ages of the animals and differences in feeding preferences. However of the 12 listed regression lines 11 showed a positive slope. Of these only 4 were found to be significant. The general increase of Hg in birds from West Greenland is in concordance with various time trends findings from the Central Canadian Arctic.

Overall conclusion

Studies of peat bogs, marine sediments and polar bears indicate that the mercury concentration in the environment has increased from pre-industrial times to about 1950, after which mercury concentration decreases in some regions and media. However, most of the high trophic comparisons from West Greenland show a tendency for an increase. This shows that different sources and processes exist in East and West Greenland. The different trends illustrate that there is no simple relationship between mercury exposure as measured as deposition from the atmosphere and levels found in marine ecosystem.

The present joint effort from different disciplines aiming at understanding the link between transport, precipitation and bioaccumulation in the Arctic environment shows that such a model is not easily established. Hopefully, continued efforts will one day enable us to

predict future trends and effects on humans and exposed target species.

However, at present this connection is not established. We need to carry out joint campaigns to study the possible connection between the atmospheric input during AMDEs, the pelagic food chain and the transfer to higher trophic levels.

7 Recommendations

Background

We have gained enough information from the conducted subprojects to make a first generation however not complete model that links emissions at mid-latitudes, atmospheric transport and atmospheric chemical conversion, deposition, washout, bio-uptake and bio-accumulation to final effects. The model will not be complete as stated above but it will make it easier to address the main uncertainties of the system illustrated in the front picture of this report.

The present project has to a large extent benefited from existing expertise and strategies. Thus atmospheric measurements were carried out in Alaska, in international co-operation. Similarly biological studies were made where knowledge of the biological system was already present. However this attempt to optimise the output of the study was to some extent counteracted by the different locations of the various subprojects.

Atmosphere

The central question is what is the mass balance for atmospheric mercury on an annual basis. Future monitoring should apply the new more cost efficient methods developed in FOMA and be carried out on an annual basis.

Melting snow and ice

The input of mercury to the marine system from snow and ice has to be determined, as no such data have yet been obtained from Greenland.

The food web

A key question for future investigations is how the mercury actually enters the pelagic food web. The high concentration of mercury associated with the fine particle fraction $< 0.45 \mu\text{m}$ indicates that the mercury is not taken up directly by the pelagic grazers together with the phytoplankton but rather enters the food web through bacterial activity and the microbial food web. The transfer of mercury in the marine ecosystems appears to be complex and therefore more recent samples are needed. Also bioaccumulation is controlled by factors not taken into account in this study.

The connection between the mercury load in the lower trophic levels and the Arctic apex carnivores has to be established. This might be done by conducting a food chain study combining the mercury load of key ecological species with their fatty acid and stable isotope profiles indicating their trophic level.

Continued time trend

Short-term trend studies on soft tissues are on-going. But the long-term time trend series of mercury in polar bear hair and teeth has to be explained by conducting sampling and analysis of recent material from the Northwest Greenland that is presently missing.

Overall recommendation

Large uncertainties on the inter-compartment fluxes still exist and future activities should be organised as joint campaigns including a more holistic approach with focus on periods and target areas with AMDEs.

Model calculation

Based on the obtained knowledge a model has to be developed that can explain the observed levels and inter compartment transport patterns. Finally scenario calculations have to be performed to demonstrate the sensitivity of the model and the system towards changes in climate, emissions and the food web.

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9 References

AMAP (2003) AMAP Assesment 2002: human health in the Arctic. Arctic Monitoring and Assessment Programme (AMA), Oslo, Norway xiv +137p.

Appleby, P.G. and Oldfield, F. (1978) The calculation of ^{210}Pb dates assuming a constant rate of supply of unsupported ^{210}Pb to the sediment. *Catena*, 5:1-8.

Appelquist, H., Jensen, K.O., Sevel, T. and Hammer, C. (1978) "Mercury in the Greenland Ice Sheet" *Nature*, Vol. 273, No 5664, pp. 657-659, June 22.

Ariya, A. P.; Niki, H.; Harris, G. W.; Anlauf, K. G.; Worthy, D.E. J. (1999) *Atmos. Environ.* 33, 931.

Barkay T, Miller SM, Summers AO. FEMS Microbiol Rev. 2003 (2-3):355-84. Review.

Bayens, W., Ebinghaus, R. and Vasiliev, O. (1996) *Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances* Proceedings of the NATO Advanced Research Workshop on Regional and Global Mercury Cycles: Sources, Fluxes and Mass Balances Novosibirsk, Russia July 10-14, 1995. Kluwer Academic Publishers The Netherlands ISBN 0-7923-4314-X.

Born, E.W., A. Renzoni & R. Dietz 1991. Total mercury in hair of polar bears (*Ursus maritimus*) from Greenland and Svalbard. *Polar Research* 9(2): 113-120.

Benoit, J.M., Fitzgerald, W.F. and Damman, A.W.H. (1994) Historical atmospheric mercury deposition in the mid-continental U.S. as recorded in an ombrotropic peat bog, in C.J. Watras and J.W. Huckabee (eds), *Mercury Pollution: Integration and Synthesis*, Lewis Publishers, Ann Arbor, Michigan, pp187-202. Cited from Bayens et al. (1996) p34

Braune B, Outridge P, Wilson S, Bignert A and Riget FF. (2003) in AMAP, 2003, AMAP Assesment 2002: Heavy Metals in the Arctic. Chapter 5: Temporal Trends. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway. (In press).

Chen, Q., Nielsen, S.P. and Aarkrog, A. (1989) Preparation of thin alpha sources by electrospraying for efficiency calibration purposes. *J. Radioanal. Nucl. Chem, Letters* 135, 2, 117-123.

Cossa, D. Coquery, M. and Martin, J.-M. (1993) Mercury in the Lena and Laptev Sea. Third Intern. Symposium on "Model estuaries: the Arctic estuaries and adjacent coastal seas. Biogeochemical processes and interactions with global change". 19-25 April 1993. Sverdlovsk, Russia. Cited from Bayens et al. (1996) p 235

Christensen, J.H. Brandt, J. Frohn, L.M. and Skov, H. (2003) "Modelling of mercury with the Danish Eulerian Hemispheric Model" *Atm. Chem. Phys.* vol. 3, 3525-3541.

Clarkson TW, Magos L, Myers GJ. (2003) The toxicology of mercury - current exposures and clinical manifestations. *N Engl J Med.* 349:1731-7.

Derome J and Fairbrother A. (2003) in **AMAP, 2003**, AMAP Assessment 2002: Heavy Metals in the Arctic. Chapter 6: Biological Effects. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway. (In press)

Dietz, R., Riget, F. and Johansen, P. (1996) Lead, cadmium, mercury and selenium in Greenland marine animals. *Sci. Total Environ.* 186: 67-93

Dietz, R., F. Riget, M.T. Olsen, C. Sonne, E. Born, Philippe Granjean, M. Kirkegaard, G. Asmund, Hans Baagøe in prep 2004a. Time trend of Hg in Greenland Polar bear teeth and hair. A 150 year survey of Hg exposure in an Arctic top predator due to anthropogenic long range transport. Technical report National Environmental Research Institute, Ministry of the Environment. Denmark.

Dietz, R., F. Riget, M.T. Olsen, David Boertman, C. Sonne, M. Kirkegaard, G. Asmund, K. Falk, J. Fjeldsaa, C. Egevang, F. Wille In prep 2004b. Time trend of Hg in feathers of selected Greenland birds of prey. A 150 year survey for long range transport of anthropogenic Hg exposure in Gyrfalcon, Peregrine and White-tailed eagle. Technical report National Environmental Research Institute, Ministry of the Environment Denmark.

Douglas, T.A. and Sturm, M. (2004) *Atm. Env.* 38, 805-820.

Ebinghaus, R. Kock, H.H. Schmolke, S.R. (2001) *Fres. Jour. Anal. Chem.* 371, 806-815

Evans, D.R. (1986) Sources of mercury contamination in the sediments of small headwater lakes in south-central Ontario, Canada, *Arch. Envir. Contam. Toxicol.* 15, 505-512.

Fitzgerald, W.F. and Mason, R.P. (1995) The global Mercury Cycle: Oceanic and Anthropogenic Aspects. In Bayens et al. (1996) p85-108

Gobeil, C. and Cossa, D. (1993) Mercury in sediment pore Water in the Laurentian Trough. *Can. J. Fish. Aquat. Sci.* 50, 1794-1800.

Gobeil and McDonald (1997) Unpublished. Mailed to the authors for inclusion in the AMAP international assessment report. Now published in A. Nilsson: Arctic Pollution Issue: A State of the Arctic Environment Report ISBN 82-7655-060-6 Arctic Monitoring and Assessment Programme, 1997 AMAP; P.O. Boks 8100 Dep., N-0032 Oslo, Norway p 107

Goodsite, M.E. Plane, J.M. and Skov, H. (2004) A theoretical study of the oxidation of Hg^0 to HgBr_2 in the troposphere. *ES&T*. vol 38, 1772-6.

Grandjean, P. Weihe, P. White, R.F and Debes, F. (1998) *Env. Res. Sec A*. 77, 165-172.

Grell, G. A., Dudhia J. and Stauffer D. R., *A Description of the Fifth-Generation Penn State/NCAR Mesoscale Model (MM5)*. NCAR/TN-398+STR. NCAR Technical Note. June 1995. Mesoscale and Microscale Meteorology Division. National Center for Atmospheric Research. Boulder, Colorado, 1995, pp. 122.

Hansen JC, and G Asmund. Trace Elements in Historic Greenlandic Hairsamples.in: *Mummies in a New Millenium* . Proc. 4th World Congress on Mummy Studies, Nuuk, Greenland Sept 4-10, 2001. Lynnerup N, Andreasen C, and Berglund J.eds. Greenland National Museum and Archives and Danish Polar Center, 69-72; 2003.

Hansen JC, Toribara TY, Muhs Ann G. (1989) *Meddr. Grønland, Man & Soc.* 12:161-167.

Hansen, L.H. & Sørensen, S.J. (2000) *FEMS Microbiology Letters* 193, 123-127.

Hansen, T.S. (2003) *Geochimica et Cosmochimica Acta.* 67, (21), 3991-4011

Hansen, J.C., Kromann, N., Wulf,H.C. and Albøge, K. (1984) Selenium and its interrelation with mercury in Wholeblood and hair in East Greenlandic population. *The Science of the total Environment*, 38 p33-40

Heidam, N.Z., Christensen, J.H., Skov, H., Wählin, P. (2004) Monitoring and modelling of the atmospheric Environment in Greenland. A review *J. of The Total Env.* vol. 331 No. 1-3, 5-28.

Heit, M., Tan, Y., Klusek, C. and Gurke, J.C. (1981) Anthropogenic trace elements and polycyclic aromatic hydrocarbon levels in sediment cores from two lakes in Adirondack acid lake region. *Water Air Soil Pollut.* 15, 441-464

Hylander L.D. and Meili, M. (2003) *STOTEN.* 304, 13-27.

Johansen, P. Pars, T. and Bjerregaard P. (2000) *STOTEN* 245, 1-3, 187-194.

Lin C-J. and Pehkonen, S.O. (1999) *Atm. Envir.* 333, 2067-2070.

Lindberg, S.E. Brooks, S. C-J. Lin, C-J. Scott, K.J. Landis, M.S. Stevens R.K. Goodsite, M. and Richter, A. (2002) *E. S.& T.* 36, 1245-1256.

Lockhart,W.L., P. Wilkinsom, R.Hunt and R.Wageman (1995) Mercury in lake and marine sediments from northern Canada. Proceedings of 1995 canadian network workshop <http://www.cciw.ca/ema...s/mercury95/part12.html>.

- Lockhart, W.L., Wilkinson, P., Billeck, B.N., Hunt, R.V., Wagemann, R., and Brunskill, G.J. (1996)** Water Air Soil Pollut. **80**, 603-610.
- Loring, D. H. and G. Asmund (1996)** Geochemical factors controlling accumulation of major and trace elements in Greenland coastal and fjord systems. *Environmental Geology* **28** (1) Juli 1996.
- Mason, R.P., Fitzgerald, W.F., and Morel, F.M.M. (1994)** The biochemical cycling of elemental mercury: Anthropogenic influences, *Geochimica et Cosmochimica Acta* **58**, 3191-3198.
- Mason, R.P. and Fitzgerald, W.F. (1996)** Sources, sinks and biochemical cycling in the ocean. In Bayens et al. (1996).
- McMurtry, G., Brill, R., Siegel, B.Z., Siegel, S.M., (1979)** Antarctic mercury distribution in comparison with Hawaii and Iceland. *US Journal of Antarctic Science* **14**, 206-209.
- Nielsen, S.P. and Asmund, G. (1998)** Lead-210 dating of sediment cores from Greenland. Risø-R-1056(EN). Risø National Laboratory, Roskilde Denmark. ISBN 87-550-2397-5 ISSN 0106-2840.
- Nielsen, S.P. and Dahlgaard, H. (1998)** Radionuclides in sediment cores from Thule, Greenland, 1991. In: Proc. Seminar on Dating of Sediments and Determination of Sedimentation Rate, Ed. E. Ilus, Helsinki 2-3 April 1997, STUK-A145, Radiation and Nuclear Safety Authority, Helsinki.
- Norton, S.A., Dillon, P.J., Evans, D.R., Mierle, G. and Kahl, J.S. (1990)** The history of atmospheric deposition of Cd, Hg, and Pb in North America: evidence from lake and peat bog sediments, in *Acidic Precipitation*, vol.3 Springer-Verlag, Berlin, pp73. Cited from Bayens et al. (1996) p 34.
- Nriagu, J.O. (1989)** A global Assessment of natural sources of atmospheric trace metals. *Nature* **338**, 47-49.
- Overgaard Nielsen, C. and Dietz, R. (1989)** Heavy metals in Greenland Seabirds *Meddelelser om Grønland, Bioscience* **29**. ISSN 0106.1054 ISBN 87-17-05957-7.
- Outridge, P. M., R.D. Evans, Wagemann, R., and Stewart, R. E. A. (1997)** Historical trends of heavy metals and stable lead isotopes in beluga (*Delphinapterus leucas*) and walrus (*Odobenus rosmarus rosmarus*) in the Canadian Arctic. *Science of the Total Environment* **203**: 209-219.
- Outridge, P. M., K.A. Hobson, McNeely, R., and Dyke, A. (2002)** A comparison of modern and preindustrial levels of mercury in the teeth of beluga in the Mackenzie Delta, Northwest Territories, and walrus at Igloodik, Nunavut, Canada. *Arctic* **55**: 123-132.
- Pacyna E.G. and Pacyna J.M. (2002)** *Water, Air and Soil Pollution*. **137**, 149-165.

Pal, B and Ariya, A. (2004) Studies of ozone initiated reactions of gaseous mercury: kinetics, product studies, and atmospheric implications. *Phys. Chem. Chem Phys.* 6, 572-579.

Petersen, G. Munthe, J. Pleijel, K. Bloxam, R. and Vinod Kumar, A. (1998) *Atm. Env.* 32, 829-843.

Pheiffer Madsen, P. (1981). Accumulation of heavy metals determined by ²¹⁰Pb dating: Experience from a marsh area in Ho Bay. Rapp. P.-v. Réun. Cons. Int. Explor. Mer, 181: 59-73.

Rada, R.G., Wiener, J.G., Winfrey, M.R. and Powell, D.E. (1989) Recent increases in atmospheric deposition of mercury to North Central Wisconsin lakes inferred from sediment analyses, *Arch. Envir. Contam. Toxicol.* 18:175-181.

Richter, A. (2002) *E. S. & T.* 36, 1245-1256. 245, 1-3.

Riget, F.F., Dietz, R. and Johansen, P. (1997) Zinc, cadmium, mercury and selenium in Greenland fish. *Meddelelser om Grønland, Bioscience* 48 ISSN 0106-1054 ISBN 87-90369-17-3.

Riget, F.F., Dietz, R. *Sci. Total Environ* in press 2004.

Risgaard-Petersen N, Nielsen LP, Rysgaard S, Dalsgaard T, Meyer RL (2003) Application of the isotope technique in sediments where anammox and denitrification coexist *Limn Oceanogr Met* 1:63-73.

Robbins, J.A. (1978) Geochemical and geophysical applications of radioactive lead. In: J.O. Nriagu (ed.), *Biogeochemistry of Lead in the Environment*. Elsevier Scientific, Amsterdam, 285-393.

Rysgaard S, Glud RN, Risgaard-Petersen N, Dalsgaard T. (2004) Denitrification and anammox activity in Arctic marine sediments *Limn Oceanogr.* 49:1493-1502.

Schroeder, W.H., Anlauf, K.G., Barrie, L.Y., Lu, A., Schneeberger, D.R. and Berg, T. (1998) *Nature.* 394, 331-332.

Skov, H. Christensen, J. Goodsite, M.E. Heidam, N.Z. Jensen, B. Wählin, P. and Geernaert, G. (2004) "The fate of elemental mercury in Arctic during atmospheric mercury depletion episodes and the load of atmospheric mercury to Arctic" *ES & T.* vol 38, 2373-2382.

Skov, H. Brooks, S. Christensen, C. Goodsite, M.E. Jensen, M. Larsen, M.R.B. Christiansen, K.Hansen, J.B. Dagaard, B. and Lohse, C. (2004a) Fate of Mercury in the Arctic: Sub-project Atmosphere. Report under preparation.

Smirnitski (1993) Cited from Bayens et al. (1996) p 235.

Somer, E. and Appelquist, H. (1974) "Changes and Differences in Mercury Level in the Baltic and Kattegat compared to the North Atlantic using *Uria Sp.* (Guillemot Sp) and *Cephus Grylle* (Black Guillemot) as Indicators. In The ninth conference of the Baltic Oceanographers, Kiel, 17-20 April.

Spicer, C. W.; Chapman, E. G.; Finlayson-Pitts, B. J.; Plastringe, R. A.; Hubbe, J. M.; Fast, J. D.; Berkowitz, C. M. (1998) Nature 394.

Swain, E.B., Engstrom, D.R., Brigham, M.E., Henning, T.A. and Brezonik, P.L. (1992) Increasing rates of atmospheric mercury deposition in midcontinental North America, Science 257, 784-787. Cited from Bayens et al. (1996)p 34.

Tolonen, K. and Jaakola, T. (1983) History of Lake acidification and air pollution studied on sediments in South Finland, Ann Bot. Fennici 20 57-78. Cited from Bayens et al. (1996)p 34.

Van Dalen, M. and Nolting, R.F. (1992). Spoor-en hoofdelementen in sediment en poriewater van het Lena-estuarium en de Laptevzee. Nederlands Institute for Sea Research. Series Data Reports. Nioz Data-Rapport 1992-5, Texel, The Netherlands. Cited from Bayens et al. (1996)p 235.

Wheatley, B., and Wheatley, M. (1988) Methylmercury in the Canadian arctic environment past and present - natural or industrial? Arctic Medical Research 47, Supplement 1: 163-167.

WHO (2000) http://www.who.dk/air/Activities/20020620_1

Zreda-Gostynska, G., P. R. Kyle, D. Finnegan, K. M. Prestbo (1997) Volcanic gas emissions from Mount Erebus and their impact on the Antarctic environment, J. Geophys. Res., 102(B7), 15039-15056, 10.1029/97JB00155.

National Environmental Research Institute

The National Environmental Research Institute, NERI, is a research institute of the Ministry of the Environment. In Danish, NERI is called *Danmarks Miljøundersøgelser (DMU)*.

NERI's tasks are primarily to conduct research, collect data, and give advice on problems related to the environment and nature.

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Publications:

NERI publishes professional reports, technical instructions, and the annual report. A R&D projects' catalogue is available in an electronic version on the World Wide Web.

Included in the annual report is a list of the publications from the current year.

Faglige rapporter fra DMU/NERI Technical Reports

2002

- Nr. 401: Dansk tilpasning til et ændret klima. Af Fenger, J. & Frich, P. 36 s. (elektronisk)
- Nr. 402: Persistent Organic Pollutants in Soil, Sludge and Sediment. A Multianalytical Field Study of Selected Organic Chlorinated and Brominated Compounds. By Vikelsøe et al. 96 pp. (electronic)
- Nr. 403: Vingeindsamling fra jagtsæsonen 2001/02 i Danmark. Wing Survey from the 2001/02 hunting season in Denmark. Af Clausager, I. 62 s., 50,00 kr.
- Nr. 404: Analytical Chemical Control of Phtalates in Toys. Analytical Chemical Control of Chemical Substances and Products. By Rastogi, S.C., Jensen, G.H. & Worsøe, I.M. 25 pp. (electronic)
- Nr. 405: Indikatorer for Bæredygtig Transport – oplæg til indhold og strategi. Af Gudmundsen, H. 112 s., 100,00 kr.
- Nr. 406: Det landsdækkende luftkvalitetsmåleprogram (LMP). Årsrapport for 2001. Af Kemp, K. & Palmgren, F. 32 s. (elektronisk)
- Nr. 407: Air Quality Monitoring Programme. Annual Summary for 2000. By Kemp, K. & Palmgren, F. 32 pp. (electronic)
- Nr. 408: Blykontaminering af havfugle i Grønland fra jagt med blyhagl. Af Johansen, P., Asmund, G. & Riaget, F. 31 s. (elektronisk)
- Nr. 409: The State of the Environment in Denmark 2001. By Bach, H., Christensen, N. & Kristensen, P. (eds). 368 pp., 200,00 DKK
- Nr. 410: Biodiversity in Glyphosate Tolerant Fodder Beet Fields. Timing of Herbicide Application. By Strandberg, B. & Bruus Pedersen, M. 36 pp. (electronic)
- Nr. 411: Satellite Tracking of Humpback Whales in West Greenland. By Dietz, R. et al. 38 pp. (electronic)
- Nr. 412: Control of Pesticides 2001. Chemical Substances and Chemical Preparations. By Krongaard, T. Petersen, K.K. & Christoffersen, C. 28 pp. (electronic)
- Nr. 413: Vegetation i farvandet omkring Fyn 2001. Af Rasmussen, M.B. 138 s. (elektronisk)
- Nr. 414: Projection Models 2010. Danish Emissions of SO₂, NO_x, NMVOC and NH₃. By Illerup, J.B. et al. 194 pp., 100,00 DKK.
- Nr. 415: Potential Environmental Impacts of Soil Spills in Greenland. An Assessment of Information Status and Research Needs. By Mosbech, A. (ed.) 116 pp. (electronic)
- Nr. 416: Ilt- og næringsstoffluxmodel for Århus Bugt og Mariager Fjord. Modelopsætning. Af Fossing, H. et al. 72 s., 100,00 kr.
- Nr. 417: Ilt- og næringsstoffluxmodel for Århus Bugt og Mariager Fjord. Modelopsætning og scenarier. Af Fossing, H. et al. 178 s. (elektronisk)
- Nr. 418: Atmosfærisk deposition 2001. NOVA 2003. Af Ellermann, T. (elektronisk)
- Nr. 419: Marine områder 2001 - Miljøtilstand og udvikling. NOVA 2003. Af Ærtebjerg, G. (red.) (elektronisk)
- Nr. 420: Landovervågningsoplande 2001. NOVA 2003. Af Bøgestrand, J. (elektronisk)
- Nr. 421: Søer 2001. NOVA 2003. Af Jensen, J.P. (elektronisk)
- Nr. 422: Vandløb og kilder 2001. NOVA 2003. Af Bøgestrand, J. (elektronisk)
- Nr. 423: Vandmiljø 2002. Tilstand og udvikling - faglig sammenfatning. Af Andersen, J.M. et al. 56 s., 100,00 kr.
- Nr. 424: Burden Sharing in the Context of Global Climate Change. A North-South Perspective. By Ringius, L., Frederiksen, P. & Birr-Pedersen, K. 90 pp. (electronic)
- Nr. 425: Interkalibrering af marine målemetoder 2002. Af Stæhr, P.A. et al. 88 s. (elektronisk)
- Nr. 426: Statistisk optimering af monitoringsprogrammer på miljøområdet. Eksempler fra NOVA-2003. Af Larsen, S.E., Jensen, C. & Carstensen, J. 195 s. (elektronisk)
- Nr. 427: Air Quality Monitoring Programme. Annual Summary for 2001. By Kemp, K. & Palmgren, F. 32 pp. (electronic)

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- Nr. 428: Vildtbestande, jagt og jagttider i Danmark 2002. En biologisk vurdering af jagtens bæredygtighed som grundlag for jagttidsrevisionen 2003. Af Bregnballe, T. et al. 227 s. (elektronisk)
- Nr. 429: Movements of Seals from Rødsand Seal Sanctuary Monitored by Satellite Telemetry. Relative Importance of the Nysted Offshore Wind Farm Area to the Seals. By Dietz, R. et al. 44 pp. (electronic)
- Nr. 430: Undersøgelse af miljøfremmede stoffer i gylle. Af Schwærter, R.C. & Grant, R. 60 s. (elektronisk)
- Nr. 432: Metoder til miljøkonsekvensvurdering af økonomisk politik. Møller, F. 65 s. (elektronisk).

This report is the final reporting of the project FONA, funded by the Danish Environmental Protection Agency with means from the MIKA/DANCEA funds for Environmental Support to the Arctic Region. The aim of the project is to study the inter-compartment mercury transport chain in the arctic area. From atmospheric deposition of mercury on sea surfaces to uptake in marine organisms, bio-accumulation, and finally mercury levels in mammals. The studies in the project are focused on the behaviour of mercury during the spring period where special phenomena lead to an enhanced deposition of mercury in the Arctic environment, at a time where the marine ecosystem is particularly active. The studies also include a comprehensive time trend study of mercury in top carnivore species. Each of these studies contributes towards establishing the knowledge necessary to develop a general model for transport and uptake of mercury in the Arctic. The report focus on the surface exchange of mercury, the uptake of abiotic mercury into the biological system, and the bio-accumulation in the first steps of the food web, and the resulting distribution and time trend of mercury in selected animals feeding on various trophic levels.

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