# AMAP Greenland and the Faroe Islands 1997-2001

Vol. 2: The Environment of Greenland

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## Preface

In 1989 a conference on protection of the Arctic environment was held in Rovaniemi with participation of all eight circumpolar countries (Canada, Denmark, Finland, Iceland, Norway, Russia, Sweden and USA). This was the start of the "Rovaniemi" process, continuing with the First Arctic Ministerial Conference in 1991, as an important step in the international cooperation for the protection of the Arctic, leading to the adoption of the Arctic Environmental Protection Strategy (AEPS).

Some of the objectives of the AEPS are:

- to protect the Arctic ecosystems, including humans
- to review regularly the state of the Arctic environment
- to identify, reduce and as a final goal, eliminate pollution.

Different work groups have been formed to implement the AEPS objectives. One of the initiatives is the Arctic Monitoring and Assessment Programme (AMAP).

The Arctic region represents one of the last frontiers of relative pristine nature but also an area vulnerable to pollution. However, results from AMAP's first phase (1994-1996) have shown that pollutants originating from anthropogenic activities at mid-latitudes are transported to the Arctic by atmospheric processes, ocean currents and rivers. Some of these pollutants accumulate in the Arctic environment.

AMAP's responsibilities are to monitor the levels and assess the effects of anthropogenic pollutants in all compartments of the Arctic environment (atmospheric, terrestrial, freshwater and marine environments, and human populations with respect to human health).

The work of AMAP has so far focused on three priority pollutants: persistent organic pollutants (POPs), heavy metals, and radioactivity. Each country has defined its own national implementation plan to meet the AMAP monitoring requirements.

Very few monitoring programmes existed in Greenland, when the international AMAP programme was adopted. To fulfil participation in the international AMAP programme Denmark initiated a national AMAP programme covering all the selected compartments and the priority pollutants in different parts of Greenland and in the Faroe Islands. The national AMAP programme has been funded by the Danish Environmental Protection Agency since 1994 as part of the environmental support program Dancea – Danish Cooperation for Environment in the Arctic.

The results from the first phase of the national AMAP programme were inter alia published in:

"AMAP Greenland 1994-1996" (Environmental Project No. 356, 1997). "AMAP Greenland 1994-1996, Data Report" (Working Report No. 29, 1997).

AMAP's first scientific circumpolar assessment was published in: "AMAP Assessment Report: Arctic Pollution Issues" Oslo 1998.

The present report is one of four containing the results and assessment of data from the second phase (1997-2002) of the national AMAP programme in Greenland and

the Faroe Islands. The four reports are compilations of a number of chapters written by different authors from several institutes. The four volumes are:

Vol. 1: Human Health.

- Vol. 2: The Environment of Greenland.
- Vol. 3: The Environment of the Faroe Islands.

Vol. 4: Data Report.

Besides these reports scientific international AMAP Assessment reports covering the circumpolar region are prepared.

## Introduction

At the Rovaniemi Ministerial meeting in 1991 it was decided to implement a programme to monitor the levels and assess the effects of contaminants in all compartments of the Arctic environment. Accordingly, between 1991 and 1996 the Arctic Monitoring and Assessment Programme, AMAP was designed and implemented as AMAP phase I. The first international assessment report was subsequently published (AMAP 1998). To fulfil the international requirements a specific Greenland AMAP programme was implemented and a Greenland Faroe Islands assessment report was produced (Aarkrog et al. 1997). The accomplishments of AMAP phase I were fully recognized by the Ministers. As such it was determined that work should continue to fill gaps in the current understanding of transport processes, spatial and temporal trends, and possible effects of contaminants, and an AMAP phase II study was initiated.

Substantial new data have been collected during AMAP phase II both in Greenland, on the Faroe Islands and in the other Arctic regions. It was decided to make a second international AMAP assessment report, which will be published in September/October 2002 prior to the Ministerial meeting of the Arctic Council in October 2002. Furthermore, it was decided also to make an assessment of the Greenland and Faroe Islands AMAP data on the background of the studies carried out since AMAP phase I. A series of four reports will be published covering human health studies, environmental studies in Greenland and Faroe Islands, respectively, and the data collected. This report deals with the environmental studies carried out in Greenland during AMAP phase II, and is organized into environmental compartments (atmospheric, terrestrial, fresh water and marine environment). A section deals with so-called other contaminants defined as contaminants of which knowledge of levels in the Greenland environment is scarce because they have not been included in the basic monitoring studies or because the focus on their possible environmental impact is rather recent. One section deals with the effect studies on ringed seals and polar bears. Conclusions and recommandations are described in the individual sections, and summarized in the last section of the report.

The present report and a significant part of the studies described have been funded by the Danish Environmental Protection Agency as part of the environmental support program Dancea – Danish Cooperation for Environment in the Arctic. The authors are solely responsible for all results and conclusions presented in the report, and do not necessary reflect the position of the Danish Environmental Protection Agency.

### 1 Atmospheric environment

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#### 1.1 INTRODUCTION

The atmospheric AMAP Assessment presented below is based on the results from the Danish programme for the Arctic atmosphere, which has been carried out in North Greenland as an interacting combination of field measurements of air pollutant concentrations and model calculations of air pollution transport in the Northern Hemisphere.

The monitoring programme and some selected results are presented in section 1.2. The model system is described in section 1.3, which also holds comparisons between measured and calculated air concentrations. This chapter also presents calculated atmospheric depositions for several pollutants at various locations in Greenland, split into quantified contributions from different and geographically distant source areas. Mercury deposition estimates for the Northern Hemisphere are also presented. In section 1.4 measurement and model data from the period since 1990 are successfully combined to demonstrate that ambient air concentrations in northeastern Greenland have decreased during the last decade. Quantified trends, attributable to emission reductions in distant source areas, are presented for several pollutants.

#### 1.2 Atmospheric Monitoring

#### 1.2.1 Location and instrumentation

The Danish atmospheric monitoring programme has been carried out by the Department of Atmospheric Environment (ATMI) at the National Environmental Research Institute (DMU) since 1990, and as an official AMAP programme since 1994. The monitoring has taken place at Station Nord, a small military air field located in north-eastern Greenland at 81°36' N, 16°40'W, see Figure 1.2.1 (left). The measurements started at the site named 'LW hut' on the map but have since 1995 been performed at the site 'Flyger's Hut', which is located approximately 3 km south of the central complex of buildings, as shown on the map in the Figure 1.2.1 (right). The building is supplied with electricity and heat and serves as the main base for the AMAP Air Monitoring Programme. The location of the AMAP station has been chosen so as to minimise influence from any local air pollution.

The instrumentation at this site consists of a filterpack-sampler operated on a weekly basis. The sampler consists of a sequence of 3 - 4 filters of which the first collects particles. The subsequent filters are specially impregnated to collect various gases, notably  $SO_2$ . The particle filters are analysed for the sulphate-, ammonium- and nitrate- ions,  $SO_4^{2^\circ}$ ,  $NH_4^+$  and  $NO_3^-$  and, by the PIXE method, for a substantial number of elements including several heavy metals. The gas filters also collect

ammonia (if any) and nitric acid,  $NH_3$  and  $HNO_3$  but since the particle phases of these nitrogen components may de-gas from the first filter onto the gas filters only the total sums of particulate and gaseous phases are reported for these nitrogen compounds.

Monitors have been used to carry out measurements with high time resolutions for ozone since 1995 and for gaseous elementary mercury since 1999 where a monitor has been operated from early winter until autumn.

The personnel at Station Nord carry out the daily supervision of the instruments. They also handle all new filters and return exposed samples together with the experimental protocol and diskettes with ozone and mercury data to DMU utilising all available flights.

Maintenance and calibration of the instruments at the field sites have been carried out regularly by the staff from DMU, usually in late winter and in late summer or early autumn/winter. The field visits have also been very useful for exchange of information and experience on instrument field performance between the laboratory staff and the station personnel. At these visits the monitors have usually been taken home for maintenance and substituted with freshly serviced instruments. The quality of measurements with monitors is regularly controlled (at least weekly) by adding standard to the sample inlet.



Figure 1.2. Greenland with the location of Station Nord (left) and the position of the air monitoring site at Station Nord. The regular AMAP site is located at Flygers' hut (right).

#### 1.2.2 Gas and aerosol measurements

The measured concentrations of a number of pollutants are shown for the period 1990 - 2001 in Figures 1.2.2 and 1.2.3. In Figure 1.2.2a the gaseous  $SO_2$  is shown on top of the shaded particulate  $SO_4^{2^2}$  and selected nitrogen compounds are shown in Figure 1.2.2b and 1.2.2c. The persistent patterns of high concentrations in winter and early spring and very low concentrations in summer, described previously (Christensen et al. 2000, 2001) are clearly to be seen for all pollutants. For sulphur in particular the maximum weekly average concentrations in the remote north-eastern Greenland are comparable to the annual mean values around 1.5  $\mu$ g S/m<sup>3</sup> found in rural districts of Denmark.

These recurrent annual cycles from low to high concentrations, separated by 2 decades of magnitude, are ascribed to the seasonal atmospheric circulation patterns characteristic of the High Arctic. In winter the circulation often favours transport into the Arctic from mid-latitudinal regions with prominent pollution sources. In summer, on the other hand, the circulation in the Arctic atmosphere is essentially local and confined within the region with its few and small emissions so the concentrations fall to very low values.



Figure 1.2 a, b, c. Weekly average concentrations through the 1990s of sulphur and nitrogen components. Total concentrations (phase sums) in *figs. a and c* are shown as red dots, and the particulate phases in *figs. a and b* as blue crosses – overlaid by smoothing curves.

The patterns of the gaseous and particulate phases of sulphur differ in that the high concentrations of  $SO_2$  appear episodically early in winter, in contrast to the slower but consistent build-up of particulate bound  $SO_4^{2-2}$  that starts somewhat later.

These patterns are probably related to the different atmospheric characteristics of the two pollutants. The occurrence of the primary pollutant  $SO_2$  is presumably controlled by meteorological switching between periods of atmospheric transport headed

directly at north-east Greenland and periods where the transport is directed elsewhere. The concentration of the secondary  $SO_4^{2-}$  depends of course also on transport from source regions, but more indirectly since it is produced from  $SO_2$  wherever it occurs by fairly slow chemical oxidation processes. These processes are induced and enhanced by increasing solar irradiation but do require time to take effect. This secondary pollutant may therefore be more widespread and, also because of its longer lifetime in the atmosphere, it may arrive at the measuring point from a broader range of directions, hence the delayed and less episodic appearance of  $SO_4^{2-}$ 

Figure 1.2. Weekly average concentrations through the 1990s of heavy metals in aerosols shown as blue crosses– overlaid by smoothing curves.

#### 1.2.3 Elements and heavy metals

The aerosol sampling and measuring of elements at Station Nord by PIXE has now been performed almost continuously for more than 10 years (since August 1990). Both the technique of sampling and the technique of elemental analysis have remained unchanged during this long time period. The results cover the weekly concentrations of a considerable number of elements and this large amount of data can be used to get a better impression of the different sources and of the average yearly cycle of the elements.

The COPREM receptor model has been used to build a data model for the elemental concentrations in the period 1991-2001. All receptor models, including factor analysis, are based on the assumption that the original receptor site concentrations can be adequately explained by a linear combination of contributions from various relevant sources with fixed composition such that

$$x_{ij} \cong \sum_{k} a_{ik} f_{kj} \tag{1.2.1}$$

where  $x_{ij}$  is the measured ambient concentration of the pollutant *i* during sampling occasion *j*. A number of relevant sources *k* are considered significant. The coefficients  $a_{ik}$  represent the constant source profiles, and  $f_{kj}$  represent the strengths of the sources found in the individual samples. Factor analysis is a general method of simplifying the problem in equation 1.2.1 in which the only necessary input is the set of numbers  $x_{ij}$ . The analysis does not give a specific solution, but merely a less complex subspace with still an infinite number of different solutions.

The Constrained Physical Receptor Model (COPREM) relies on the same basic receptor model as factor analysis (equation 1.2.1). The equation is solved by an iterative method to determine the source strengths  $f_{kj}$  and the source profiles  $a_{ik}$  (Wåhlin, 1993). The chi-square statistic

$$\chi^{2} = \sum_{j} \sum_{i} \frac{(x_{ij} - \sum_{k} a_{ik} f_{kj})^{2}}{\sigma_{ij}^{2}}$$
(1.2.2)

measures the total squared distance between the measurements and the model in units of the uncertainties of the data  $\sigma_{ii}$ .

Built-in model constraints exclude non-physical solutions (negative coefficients in the source profiles and negative source strengths), and additional constraints can by means of a form matrix be included to fix profile components in constant ratios, partly or entirely. The chi-square statistic is minimised within the limits imposed by constraints. An initial profile matrix is set up in which the source vectors have the main characteristics of known sources, and the form matrix is set up to maintain these characteristics, and to prevent the profiles from mixing together during the iteration. In this way any a priori knowledge about the character of the sources can be used to achieve a polarised solution as elements can be allowed to enter only in certain source profiles. The COPREM also take into account uncertainties, which is of particular importance for measurements near the detection limit. Chemical compounds, which do not fit into the simple linear model and therefore need special handling, are easily recognised.

At Station Nord the measured concentration data for all PIXE elements except S, Cl and Br can be expressed as combined contributions from only 4 sources. These comprise a crustal source (soil), a marine salt source (sea), a prominent anthropogenic source (combustion), and an additional anthropogenic source (metal) with contributions of the metallic elements Ni, Cu and Zn.

Local sources (*i.e.* anthropogenic emissions from Station Nord itself) are normally negligible. Only very few episodes of substantial local air pollution (caused by waste burning in the summer) has been noticed since the start of aerosol measurements at Station Nord in 1990.

All samples are week samples starting Monday 0:00 UTC and they can therefore be assigned a specific week number in the range 1-53 for every year. The average yearly variation of each element as a function of the week number was calculated by averaging concentrations with the same week number for all years. In this way, a lot of week-to-week scatter in the influx from the different sources is smoothed out, and the gross seasonal variation is more easily observed. The average annual variations of the concentrations of selected PIXE-elements at Station Nord in the years 1991-2001 is shown below in Figure 1.2.4 ordered by their atomic number. In this figure the results of COPREM receptor analysis on source contributions are also shown.



Figure 1.2. Annual elemental concentrations averaged over 1991 – 2001, as a function of week number. The source apportionments according to COPREM are shown for the four main sources. The colours indicate: Soil (green), sea spray (blue), combustion (red) and copper smelters (yellow).

Elements such as Al, Si, and Ti are of almost pure crustal origin, and it can be seen clearly that their seasonal variations are very much the same, and can be fitted with the same soil source time signal with peaks in spring and late summer.

The elements Fe, Mn, V, As and Pb are in this order under increasing influence of the combustion source compared to the soil source. The elements As and Pb in the lower right corner of the figure have almost the same seasonal variation showing the pure combustion time signal with peaks in the winter and almost total absence in the summer, which is typical for *Arctic Haze*. As described earlier the time signal for total-S is a little different, probably due to a longer lifetime of sulphur particles in the atmosphere compared with sulphur dioxide. Sulphur dioxide peaks in the winter, while sulphate/sulphuric acid peaks in the spring (after Polar Sunrise).

The elements Ca, K and Sr are abundant in seawater and in aerosols created by sea spray. The elements, which also have a crustal and a combustion origin, are in this order under increasing influence of the sea source. The sea signal has peaks in the winter half-year showing the influence at Station Nord of ocean storms.

The elements Zn, Ni and Cu have additional winter peaks not found in the common anthropogenic combustion signal. The deviations can be described by an additional anthropogenic source involving particularly high emissions of these metallic elements. The elements are in this order under increasing influence of the metal source.

#### 1.2.4 Ozone and mercury measurements

Mercury is found at high levels in marine animals at many places in the Arctic and North Atlantic Ocean. It has been shown that the present levels of mercury in sea animals have a negative effect also on the health of the local populations, dependent on these animals as food supply (Grandjean et al. 1998).

The lifetime of atmospheric elemental mercury (GEM) (95% of atmospheric mercury) is in general about 1 year (Lin & Pehkonen, 1999). In the Arctic during spring, the lifetime of GEM is significant shorter and GEM is observed to be depleted in less than one day during mercury depletion episodes (MDE), (Schroeder et al. 1998, Lindberg et al. 2002, Skov et al. 2002). GEM is converted to oxidised mercury in the gas phase the socalled reactive gaseous mercury (RGM) that is fast deposited to the ground (Goodsite et al. 2002). Recently MDE's have been observed also in Antarctic (Ebinghaus et al. 2002). MDE occurs at the time where the Arctic ecosystems are extremely active. Therefore it is hypothesised that there is a higher efficiency of bioaccumulation of mercury that would be expected from extrapolating data from mid-latitudes to Arctic and therefore it is very important to get a fully understanding of the processes leading to MDE's. The improved knowledge of the concentrations, deposition and atmospheric processes in the Arctic is intended to lead to better performance of atmospheric chemical transport models and thereby an improved understanding of the source-receptor relationship for atmospheric mercury. At present it is not clear what the benefits are to improved ecosystem quality in the Arctic, if emission reduction strategies are proposed because of the lack of understanding of the processes controlling atmospheric mercury. Only improved model performance and confidence in the calculations will help in the decision making process.

Ozone has been observed to be depleted during spring for nearly ten years and it is well accepted that it is due to photochemical degradation after the polar sunrise. More recently it has been demonstrated that GEM is depleted as well and it is strongly correlated with ozone during MDE (Schroeder et al. 1998) and that the GEM depletion is triggered by solar radiation (Lindberg et al. 2002). However, very little is known about the reaction mechanisms. Several hypotheses have been proposed where Cl and/or Br atoms or ClO and/or BrO are common candidates. In this section, measurements of tropospheric mercury and ozone at Station Nord, Northeast Greenland are presented. The data are treated using basic reaction kinetic theory and physical theory for mixing of gases in the atmosphere.

#### 1.2.4.1 Experimental

The analytical techniques for measuring ozone and GEM have been presented in a previous AMAP report, Christensen et al. (2001), and will only be described shortly here.

Ozone is measured with an UV absorption monitor, Monitorlab 8810, with a detection limit of 1 ppbv and an uncertainty of 3 % for concentrations above 10 ppbv and 6 % for concentrations below 10 ppbv, (all uncertainties are at a 95% confidence interval). GEM is measured by a TEKRAN 2537A mercury analyser where GEM is collected from the sample air on a gold trap from where mercury is thermally desorbed using argon as carrier gas and then analysed with cold vapour atomic fluorescence spectroscopy. The detection limit is 0.1 ng/m<sup>3</sup> and the reproducibility for concentrations above 0.5 ng/m<sup>3</sup> is within 20% on a 95% confidence interval. It is not at present possible to give the combined uncertainty, as the exact identity of the measured mercury is unknown though GEM is determined as the dominant compound

#### 1.2.4.2 Results

The results of ozone and GEM measurements are shown in Figure 1.2.5. It is seen that ozone is rather stable from September/October until the end of February/beginning of March, then a highly perturbed period is occurring where ozone and GEM at about 40 ppb and 1.5 ng/m<sup>3</sup>, respectively, are depleted within hours to 0. They remain at 0 for up to several days until they suddenly rise again. In July the ozone concentration stabilises around a little above 20 ppbv for slowly increase to about 40 ppbv in September/October.



Figure 1.2. Ozone mixing ratios measured from 1999 to 2001 at Station Nord. Gem is measured in the period from 25. September 1999 to 23. August 2000 and again 14. February 2001 to 23. August 2001.

GEM was only measured from February to end of July or to the beginning of August. The measurements were focusing on the description of the highly perturbed period where ozone was depleted. Previously Schroeder et al. (1998) have described that ozone and GEM are highly correlated and this is indeed confirmed from the present data set, see Figure 1.2.6. Data was selected from periods where at least 3 consecutive concentrations were decreasing on both ozone and GEM and where the initial GEM

concentration was above 0.4 ng/m<sup>3</sup>. After the depletion period some very high concentrations of GEM appeared with values up to above 2 ng/m<sup>3</sup>. Similar observations were also observed at Alert (Schroeder et al. 1999) and at Barrow (Lindberg et al. 2002) and they are attributed to reemission of mercury to the atmosphere. The interruption of the time series of GEM at Station Nord makes it difficult to further interpret if reemission is occurring at Station Nord.

A plot of GEM versus ozone at Station Nord is shown in Figure 1.2.6. There is a significant linear correlation (99.9 % significance level) between them. The slope is  $0.034 \pm 0.001 \text{ ng/m}^3/\text{ppbv}$  and the intercept is  $0.023 \pm 0.03 \text{ ng/m}^3$ . The slope is practically identical with the one obtained by Schroeder et al. (1998) at respectively  $0.04 \text{ ng/m}^3/\text{ppbv}$  and  $0.39 \text{ ng/m}^3$  for the slope and the intercept confirming that it is the same process observed leading to MDE at Station Nord and at Alert, Canada.



Figure 1.2. GEM against ozone concentrations at Station Nord including a regression line obtained by classical regression analysis.

#### 1.2.4.3 Discussion Reaction Kinetics

The interpretation of the correlation between ozone and GEM is not simple. The strong correlation indicates that ozone and GEM are dependent on a mutual factor. A direct reaction between ozone and GEM can be ruled out due to the long lifetime of GEM with respect to the present ozone concentrations. Hausmann & Platt et al. (1994) have shown that when ozone is decreased BrO is building up due to the reaction:

$$O_3 + Br \longrightarrow O_2 + BrO \tag{1.2.3}$$

and therefore serious candidates for GEM removal are Br or BrO. However Cl and ClO cannot be ignored as significant Cl removal of organic compounds have been observed during MDE (e.g. Boudries & Bottenheim, 2000) and their importance depend on their reactivity towards GEM.

The lifetime of GEM is observed to be typically about 10 hours during MDE. Hausmann & Platt observed up to 20 pptv of ClO and BrO and thus the resulting rate constants for the reactions can be estimated to be in the order of  $6 \times 10^{-14}$  cm<sup>3</sup> molec<sup>-1</sup> sec<sup>-1</sup>, which is reasonable.

BrO and/or ClO should then react with GEM

$$Hg + BrO \longrightarrow HgO + Br$$
 (1.2.4)

or

$$Hg + ClO \longrightarrow HgO + Cl$$
 (1.2.5)

in competition with other reactions regenerating Cl and Br (ignoring heterogeneous reactions):

$$BrO + BrO \longrightarrow 2Br + O_2 \qquad (1.2.6)^1$$
$$BrO + ClO \longrightarrow Br + ClOO \qquad (1.2.7)^2$$

If BrO is the main responsible for the GEM removal and we write the formation rate of Br from reaction 1.2.4, 1.2.6 and 1.2.7 and assuming steady state for the Br concentration the following equation can be deduced.

$$k_{1,2,3}[O_3] = k_{1,2,4}[Hg] + (k_{1,2,6}[BrO] + k_{1,2,7}[ClO])$$
(1.2.8)

 $k_{1,2x}$  is the reaction rate constant for reaction 1.2.x.

The part in parenthesis has to be negligible compared to  $k_{1,2,4}$ [Hg] in order to explain the strong linear correlation between ozone and GEM with a close to zero intercept observed in Figure 1.2.6. However both  $k_{1,2,4}$  and  $k_{1,2,5}$  are at least a factor 100 larger than  $k_{1,2,4}$  (DeMore et al. 1997) and the concentrations of GEM, CIO and BrO are of the same magnitude, so the part in parenthesis is not negligible. The same considerations are valid if CIO is assumed to represent the main sink for GEM. Therefore the reactions of BrO and CIO with GEM most probably are of negligible importance.

The strong correlation observed in Figure 1.2.6 indicates that ozone and GEM is directly dependent on one another. Therefore the data was analysed assuming relative rate conditions between ozone and GEM. The method is widely used under laboratory conditions where the reaction of interest is running in competition with another reaction where the reaction rate constant is well established. So the system here is:

$$O_3 + X \to product$$
 (1.2.9)

and

$$Hg + X \rightarrow product$$
 (1.2.10)

where X is either Br or Cl.

<sup>&</sup>lt;sup>1</sup> Only the dominant reaction product is shown

<sup>&</sup>lt;sup>2</sup> Other products are formed in the reaction as OCIO and BrCl where the last product photolysis fast to Cl and Br

The kinetic equations for reaction 1.2.9 and 1.2.10 are:

$$\int_{[O_3]_0}^{[O_3]} d\ln[O_3] = -k_{1,2,9} \int_0^t [X] dt \qquad (1.2.11)$$

and

$$\int_{[GEM]_{b}}^{[GEM]} d\ln[GEM] = -k_{1,2,10} \int_{0}^{t} [X] dt \qquad (1.2.12)$$

respectively.

Dividing equation 1.2.11 with 1.2.12 the relative rate expression is obtained.

$$\ln\left(\frac{[GEM]_0}{[GEM]_t}\right) = \frac{k_{1,2,10}}{k_{1,2,9}} \bullet \ln\left(\frac{[O_3]_0}{[O_3]_t}\right)$$
(1.2.13)

A plot of  $\ln([GEM]_0/[GEM]_t$  against  $\ln([O_3]_0/[O_3]_t$  should then give a straight line with intercept 0 and where the slope is equal to  $k_{1,2,10}/k_{1,2,9}$ . Figure 1.2.7 shows such a plot using the data from Station Nord where data has been selected for periods where the initial concentration of GEM was above 0.4 ng/m<sup>3</sup> and where three consecutive measurements of both ozone and GEM are decreasing. All measurement included were for periods with 24 hour daylight.



Figure 1.2. The natural logarithm to the relative concentrations of GEM and ozone during Depletion episodes in 2000 and 2001. The regression analysis is carried by orthogonal regression analysis. Only data are included where three consecutive measurements of both ozone and GEM are decreasing and where the initial concentration of GEM is larger than 0.4 ng/m<sup>3</sup>.

In fact there is a strong linear correlation (>99.9% significance). A straight line is obtained by orthogonal regression with intercept close to zero as expected from equation 1.2.13. The slope is 1.437 and significantly different from 1. A slope equal to one is expected if the correlation was only caused by dilution due to mixing of air masses. So first of all Figure 1.2.7 proves that ozone and GEM have a mutual dependence that cannot be explained solely by meteorology.

The rate constant of ozone with Br and Cl atoms is very well known due to their importance in the depletion of stratospheric ozone depletion (DeMore et al. 1997). Table 1.2.1 shows the calculated rate constants for GEM assuming respectively Cl reaction and Br reaction together. In the Table is also listed available data from the literature.

TABLE 1.2. THE CALCULATED REACTION RATE CONSTANTS FOR THE REACTIONS BETWEEN GEM AND BR AND CL BASED ON FIGURE 1.2.7 AND THE REACTION RATE OF CL AND BR WITH OZONE FROM DEMORE ET AL. 1997. THE RATE CONSTANTS OBTAINED IN THIS STUDY ARE CALCULATED USING A REACTION RATE FOR OZONE AT 233 K AND 263 TO BE REPRESENTATIVE FOR THE CONDITIONS IN ARCTIC.

Reactant	10 <sup>12</sup> cm <sup>3</sup> molec <sup>-1</sup> sec <sup>-1</sup>	Kelvin	Reference
Br	0.8	233	This Study
Br	1.2	263	This study
Br	0.2 ± 0.08	295	Sommar et al. (2001)
Br	0.3*	120-170	Greig et al. (1970)
Br	3.2 ± 0.4	298	Ariya et al. (2002)
Cl	14	233	This Study
Cl	16	263	This study
Cl	15*	120-170	Horne et al. (1968)
Cl	10 ± 4	298	Ariya et al. (2002)

\*Correct within a factor 3

The reactions of halogens with Hg are independent of temperature (Horne et al. 1968, Grieg et al. 1970) and therefore results of the various studies should be directly comparable. The ozone reactions with halogen atoms are temperature dependent and the rate constants of Hg are calculated at 233 K and 263 K representative for the conditions in Arctic during mercury depletion. There are very few studies of the rate constant of Hg with Cl and Br. Horne et al. and Grieg et al. indicate that the results from their studies are correct within a factor 3.

In case of Br the reaction rate constant there is a factor 16 between the studies of Sommar et al. and Ariya et al. and the value obtained here is in between those values. Both groups used the relative rate technique in their study and more studies are needed in order to establish the correct reaction rate constant. For the reaction between Cl and Hg there appears to be an excellent agreement between the laboratory study of Ariya et al. and the results obtained in the field experiment.

In general the half-life of GEM at Station Nord is about 10 hours during MDE. Using rate constants of Ariya et al. (the largest values for the reaction rate constants) this corresponds to a concentration of either Br or Cl at 1 pptv and 0.1 pptv, respectively. Most laboratories report Cl concentrations in Arctic during MDE from 0.001 to 0.004 ppt (e.g. Boudries & Bottenheim, 2000, Röckmann et al. 1999, Jobson et al. 1994) at least a factor of 100 lower concentration than needed for the observed GEM depletion. Br in the ppt level is reported by many authors (e.g. Boudries & Bottenheim, 2000, Tuckermann et al. 1997, Jobson et al. 1994). Therefore it can be concluded that the direct reaction of Cl with GEM is not an important removal process during mercury depletion episodes but that Br is a serious candidate for the depletion. Based on the results presented above the most important reactant for GEM removal is Br. However, there are still large uncertainties involved before a definitive answer can be given about the mechanisms of MDE's. For example there is as previously mentioned a factor 14 difference between the results obtained in laboratory studies for the reaction of Hg with Br. To the knowledge of the authors there is not any study of the reaction rates constant of the reactions between Hg and ClO or BrO. The lack of temperature dependence and an eventual effect of pressure need to be documented as well.

#### 1.2.4.4 Atmospheric implications

The measured GEM at Station Nord confirms atmospheric mercury as a global pollutant and that mercury depletion events (MDE's) are phenomena connected to all coastal areas in Arctic during Arctic Spring. The MDE occurs in parallel with ozone depletion each spring in Arctic.

Strong indication for the reaction between Br and Hg as responsible for MDE's in Arctic is found and therefore model calculation of atmospheric mercury has to include this reaction in the reaction scheme. Organobromides, sea ice and sea salt have been suggested to be sources of Br in the arctic troposphere. It is now generally accepted that releases from sea ice and sea spray are the main sources (Platt sand Moortgat, 1999 and references in there). Therefore model calculations of MDE should be restricted to air masses influence by marine air.

The reaction with Br with GEM leads to a monovalent mercury radical species. The further fate of this species is at present unknown but evidence is found for that it reacts further to form reactive gaseous mercury (Lindberg et al. 2002) which various divalent mercury compounds. The identity of RGM is at present unknown and it will be the future challenge of the scientific community to identify and describe the fate of RGM. How much is deposited to the snow surface and how much is reacting further for example with particles?

#### 1.3 Atmospheric Modelling

A model is a mathematical tool for the study of processes and mechanisms of complex systems such as the atmosphere and the processes inside the atmosphere as f.ex. transport of air pollution. This tool should therefore take into account all processes, which the transports depend on. The air pollution in the Arctic depends on the emissions from the sources, transport from the emissions area into the Arctic by the wind, dispersion of the pollution by diffusion, chemical transformations during the transport, removal of pollutants due to precipitation and deposition on the surface. An air pollution model for the Arctic must take into account all these physical and chemical processes. The different processes must be described very precisely to reduce the uncertainties in the model. It is only possible to handle such a model on a very powerful computer, because the processes and the interactions between the different processes are very complex.

There are several reasons why one should use a model. A model is a good tool for improving the understanding of the atmospheric pathways to the Arctic. The model can also be used to trace the measured pollution back to different sources in the Northern Hemisphere and estimate their contributions to the Arctic atmospheric pollution, which is done in the following section 1.3.2. The model can also be used to quantify the importance of different processes as f.ex. mercury depletion for the transport of mercury into Arctic as shown in section 1.3.3. Finally the model can also be used for trend analysis of the measurements, e.g. by normalising the

measurements for the meteorological factor, i.e. estimate the variations in the measurements that are due to changes in the meteorological conditions and then estimate the trend of the concentrations due to changes in the emissions. This is done in section 1.4.

The current state of atmospheric modelling of the pollution in the Arctic is highly developed. This is mainly caused by the development over the years of both 1) weather forecast models, which gives comprehensive knowledge about the physical processes in the atmosphere and provide reliable meteorological data for the models, and 2) the development of comprehensive regional transport chemistry models for the mid-latitudes with a detailed description of both the physical and chemical processes in the atmosphere. There are only few existing atmospheric long-range transport models, which have been used to study the atmospheric transport of pollution to the Arctic. These models are all three-dimensional Eulerian models, which contain a detailed description of the physical processes. Examples of such models are the three-dimensional hemispheric model developed by Iversen (1989) and Tarrason & Iversen (1992, 1997), the three-dimensional global sulphur and mercury model by Dastoor and Pudykiewicz (1996), MSC-E Hemispheric Model developed by EMEP-EAST in Moscow, and the Danish Eulerian Hemispheric Model (DEHM) by Christensen (1995,1997).

The DEHM model has been used for this assessment. The DEHM model has earlier been used in AMAP phase 1 (see Kämäri et al., 1998), and the model has been described in several papers, see e.g. Christensen (1997, 1999), Barrie et al. (2001), Lohmann et al. (2001) and Roelofs et al. (2001). Model results from the Danish Eulerian Hemispheric Model will be presented in the following.

#### 1.3.1 The DEHM modelling system

The system consists of two parts: a meteorological part based on the PSU/NCAR Mesoscale Model version 5 (MM5) modelling subsystem (see Grell et al, 1995) and an air pollution model part, the DEHM model (see Figure 1.3.1). The MM5 model produces the final meteorological input for the DEHM model. Global meteorological data, used as input to the MM5 mesoscale modelling system, are obtained from the European Centre for Medium-range Weather Forecasts (ECMWF) on a  $2.5^{\circ}x2.5^{\circ}$  grid with a time resolution of 12 hours. The whole system includes 2-way nesting capabilities, so it is possible to do finer (150 km  $\rightarrow$  50 km  $\rightarrow$  16.67 km, etc) model calculations over e.g. the Arctic Ocean or Greenland. 23 years of meteorological data from 1979 to 2001 are available, but the MM5 model system for the model system with 1 nest has been run for the period 1995-2001 for Europe (50 km) and 1 month for Greenland (50 km) as demonstration.

In the version used here the model has been run for only the hemispheric domain.



FIGURE 1.3.1. OVERVIEW OF THE DEHM MODEL SYSTEM.

The DEHM model is based on set of coupled full three-dimensional advectiondiffusion equations, one equation for each species. The horizontal mother domain of the model is defined on a regular 96x96 grid that covers most of the Northern Hemisphere with a grid resolution of 150 km × 150 km at 60°N. The vertical discretization is defined on an irregular grid with 20 layers up to  $\approx$  15km that reflects the structure of the atmosphere.

The vertical diffusion is parameterised by using a  $K_z$  profile for the surface layer based on the Monin-Obukhov similarity theory, and this  $K_z$  profile for the surface layer is extended to the whole boundary layer by using a simple extrapolation (see Christensen, 1997).

#### 1.3.2 Modelling of sulphur and lead

In the basic version the emissions of anthropogenic sulphur and lead are based on the global GEIA inventory of sulphur, version 1A.1, for 1985 (see Benkowitz et al., 1996) and the global GEIA inventory of lead, Version 1, for 1989 (see Pacyna et al, 1995), both on a  $1^{\circ}x1^{\circ}$  grid. These emissions are redistributed to the grid used in the model. The EMEP emissions of sulphur (for Europe) for the years 1990-1997 are used for the part of the grid, which is equal to the EMEP grid.

The sulphur chemistry is simple linear, where the oxidation rate of  $SO_2$  to  $SO_4^{2-2}$  depends on the latitude and the time in the year, while for Lead there are no chemical transformations.

The dry deposition velocities of the species are based on the resistance method. The wet deposition is parameterized by using a simple scavenging ratio formulation with different in-cloud and below-cloud scavenging. The removal rates for Pb are equal to the rates for  $SO_4^{2^2}$ .

The model has been run from October 1990 to May 2001. In Figure 1.3.2 the mean concentrations of  $SO_x$  (= $SO_2 + SO_4^2$ ) for the surface level and the total depositions are shown. The similar figures for Pb are given on Figure 1.3.3. The general pattern of both the SO<sub>x</sub> and Pb is quite similar. The main pathway for the transport is from Russia into the Arctic. For Greenland the highest concentrations levels of both SO<sub>x</sub>

and Lead are in the northeast Greenland, while the highest depositions are in south Greenland in connection higher precipitation rates and more open water. The dry deposition to ice and snow is very low.





Figure 1.3.3 The mean concentrations for the surface layer of PB in ng Pb/m<sup>3</sup> (left) and the total deposition of PB in mg Pb/m<sup>2</sup>/year (right).

For the Arctic areas the model has been compared with measurements from Station Nord for the whole period, The results show that there is a rather good agreement between the calculated and observed concentrations of  $SO_2$ ,  $SO_4^{-}$  and Pb, see Figure 1.3.4 and 1.3.5.



Figure 1.3.4 Comparisons between observed and calculated weekly mean of SO  $_{_2}$  and SO  $_{_4}^{=}$  for Station Nord in North-Eastern Greenland



Figure 1.3.5. Comparisons between observed and calculated weekly mean of Pb for Station Nord in North-Eastern Greenland

In Figures 1.3.6 and 1.3.7 the vertical distributions of  $SO_x$  and Pb and the contribution from different anthropogenic sources to these vertical distributions for 6 different areas at Greenland are shown. The areas are: Station Nord, Daneborg-Scoresbysund area, South Greenland, Nuuk area, Thule and Summit. As mentioned earlier the highest concentrations of both sulphur and lead are in the northern part of Greenland and it is in lowest 2 km of the atmosphere, while the lowest concentrations are at the icecap of Greenland (Summit). The highest concentration levels are a factor of 10 lower than the similarly calculated concentrations for Denmark.



Figure 1.3.6. The vertical distribution of SOX and contributions from different sources to the vertical contributions for Station Nord (upper left), Daneborg-Scoresbysund area (upper right), South Greenland (middle left), Nuuk area (middle right), Thule (lower left) and Summit (lower right)

The largest contribution to the atmospheric burden of sulphur and Pb is coming from the Russian sources with a contribution up to more than 50% in the northern part of Greenland, while in the southern and western part the most important sources are from North America (up to 50% for sulphur and 35% for lead). At higher levels for whole Greenland there are larger contributions from the sources in North America.



Figure 1.3.7. The vertical distribution of Pb and contributions from different sources to the vertical contributions for Station Nord (upper left), Daneborg-Scoresbysund area (upper right), South Greenland (middle left), Nuuk area (middle right), Thule (lower left) and Summit (lower right)

In Figures 1.3.8 and 1.3.9 the total deposition and the contribution from different sources are shown for the same 6 areas as shown above. The largest deposition of both sulphur and lead is in the southern part of Greenland and the lowest is at the icecap. The deposition levels for sulphur are a also factor 10 lower than the calculated deposition levels in Denmark, and for lead the deposition is a factor of 15 lower. The largest contribution to the deposition in Northern part of Greenland is coming from Russian sources (up to 60%), while for the Eastern part there are larger contributions from European sources (65%). In the southern and western part the most important source for the deposition is from North America (up to 73% for sulphur and 55% for lead)



Figure 1.3.8. The contribution from different sources to the total deposition of sulphur for Station Nord (NOR), Daneborg-Scoresbysund area (EAS), South Greenland (SOU), Nuuk area (WES), Thule (THU) and Summit (SUM)



Figure 1.3.9 The contribution from different sources to the total deposition of Pb for Station Nord (NOR), Daneborg-Scoresbysund area (EAS), South Greenland (SOU), Nuuk area (WES), Thule (THU) and Summit (SUM)

#### 1.3.3 Modelling of mercury

In general, activities aimed at modeling Hg are less developed, although major improvements in regional (European) and global modeling of Hg have been made. An example of a mercury model is the mercury version of the Danish Hemispheric Eulerian Model system (DEHM), which have been used to study the transport of mercury into the Arctic. The main reason for the development of the model was fulfill the recommendation from the AMAP workshop: "Modelling and sources: A workshop on Techniques and associated uncertainties in quantifying the origin and long-range transport of contaminants to the Arctic. Bergen, 14-16 June 1999" to "Assess spring Hg and O3 depletion using atmospheric model with high-resolution boundary layer".

In the present mercury version of DEHM there are 13 mercury species, 3 in gasphase (Hg<sup>0</sup>, HgO and HgCl<sub>2</sub>), 9 species in the aqueous-phase and 1 in particulate phase.

In the current version the emissions of anthropogenic mercury are based on the new global inventory of mercury emissions for 1995 on a  $1^{\circ}x1^{\circ}$  grid (Pacyna & Pacyna, 2002), which includes emissions of Hg<sup>0</sup>, reactive gaseous mercury (RGM) and particulate mercury. There are no re-emissions from land and oceans, instead a background concentration on 1.5 ng/m<sup>3</sup> of Hg<sup>0</sup> is used as initial concentrations and boundary conditions.

The chemistry is based on the scheme from the GKSS model, see Figure 1.3.10 and Petersen et al. (1998). The mercury chemistry is depending on the concentrations of  $O_3$ ,  $SO_2$ ,  $CI^{-}$  and Soot. Constant values of  $CI^{-}$  and Soot concentrations are used, while  $O_3$  and  $SO_2$  concentrations are both obtained from the photochemical version of DEHM. During the polar sunrise in the Arctic an additional fast oxidation rate of Hg<sup>0</sup> to HgO is assumed: Inside the boundary layer over sea ice during sunny conditions it is assumed that there is an additional oxidation rate of  $\frac{1}{4}$  hour<sup>-1</sup>. The fast oxidation stops, when surface temperature exceeds  $-4^{\circ}C$ . The removals of Hg0 are due to the chemistry and the uptake by cloud water.



Figure 1.3.10. The GKSS chemical scheme used in the mercury model (from Petersen et al., 1998). The red arrow shows the additional fast oxidation rate of Hg<sup>°</sup> to HgO during Polar Sunrise (PS).

The dry deposition velocities of the reactive gaseous mercury species are based on the resistance method, where the surface resistance similar to  $HNO_3$  is used. The wet deposition of reactive and particulate mercury is parameterized by using a simple scavenging coefficients formulation with different in-cloud and below-cloud scavenging coefficients (see Christensen, 1997).

The mercury model has been run for October 1998 to December 2000. For the Arctic areas the model has been compared with measurements from Station Nord in northeast Greenland. The results show that there is some agreement between the calculated and observed concentrations of elemental mercury (Hg<sup>0</sup>), see Figure 1.3.11. The calculated concentrations of reactive gaseous mercury (RGM) and particulate mercury are also shown, and during the depletion period the levels of both species increase considerably.

Because the dry deposition velocity of RGM is very high, these high concentrations of RGM result to a dramatically increased deposition of mercury, which are shown in both Figures 1.3.12 and 1.3.13.



Figure 1.3.11. Comparisons between observed (blue curve) and calculated daily mean of Hg° with two model versions, one without depletion (red) and one with depletion (black) (top), the total particulate mercury (middle) and total reactive gaseous mercury (bottom) for Station Nord in North-Eastern Greenland.



Figure.1.3.12. The total deposition of mercury without Arctic mercury depletion (left) and with (right) in  $\mu$ g Hg/m<sup>2</sup>/month.

In Figure 1.3.12, the total deposition of mercury for the 1999 and 2000 is shown. This example shows the importance of the mercury depletion in the Arctic for the total deposition of mercury. The total deposition increases in the whole Arctic and the surrounding areas, and for the area north of the Polar Circle the total deposition of mercury increases from 89 to 208 tonnes pr. year due to the depletion according to the model runs.

In Figure 1.3.13 the total deposition of mercury in  $\mu g Hg/m^2/year$  for 8 different localities (6 in Greenland, Faeroe Island and Denmark) are shown. The total deposition is splitted up in three components: the contribution from the deposition of RGM, chemical made particulate mercury and directly emitted particulate mercury. At the figure it is shown very clearly how important the depletion phenomena is for the deposition of mercury for the northern, western and Eastern Greenland. F.ex for the Thule area the total deposition of mercury is increased with a factor 3, while for the southern part for Greenland the depletion phenomena have only a minor influence on the mercury deposition. For all places closed to the ocean the total deposition is at the same levels at the southern part of Greenland and slightly lower than the depositions in Denmark. It is also shown that it is the increased deposition of RGM, which contributes mainly to the higher deposition rates. The contribution from directly emitted particulate mercury is very small in Greenland. It is mainly the large atmospheric reservoir of elemental mercury, which contributes to the deposition, and which all global emissions both anthropogenic and natural contributes to.



Figure 1.3.13. Total deposition of Mercury in µg Hg/m²/year splitted up in deposition of Reactive Gaseous Mercury, chemical made particulate mercury and directly emitted particulate mercury for two different model runs: without depletion (left) and with depletion (right), and for 8 different localities: Station Nord (NOR), Daneborg-Scoresbysund area (EAS), South Greenland (SOU), Nuuk area (WES), Thule (THU), Summit (SUM), Faeroe Island (FAE) and Denmark (DEN)

#### 1.4 TREND ANALYSIS

#### 1.4.1 Method and results

The chemical compounds and elements measured by IC and PIXE analysis in TSP samples and impregnated filter samples collected at Station Nord have been apportioned to four main source categories (Aarkrog er al. 1997). These are a 'soil' source, (wind blown dust), a 'sea' source (sea spray), a 'combustion' source (a general anthropogenic source due to a variety of distant activities), and a 'metal' source (probably due to copper-nickel production in the Arctic area). This is illustrated in Figure 1.2.4. Some elements have both an anthropogenic and a natural origin (e.g. vanadium, manganese and iron) while others are almost exclusively of anthropogenic origin: sulphur (except for a small amount of sea-salt sulphate), copper, nickel, zinc, arsenic and lead. These elements show a strong seasonal variation with high values in the winter/spring and very low values in the summer. Total sulphur (the sum of sulphur measured as sulphur dioxide and sulphate measured in the TSP samples) shows the same seasonal variation as the other anthropogenic elements. But the partition of the two components changes during the winter/spring season from a high content of sulphur dioxide during the dark winter period to a very low content after the polar sunrise in early spring.

Station Nord is almost not influenced by local or regional air pollution and can be considered as a remote watchtower from where the average emissions in a huge emission area in the eastern part of Europe and Russia can be followed. A study of the general emission trends is therefore possible using the long-time series of measurements during the last decade of the anthropogenic elements: Sulphur, copper, nickel, zinc, arsenic and lead. But, unfortunately, the measured concentrations depend strongly upon the meteorological conditions along the pathway to the Arctic. In the summer time the emissions never get to the Arctic, and during the winter the transport time can change much from week to week. Therefore, the single samples reflect only poorly the actual emissions in the source areas, and a trend analysis on the raw concentration data might give misleading results. Fortunately, a relevant way to handle this problem was possible using the results of the hemispheric Eulerian model DEHM.

The DEHM model was run with emission data for the year 1989 for lead and with emission data for the year 1990 for sulphur for the 11-year period 1991-2001, where the emissions were kept constant through all the years. All the variations of the modelled concentrations at Station Nord are therefore due to changes in the meteorological conditions from day to day. The raw concentration data for lead (Pb) are shown in a logarithmic presentation in Figure 1.4.1, and the model calculations
are shown in an analogous way in Figure 1.4.2. It is evident that the model to a high extent grasps the meteorological variations, although it underestimates the annual relative span. It might also be suggested from a comparison of the two figures that the measured data have a decreasing trend. The trend is much more clear in Figure 1.4.3 where the ratio Pb(measured)/Pb(model) has been calculated by weighted regression analysis for each of the years 1991-2000 (Wåhlin et al., 2002). The values are fitted by an exponential function of time. It can be seen that this trial function does not disagree statistically with the data points when the uncertainties (standard deviations) are taken into account. Thus, assuming an exponential decay of the emissions, the half-value period and its standard deviation could be estimated at  $11 \pm 3$  years.



Figure 1.4.1. Concentrations of particulate lead (PB) measured at Station Nord in the years 1990-2001.



Figure 1.4.2. Concentrations of airborne particulate lead (PB) at Station Nord calculated using the Hemispheric Eulerian model with constant emission data (for the year 1989).



Figure 1.4.3. Ratios determined by regression analysis of measured values and constant emission model values of lead (Pb) for each of the years 1991-2000. The values are fitted by an exponential function of time with a half-value period of 11  $\pm$  3 year

The measurements of arsenic (As) and zinc (Zn) are highly correlated with lead on a sample to sample basis, and also the measurements of nickel (Ni) and copper (Cu) on a seasonal basis. Therefore, it makes sense to use the model values of lead for an equivalent analysis of trends for the other elements. The influence of the large scale meteorological conditions seems to be very similar. Ratios and exponential trend functions were determined by the same technique used for lead. The results are presented in Table 1.4.1 and Figures 1.4.4-1.4.7. The constant exponential trend seems to give a good description for all elements.

Table 1.4.1. Ratios (measured mass/model mass) determined by regression analysis, and half-value periods of fitted exponential functions.

	Cu/Pb(model)	Zn/Pb(model)	Ni/Pb(model)	As/Pb(model)	Pb/Pb(model)
1991	0.50±0.05	2.2±0.2	0.30±0.03	0.29±0.03	1.9±0.3
1992	0.44±0.04	1.8±0.2	0.23±0.02	0.24±0.02	1.27±0.14
1993	0.42±0.04	1.8±0.2	0.24±0.02	0.26±0.03	1.30±0.15
1994	0.65±0.10	2.1±0.3	0.27±0.03	0.33±0.04	1.4±0.2
1995	0.42±0.05	1.23±0.11	0.19±0.02	0.156±0.013	0.88±0.08
1996	0.49±0.08	1.6±0.2	0.20±0.03	0.22±0.03	1.1±0.2
1997	0.42±0.07	1.7±0.3	0.17±0.03	0.21±0.03	1.1±0.2
1998	0.32±0.04	1.5±0.2	0.15±0.02	0.20±0.03	1.1±0.2
1999	0.25±0.03	1.11±0.14	0.12±0.02	0.15±0.02	0.79±0.09
2000	0.36±0.07	1.5±0.3	0.16±0.03	0.24±0.04	1.2±0.2
Half-value period	12 ± 3	12 ± 3	8.1 ± 1.3	12 ± 3	11 ± 3
in years					



Figure 1.4.4. Ratios determined by regression analysis of measured values of copper (Cu) and constant emission model values of lead (Pb) for each of the years 1991-2000. The values are fitted by an exponential function of time with a half-value period of 12±3 year.



Figure 1.4.5. Ratios determined by regression analysis of measured values of zinc (Zn) and constant emission model values of lead (Pb) for each of the years 1991-2000. The values are fitted by an exponential function of time with a half-value period of  $12\pm3$  year.



Figure 1.4.6. Ratios determined by regression analysis of measured values of nickel (Ni) and constant emission model values of lead (Pb) for each of the years 1991-2000. The values are fitted by an exponential function of time with a half-value period of  $8.1\pm1.3$  year.



Figure 1.4.7. Ratios determined by regression analysis of measured values of arsenic (As) and constant emission model values of lead (Pb) for each of the years 1991-2000. The values are fitted by an exponential function of time with a half-value period of 12±3 year.

The anthropogenic sulphur is emitted to the atmosphere as sulphur dioxide and is converted to sulphuric acid (sulphate) by photochemical processes. The Hemispherical Eulerian Model (DEHM) takes this conversion into account, and also the different deposition rates of sulphur dioxide (gas) and sulphate (particles) are included in the model. The DEHM model was run with constant sulphur emission data for the year 1990 for the 11-year period 1991-2001. The results for Station Nord were expressed as total-sulphur SO<sub>x</sub>-S (sum of the elemental sulphur mass in sulphur dioxide and sulphuric acid/sulphate, SO<sub>2</sub>-S+SO<sub>4</sub>-S) and compared with the

corresponding measured values of  $SO_x$ -S. No correction for sea salt sulphate was made as the average amount at Station Nord is relatively small (approx. 7%). Following exactly the same procedure as for lead, the ratio  $SO_x$ -S(measured)/SO<sub>x</sub>-S(model) was calculated by regression analysis for each of the years 1991-2000. The results are shown in Figure 1.4.8 and Table 1.4.2. It can be seen the declining trend is similar to the trend of the other anthropogenic elements.



Figure 1.4.8. Ratios determined by regression analysis of measured values of sulphur (SO<sub>x</sub>-S) and constant emission model values for each of the years 1991-2000. The values are fitted by an exponential function of time with a half-value period of 11 $\pm$ 2 year.

TABLE 1.4.2. RATIOS (MEASURED MASS/MODEL MASS) DETERMINED BY REGRESSION ANALYSIS, AND HALF-VALUE PERIOD OF A FITTED EXPONENTIAL FUNCTION.

Half-value period	11 ± 2 year
2000	0.82±0.13
1999	0.71±0.09
1998	0.76±0.09
1997	0.91±0.11
1996	0.96±0.12
1995	0.67±0.06
1994	1.06±0.12
1993	1.14±0.13
1992	1.21±0.14
1991	1.26±0.14
	SO <sub>x</sub> -S/SO <sub>x</sub> -S(model)

#### 1.5 CONCLUSIONS

The High Arctic is burdened with a considerable atmospheric pollution, consisting of a wide variety of acidic and toxic compounds, which originate in mid-latitude industrial areas. That has been demonstrated by the combined use of long-term field measurements and sophisticated large-scale meteorological and chemical transport models. The pollution reaches it's maximum in late winter and early spring when atmospheric circulation favours transport from these source areas into the Arctic region. This *Arctic Haze* is accompanied by an intense photochemical activity induced

in the Arctic atmosphere by the Polar sunrise. Much of this pollution leaves the Arctic region again but a considerable amount is deposited on land and sea surfaces, leading to detrimental effects on the vulnerable eco-systems in this pristine region.

Particular interest has been attached to mercury as an atmospheric pollutant. It has been found that this volatile heavy metal has a unique behaviour in the Arctic spring atmosphere. After Polar sunrise in February gaseous elemental mercury (GEM) is abruptly depleted from the atmosphere in the so called mercury depletion episodes lasting from hours to days whereupon it is equally abruptly restored to the original concentrations of about 1.5 ng·m<sup>-3</sup>. MDE has been found at several Arctic stations and MDE therefore seems to be a ubiquitous phenomenon in Arctic. The MDE leads to deposition of atmospheric mercury at a time where the Arctic biological system is extremely active and thus the deposited mercury may be bioaccumulated much more effectively than predicted from mid-latitudes studies.

MDE occurs simultaneously with the depletion of ozone. Halogen radicals as Cl, ClO, Br and BrO have been suggested to be responsible for MDE. In the present report strong evidence is found for that Br is the only important reactant.

The model calculations have shown that different source regions have a different influence in various parts of Greenland because of differing pathways. Thus the atmospheric concentrations of sulphur in the central, southern and south-western areas of Greenland are dominated by source regions (in order of decreasing dominance) in North America, Russia and Western Europe. The concentrations in the northern and eastern Greenland are dominated by sources in Russia, North America and Europe as a whole. For lead the influences are much the same, but with a tendency for higher relative contributions from Western Europe. The average concentrations are by far the largest in northeast Greenland.

For deposition of sulphur and lead it has been found that Russian sources dominate in the North and East over contributions from European sources. In the West and the South the contributions to the deposition come primarily from North America and secondarily from Europe. The depositions are largest in the South and East with north-eastern Greenland a close third.

The combination of field data and model calculations has also been highly useful in assessing trends in atmospheric concentrations. A glance at the concentrations during the 1990s shown in Figures 1.4.1 and 1.4.2 may, depending on the reader's subjective assessments, either lead to a conviction that there is a downward trend in these data or that there is no trend because of a large spread in data. This large spread is mainly caused by the varying meteorological conditions in the different years. Most likely a simple statistical analysis would show that there is a downward trend but that it is not significant.

A much smaller scatter is found when experimental data and are compared to model data, calculated under the assumption that emissions have remained unchanged during the decennium. The ratios between measured and model values were found for each of the years 1991-2000 using regression analysis. An assessment of these timeseries have shown that there indeed are significant decreases in the concentrations, contrary to the built-in assumption that emissions have been unchanged. Since the DEHM model estimates that more than 70% of the sulphur and lead measured at Station Nord is emitted in the area covering the former Soviet Union the results of the trend analysis indicate that the general anthropogenic atmospheric emissions decreased significantly in this region in the nineties. Whether the internationally agreed emission reductions that have mainly been effected in Western Europe and North America also influence the results from Station Nord is, however, not clear. Thus the effect on ambient concentrations of the stronger decline

of the lead emissions compared with the decline of the sulphur emissions, which has been observed in Western Europe, is not observed at Station Nord.

It can however be stated that the smaller emissions in the source areas have taken effect also in the High Arctic and that the decreasing trends for Pb, Zn, Ni, As, Cu and S can be characterised by a half-life of about 11 years.

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# 2 Terrestrial Environment

Citation: Riget, F<sup>1</sup>., M. Goodsite<sup>2</sup>, H. Dahlgaard<sup>3</sup>, W. Shotyk<sup>4</sup>, D.Muir<sup>5</sup>, P. Johansen<sup>1</sup> & G. Asmund<sup>1</sup>: Chapter 2. Terrestrial Environment. In: Riget, F., J. Christensen & P. Johansen (eds). AMAP Greenland and the Faroe Islands 1997-2001. Ministry of Environment, Denmark

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#### 2.1 INTRODUCTION

The contaminant data available for the terrestrial environment since AMAP phase 1 have been collected in connection with the following AMAP projects: "Biological core programme", "Mercury in dated peat bogs", Regional differences in heavy metal concentrations in reindeer", "Contaminants in Greenland human diet", "Long term Atmospheric Records of Hg, Pb, Cd and POPs in the Arctic","Radionuclides, remaining phase 2 data, 2001","Radionuclides 2000" and "Anthropogenic radionuclides in Greenland and the Faroe Islands".

The description of contaminant levels, spatial trends and short-term temporal trends is focusing on the heavy metals Cd and Hg (Se) and on the organochlorines PCBs, DDTs, HCHs, HCB and chlordanes. Appendices A and B shows descriptive statistics of the new available data of heavy metals and organochlorines, respectively. The peat core studies have focused on long-term temporal trends of Hg and Pb. The radionuclide studies focus on deposition of <sup>137</sup>Cs and <sup>239,240</sup>Pu from 4 different regions in Greenland.

#### 2.2 HEAVY METALS

## 2.2.1 Levels and spatial trends

In AMAP phase I, metals were determined in soil, humus, lichens and moss at four location in Greenland and caribou at two locations (Riget et al. 2000a, Aastrup et al. 2000). In general no obvious spatial trends were seen. Differences in metal levels mostly could be explained by natural causes such as bedrock geology, feeding behaviour rather than as consequences of contamination (Aakrog et. al. 1997).

Since AMAP phase I, heavy metal data have become available for lichens (*Cetraria nivalis*), crowberry (*Empetrum hermaphroditum*), Arctic blueberry (*Vaccinium uliginosum*), ptarmigan (*Lagupus mutus*), sheep (*Ovis sp.*), Arctic hare (*Lepus arcticus*), caribou (*Rangifer tarandus*) and musk ox (*Ovibos moschatus*). Appendix A shows aggregated data together with basic information.

## Cd

Cd concentrations in lichens from Nuuk and Qaqortoq in 1999 were at a similar level as observed during AMAP phase I at four locations around Greenland (Riget et al. 2000a). The Cd concentrations collected in 1999 did not differ between the two locations (t-test of log-transformed data, p=0.96).

Cd concentrations in berries (crowberry and Arctic blueberry) from southwest Greenland were low (0.004 and 0.028 mg/kg ww, respectively).

Cd concentrations in ptarmigans from Nuuk and Qeqertarsuaq in 1999 show increasing level in the order muscle, liver and kidney. No significant difference was observed in Cd concentrations in liver and kidney between the two locations (t-test of log-transformed data, p=0.62 and p=0.74, respectively). No previous data exist on terrestrial bird species in Greenland. The Cd levels in liver and kidney were similar to those from northern Scandinavia and lower than samples from the Canadian Arctic (AMAP 1998).

Cd concentrations in muscle from domestic sheep, Arctic hare and musk ox were low and at a similar level as in caribou. In liver of these terrestrial mammals, Cd concentrations ranged from 0.051 mg/kg ww in musk ox to 0.186 mg/kg ww in Arctic hare, which appears lower than in caribou (se Appendix A). Also in the kidney, the Cd concentrations appeared little lower than in caribou, except for Arctic hare (3.81 mg/kg ww).

Cd concentrations in muscle of caribou were at or below the detection limit (0.003 mg/kg ww). Figure 2.2.1 shows the Cd concentrations in liver of caribou from different locations at West Greenland. Cd concentrations in caribou from Akia and Isortoq appear higher than in Kangerlussuaq and Ittinera. Several metals showed the same tendency with the highest levels in caribou from Isortoq and Akia and this probably is caused by higher availability of lichens as winter forage in these areas (Aastrup et al. 2000). The samples in Akia and Kangerlussuaq 1996 and 1997 were taken in the early winter (September 1996) and in the late winter (March 1997). In both areas a small increase of Cd was found from 1996 to 1997 indicating seasonal variation in Cd concentrations.

In general, Cd levels in Greenland caribou are similar to levels found in eastern Arctic Canada, but lower than levels found further south in Norway and in Yukon in Canada (Aastrup et al. 2000).

#### <u>Hg-Se</u>

Hg concentrations in lichens from Nuuk and Qaqortoq in 1999 were similar to those found in AMAP phase I at four locations around Greenland (Riget et al. 2000a). Both Hg and Se concentrations in lichens from Isortoq in 1999 were significantly higher than in lichens from Nuuk the same year (t-test on log-transformed data, p=0.04 and p<0.01, respectively).

Hg and Se concentrations in berries (crowberry and Arctic blueberry) from southwest Greenland were very low.

Hg and Se concentrations in ptarmigans from Nuuk and Qeqertarsuaq in 1999 show increasing level in the order muscle, liver and kidney, however not as pronounced from liver to kidney as was the case for Cd. Hg concentrations in ptarmigans from Qeqertarsuaq was higher than in birds from Nuuk, however, this was only significant in case of liver tissue (t-test on log-transformed data, p=0.04 and 0.22, respectively). Se concentrations were not significantly different between the two locations (t-test of

log-transformed data, liver p=0.87 and kidney p=0.77). No previous data existed on terrestrial bird species in Greenland. Hg levels in West Greenland ptarmigan liver and kidney were high compared to ptarmigans from Arctic Canada and considerably higher than in birds from northern Scandinavia (AMAP 1998).



Figure 2.2.1. Cd (black) and HG (grey) concentrations mg/kg ww (mean + SD) in caribou liver in Greenland

Hg and Se concentrations in liver and kidney of caribou were highest in Isortoq and Akia, the two locations with highest availability of lichens as winter food (Aastrup et al. 2000). This geographical pattern was also seen for Cd. The Hg concentrations found in 1999 in caribou from Isortoq (liver: 0.142 mg/kg ww) were lower than found in 1995 (liver: 0.651 mg/kg ww), but still relatively high compared to the concentrations at the other locations (see Appendix A). Hg and Se levels were relatively high, especially at some locations, compared to the levels found in other Arctic regions (AMAP 1998 and Aastrup et al. 2000).

## 2.2.2 Temporal trends

New heavy metal data from the terrestrial environment makes it possible to compare with previously found levels. However, possible differences between levels found in only few years cannot be interpreted as a temporal trend but may be caused by random year-to-year variation. The results may therefore only be indicative. Table 2.2.1 shows the results of the statistical analyses of temporal trends.

## Cd

Cd concentrations in lichens from Nuuk and Isortoq collected in 1999 can be compared with the concentrations found in 1994 at the same locations. Similarly it is possible to compare the Cd concentrations in liver of caribou collected in Isortoq 1999 whose those collected in 1995.

Table 2.2.1. Results of statistical tests for difference in mean metal concentrations between years in lichens and caribour.\* denotes significance at 5% level and \*\* denotes significance at 1% level. The power of the test is given if no significant difference was found.

				Trend	Test	significance (p)	power (p)
Cd	Lichens		Nuuk	94<99	t-test	0.35	0.16
			Isortoq	94>99	t-test	0.05*	
	Caribou	Liver	Ittinera	95<96,96>97,9	7<99 ANOV	A 0.92	0.16
		Liver	Isortoq	95<99	t-test	0.83	0.06
Hg	Lichens		Nuuk	94>99	t-test	0.43	0.26
•			lsortoq	94<99	t-test	0.15	0.27
	Caribou	Liver	Ittinera	95<96,96>97>9	99 ANOVA	<0.01**	
		Liver	Isortoq	95>99	t-test	<0.01**	
Se	Lichens		Nuuk	94>99	t-test	0.03*	
			Isortog	94>99	t-test	0.31	0.10
	Caribou	Liver	lsortoq	95>99	t-test	<0.01**	

In lichens from Isortoq, the Cd concentrations were significantly lower in 1999 than in 1994 (t-test on log-transformed data). However, in liver of caribou, the Cd concentrations were higher in 1999 than in 1995, but not significantly (t-test on logtransformed data). In lichens and caribou from Ittinera, Nuuk no significant difference was found between 1994 and 1999 in case of lichens (t-test on logtransformed data) and between years 1995, 96, 97 and 99 in case of caribou (ANOVA on log-transformed data).

## <u>Hg/Se</u>

Hg and Se concentrations in lichens from Ittinera, Nuuk and Isortoq collected in 1999 can be compared with the concentrations found in 1994 at the same locations. Similarly it is possible to compare the Hg concentrations in liver of caribou collected in Isortoq 1999 to those collected in 1995 and to compare the concentrations in liver samples from Ittinera collected in 1999 with those collected in 1995, 96 and 97.

No significant difference in Hg concentrations in lichens from Isortoq between 1994 and 1999 was found (t-test on log-transformed data). In caribou liver from the same area, the Hg concentrations were significantly lower in 1999 than in 1994 (t-test on log-transformed data). In both lichens and caribou from Ittinera, Nuuk, the Hg concentrations were lower in 1999 than in 1994 (in case of lichens) and 1995, 96 and 97 (in case of caribou), however, the difference was only significant for caribou (ANOVA on log-transformed data).

Se concentrations in lichens and caribou from Isortoq were lower in 1999 than in 1994 (lichens) and 1995 (caribou), however this was only significant in case of caribou (t-test on log-transformed data). Also in Ittinera, Se concentrations in lichens and liver of caribou were lower in 1999 than in 1994 (lichens) and 1995, 96 and 97 (caribou), but this was only significant for caribou (ANOVA on log-transformed data).

#### 2.3 PEAT CORE STUDY

Peat cores were collected from ombrogenic and minerogenic peat deposits in Switzerland, Denmark, Scotland, the Shetland Islands, the Faroe Islands, Finland, Iceland, SW Greenland and the Carey Islands, as well as in the High Arctic of Canada (Bathurst Island, Nunavut). Data have become available from the following AMAP projects: "Long term records of atmospheric deposition of Hg, Cd, Pb and persistent organic pollutants (POPs) in peat cores from Arctic bogs (Carey Islands, Greenland and Faroe Islands)", "Dating of Mercury in Peat Bogs" and "The dating of transboundary air pollution in the Arctic". Data also come from the following Swiss and US grants: "Sources and rates of atmospheric mercury accumulation in the High Arctic of Canada and Europe: long term records (9,000 <sup>14</sup>C yrs) using peat cores".Swiss National Science Foundation, "Long term records of the changing rates and sources of atmospheric metal deposition using peat cores from bogs". Swiss National Science Foundation, "Long term records of atmospheric deposition of Hg, Cd, Pb and persistent organic pollutants (POPs) in peat cores from Arctic bogs, and comparison with bogs in the temperate zone". International Arctic Research Centre, Fairbanks, Alaska.

The focus of the projects have been to obtain peat profiles in Arctic regions and analyse them geochemically as well as paleoecologically and date the profiles with as high resolution as possible. The goal has been to establish long term records of Hg, Pb, Cd and POPs in the Arctic, and compare them with continental records. Our primary focus has been mercury, whereas Cd and POP data are not yet available. The data may be used as input for models and obtaining knowledge of past background variations with climate. The distribution of mobile trace elements such as Ca and Sr and redox-sensitive trace elements such as U in the profiles was used to indicate the ombrogenic sections of the peat profiles where Hg was supplied exclusively by atmospheric processes. Age dating of these sections, using both <sup>210</sup>Pb and <sup>14</sup>C, allows the rates of peat formation to be quantified and this, in turn, is used to calculate the rates of atmospheric Hg accumulation. The fluxes of atmospheric Hg from the post-Industrial period can be compared with those of pre-Industrial and ancient samples, in an effort to distinguish between natural and anthropogenic fluxes. In the modern time the fluxes can also be compared with the <sup>210</sup>Pb flux since this is considered atmospheric input as well. The cores represent up to 12,000 <sup>14</sup>C years of peat accumulation.

With respect to the cores from SW Greenland and Denmark, a high resolution chronology ( $\pm 2$  yrs) has been established for past 50 years using <sup>14</sup>C to reconstruct the atmospheric bomb pulse curve (Goodsite et al., 2001). In Greenland, Hg concentrations in the peat samples dating from the 1950's are up to 14 times higher than samples dating from AD 890-985 (Shotyk et al., 2002). A similar Hg chronology has been obtained for Hg accumulation in Denmark, but the concentrations tend to be approximately twice those of Greenland. Work is presently focussed on providing reliable estimates of Hg "flux" or net accumulation, since Hg concentrations can appear to be misleading in cores as Hg is concentrated through time in peat, due to natural decomposition of the organic material, and the possibility of perterbation of the true depositional signature/profile due to diagenitic processes/post depositional transformation and mobility are still being studied..

With respect to the cores collected from Bathurst Island, Nunavut, Hg concentrations in surface samples exceed those of deeper, older peat layers by 7 to 17 times. Work is now underway to try to also date these cores using the <sup>14</sup>C atmospheric bomb pulse.

With respect to the cores collected from lower latitudes, the greatest Hg concentrations were found on the Faroe Islands (up to 700 ng/g) with maximum Hg

concentrations decreasing in the order Faroes > Shetland > Scotland > Switzerland. Peat samples dating from the post-Industrial period are clearly enriched in Hg, relative to pre-Industrial samples, at each of these sites. However, at least in the peat core from the Faroe Islands, the relationship between Hg enrichment in the subsurface and redox-related Fe transformations of Fe, requires further study.

The cumulative, longterm rates of atmospheric Hg accumulation ( $\mu$ g/m<sup>2</sup>/yr), averaged over the past 1 to 5 millenia, are Switzerland (2.0-2.3), Scotland (5.1-6.1), Faroes (6.1-7.8), and Shetland (7.9-9.7). The elevated Hg concentrations and net accumulation rates found in deeper peat layers from Scotland, Shetland, and the Faroe Islands, compared to the peat core from an ombrogenic bog in Switzerland, suggests that there may be a significant natural source of Hg in the N Atlantic region. The most obvious possible Hg source is volcanic emissions and degassing of the earth's mantle in Iceland. The Hg concentrations and fluxes which will be obtained using peat cores from Iceland will test this hypothesis.



Figure 2.3.2. Lead deposition in a Danish ombrogenic peat bog has been been successfully modelled and demonstrated on the regional level. We hope to extend our collaboration with the modelling groups to provide them useful information to test/calibrate their models of transport to the Arctic. Figure from: Umweltschadstoff Blei: Ist die Gefahr gebannt? C. Hagner, F. Feser, M. Costa-Cabral, H. v. Storch, Institut für Küstenforschung, GKSS-Forschungszentrum, Geesthacht and GKSS Jahres Berich 2000/2001 (used with permission). Pb data in a Danish bog from Shotyk et al., 2002 in revision.

Conclusions and recommendations:

It appears that peat records of deposition, correlate well with changes in emission – peaking when they should and falling overall since the late 80's/90's correlating with for example, closure of former East German chlor alkali plants and coal fired power plants (Gerhard Petersen, as cited in Goodsite et al. 2001). Mercury is used in great quantities in this process. Overall, the conclusion and general trends shown in the peat record are in agreement with the other environmental archives which have been studied in AMAP (i.e. ice core records, lake and ocean sediments).

The challenging scientific issue regarding interpretation of these records is the lack of scientific understanding of post depositional processes. While it is well documented that Pb is very well preserved, and that data obtained from ombrogenic peat bogs are generally in good correlation with detailed regional models of lead deposition (Figure 2.3.2), there is still much work to be done to show the same for Hg and Cd. For example: the change in time of concentrations or net accumulation recorded in the peat are too fast: i.e. the "slopes" of the deposition versus time in the various media - seem to be much faster than normal atmospheric chemistry and deposition processes allow.

Certainly the climate and associated effects greatly affect the total input of mercury, just as things that might have effected the climate in the past (e.g. large amounts of volcanic activity) might have released large amounts of mercury. More study is needed, and a closer look needs to be taken at the data provided by environmental archives to determine if climatic effects outweigh those of anthropogenic effects with respect to end deposition in the Arctic. Certainly there is interdependency, and most likely a synergistic effect. There is yet to be found true ombrogenic peat in the Arctic. The peat deposits found are either minerogenic, or nourished by bird droppings (deposits on top of cliffs like on the Carey Islands). Much work needs to be done, and is underway by the group and others, to be able to properly interpret the profiles measured in Arctic peat. To better understand the supplementary and complementary functions of different environmental archives especially, peat and lake sediment, we need a study, that for the same catchment compares the profiles of e.g. Hg recorded in peat and lake sediment. Research on peat in the future should focus on answering the above questions and should be supplemental to research with other environmental archives.

#### 2.4 Organochlorines

Prior to AMAP II very little knowledge existed of OC levels in the Greenland terrestrial biota. Few and relatively old studies existed dealing with OCs in terrestrial species such as Arctic fox (*Alopex lagopus*), sheep (*Ovis aries*), peregrine falcon (*Falco peregrinus*), see review by Fromberg et al. (1999). In the project "Contaminants in Greenland human diet" OC data have become available for ptarmigan, hare, lamb and musk ox sampled in 1999 from West Greenland (Appendix B). The National Water Research Institute, Canada (NWOC) has conducted all the OC analyses.

In general, OC levels are very low in terrestrial biota compared to marine species (see chapter 4.4). For example in muscle tissue, PCB levels are 10 to 60 times lower in terrestrial than in marine mammals. Even in fat OC levels are low in terrestrial mammals and only slightly higher than in muscle. This is a contrast to marine mammals, in which blubber has the highest OC levels. In Greenland PCB levels in fat are 100 to 1000 times lower in terrestrial than in marine mammals. The dominant OC were  $\Sigma$ PCB. Chlordanes,  $\Sigma$ HCH, and HCB levels were lower and  $\Sigma$ DDT even lower than these. The sum of 10 PCB congeners (28, 31,52, 101, 105, 118, 138, 153, 156, 180) ranged from 0.10 µg/kg ww in hare liver to 2.04 µg/kg ww in lamb liver.

## 2.5 RADIONUCLIDES

Artificial radionuclides have been monitored in the Greenland environment since the 1960's. The Greenland data have been reviewed in the first Arctic Monitoring and Assessment (AMAP) reports (Aarkrog et al. 1997; Strand et al. 1998). Since the AMAP I assessment, no radioactive contamination of the Greenland environment of significance has been detected. As compared to the previous assessment, the levels

measured are thus mainly influenced by environmental redistribution and continued decay and dilution with time. The present account shows averaged values. For individual analytical results, consult the data compilation.

The sampling regions are given in Figure 2.5.1.

A sampling campaign was carried out to determine the deposition of <sup>137</sup>Cs and <sup>239,240</sup>Pu from 4 different regions in Greenland. Three soil profiles were taken from different areas in each region. The samples were taken with available tools, i.e., no standard soil profilers were used. The aim was to get area-representative soil samples from relatively flat regions split in 10 cm depth sections. The raw data showed a large variation: in most profiles, only the top 5 or 10 cm were above detection limit, whereas other profiles seemed to have <sup>137</sup>Cs distributed to 40 or 50 cm. <sup>239,240</sup>Pu was only analysed in the uppermost layers. As <sup>137</sup>Cs from fallout, at some sites, has penetrated to 50 cm or more, it should also be expected that a fraction of the <sup>137</sup>Cs and the <sup>239,240</sup>Pu have been washed out to streams, lakes and fjords. In the results compiled in Table 2.5.1, the significant results have been summed up.



FIGURE 2.5.1 SAMPLING REGIONS

In spite of the variability, the data gives a picture similar to what was seen earlier (Aarkrog et al., 1997), i.e. highest fallout to the south parallel to high precipitation rates. The <sup>239,240</sup>Pu / <sup>137</sup>Cs activity ratio in integrated global fallout was estimated as 0.0116 without decay correction (Beck & Bennettt, 2002). Decay correcting from 1962 to 2002 changes this ratio to around 0.029, which is relatively close to the measured values. Due to limitations described above, the values given in Table 2.5.1 do not represent the total integrated fallout. The <sup>239,240</sup>Pu / <sup>137</sup>Cs ratios from Zackenberg are apparently higher than for the other sites and for the samples taken in 1994 (Aarkrog et al. 1997).

· · · · ·		Depth		<sup>137</sup> Cs		2	<sup>39,240</sup> Pu		Ratio
Location	Year	cm	Bq kg dry	Bq m⁻²	SD %	Bq kg <sup>-1</sup> dry	Bq m <sup>·</sup> ²	SD %	<sup>239,240</sup> Pu/ <sup>137</sup> Cs
Zackenberg (Salix)	1999	0-10	1.10	122	14.5	0.054	6.0	12.4	0.049
Zackenberg (Cassiope)	1999	0-10	0.32	27	36.7	0.014	1.2	37.8	0.045
Zackenberg (Dryas)	1999	0-10	1.57	146	11.0	0.071	6.6	10.9	0.045
Isortoq, profile 1	1999	0-10	74.4	2034	0.6	2.120	58.O	5.8	0.028
Isortoq, profile 2	1999	0-10	16.6	1113	1.5	0.541	36.2	6.4	0.033
Isortoq, profile 3	1999	0-10	14.2	1423	1.7	0.438	44.0	6.7	0.031
Itinnera, profile 1	1999	0-7	28.5	320	2.0	1.001	11.2	15.1	0.035
Itinnera, profile 2	1999	0-17	30.5	320	3.6	0.648	6.8	1.4	0.021
Itinnera, profile 3	1999	0-25	33.4	343	2.3	0.647	6.6	0.8	0.019
Pituffik, profile 1	2000	0-10	<0.7		DL	0.012		30.3	
Pituffik, profile 2	2000	0-10	16.7		3.7	0.391		7.5	0.023
Pituffik, profile 3	2000	0-10	0.62		25.6	0.013		31.0	0.021

TABLE 2.5.1. <sup>137</sup>Cs and <sup>239,240</sup>Pu in soil samples from 4 Greenland regions.

Table 2.5.2 gives <sup>137</sup>Cs concentrations in various terrestrial plants. The lichens and moss plants are retaining the global fallout and the Chernobyl contamination with relatively high concentrations due to a slow growth rate whereas the present grass samples are supposed to be contaminated by root uptake.

Species	Location	Region	Yr	<sup>137</sup> Cs			<sup>137</sup> Cs		
				Bq kg⁻¹	SD	n	Bqm⁻²	SD	n
				d.w.					
Lichen/moss	Faroe Islands	FR	1999	708		1			
Moss	Faroe Islands	FR	1999	196	147	2			
Grass	Faroe Islands	FR	1999	11	14	3			
Cetraria nivalis	Zackenberg	NE	1999	59	29	3			
Lichen	Scoresbysund	NE	1999	189	71	2			
Vaccinium	Scoresbysund	NE	1999	70		1			
uligonosum									
Lichen	lsortoq	SW	1999	292	175	5			
Grass	lsortoq	SW	1999	80	144	5	826	1160	2
Grass	ltiennera	CW	1999	39	21	3	4	2	3
Lichen	Thule air Base	NW	2000	90	14	3			

TABLE 2.5.2. CS-137 (BQ KG<sup>1</sup> DRY WEIGHT) IN VARIOUS TERRESTRIAL PLANTS.

Table 2.5.3 gives <sup>137</sup>Cs concentrations in meat from lamb, caribou and ptarmigan. In 1997, a special sampling of reindeer was performed to evaluate the effect of lichenrich and lichen-poor areas on the level of <sup>137</sup>Cs. This was initiated because the food chain transfer of <sup>137</sup>Cs from lichen to reindeer is known to be important for <sup>137</sup>Cs (Ahman et al., 2001). The levels observed in Greenland are intermediary between the low Icelandic levels, explained by a low frequency of lichens, and the Norwegian pre-Chernobyl values (Palsson et al., 1994). There was no significant difference between the two groups of caribou sampled. The test is weakened by the fact that the two groups of caribou were shot 16. - 17 September 1997, which is before the main lichen-grazing period. Although lower than in caribou, the transfer of caesium to lamb in south Greenland is high. As seen in the Faroe Islands, high levels in lamb are explained not only by a high fallout, but also by long ecological half-lives and high transfer parameters due to special environmental conditions (Joensen, 1999). This phenomenon deserves further study in Greenland.

Species	Location	Region	Year	<sup>137</sup> Cs		
		-		Bq kgʻʻ	SD	n
				fr.w.		
Lamb	Bøur	FR	1999	5.10	2.00	2
Lamb	Sandur	FR	1999	4.90	0.10	2
Lamb	Narssaq	SW	1999	19	18	3
Caribou	Isortoq	SW	1999	79	6	3
Caribou	Akia (Lichen rich)	CW	1997	65	9	5
Caribou	Itinnera (Lichen poor)	CW	1997	59	13	10
Ptarmigan	Qeqertarsuaq	CW	1999	0.76	0.33	6

TABLE 2.5.3. CS-137 (BQ	/ KG FRESH WEIGHT)	IN MEAT FRO	M LAMB,	CARBOU AND PTARM	IIGAN.
				107	

Conclusions and recommendations

- To be representative, a total soil inventory estimate of man-made radionuclides requires more sampling and analytical work than available in the present project.
- Caribou and lamb hold the largest <sup>137</sup>Cs concentrations in the terrestrial environment, and long ecological halflives are seen because of the special environmental conditions.
- A survey of the level of <sup>137</sup>Cs in caribou and lamb should be continued from earlier sampling areas and preferably extended in south Greenland. A special study of the environmental parameters responsible for the high and persistent transfer of <sup>137</sup>Cs to lamb should be performed

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## 3 Fresh Water Environment

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#### 3.1 INTRODUCTION

The contaminant data available for the Greenland fresh water environment since AMAP phase I have been collected in connection with the following projects: "Biological core programme", "Temporal time trend programme", "Radionuclides, remaining phase 2 data, 2001", "Radionuclides 2000" and "Anthropogenic radionuclides in Greenland and the Faroe Islands".

Arctic char (*Salvelinus alpinus*) is the only fresh water species where new contaminant data is available. The description of contaminant levels, spatial trends and short-term temporal trends focuses on the heavy metals Cd and Hg (Se) and on the organochlorines PCBs, DDTs, HCHs, HCB and chlordanes. Appendices A and B show descriptive statistics of the new available data of heavy metals and organochlorines, respectively. Stable isotopes have been analysed in order to facilitate the interpretation of levels and trends. The radionuclides focus on concentrations of <sup>137</sup>Cs and <sup>90</sup>Sr in fresh water sampled in 4 Greenland regions and the Faroe Islands and <sup>137</sup>Cs in Arctic char.

#### 3.2 STABLE ISOTOPES

Stable-nitrogen and stable-carbon isotope ratios were measured in muscle of Arctic char sampled in 1999 and 2000 according to Hobson et al. (1997) at the laboratory of Prairie and Northern Wildlife Research Center, US. Stable isotopes data can be informative about feeding preferences and trophic level (Hobson & Welch, 1995). The reason is that the abundance of  $15 \text{ (}^{15}\text{N/}^{14}\text{N}$ ) in the tissues of consumers is typically enriched over that in their prey owing to the preferential excretion of the lighter <sup>14</sup>N during protein transamination and deamination (Hobson & Welch ibid). Different feeding preferences among populations may lead to different levels of bioaccumulating contaminants, therefore information about stable isotopes is useful when interpreting contaminant levels.

Stable isotopes have been determined in the Arctic char sampled in Qaqortoq and Zackenberg, 1999 and in Ittoqqortoormiit, 2000. Table 3.2.1 shows stable-nitrogen and carbon isotope values from the Arctic char populations.

No significant difference (p<0.05) in  $\div$ <sup>15</sup>N among populations were found (analysis of covariance with fish length as covariate).  $\Rightarrow$ <sup>15</sup>N increased significantly with fish length. Hobson & Welch (1995) also report of a positive correlation between fish

length and  $1^{35}$ N in an Arctic char population in Arctic Canada.  $1^{33}$ C in chars from Iittoqqortoormiit, 2000 was significantly higher (p<0.05, analysis of covariance with fish length as covariate) than in the two other populations. No correlation between  $1^{33}$ C and fish length was found. Stable-carbon isotope ratios of primary producers in freshwater food webs are typically less enriched in  $1^{33}$ C than those of marine food webs and this difference is passed on to higher order consumers (Fry and Sherr 1988). The relative high  $1^{33}$ C and the relatively low Hg levels (see chapter 3.3.1) in chars from Ittoqqortoormiit, 2000 give strong indication that these chars are anadrome.

Table 3.2.1. Stable-nitrogen and carbon values (mean  $\pm$  SD) of muscle from Arctic char.

Location	n	<sup>15</sup> N (‰)	⊷ <sup>13</sup> C (‰)
Qaqortoq, 1999	20	$10.4 \pm 0.4$	-21.6 ± 0.8
Zackenberg, 1999	21	9.6 ± 2.0	-20.5 ± 2.1
Ittoqqortoormiit, 2000	20	$10.0 \pm 2.0$	$-17.7 \pm 3.2$

#### 3.3 HEAVY METALS

## 3.3.1 Spatial and temporal trends

Arctic char is the only fresh water species from which new data are available since AMAP phase I.

## Cd

Cd concentrations in muscle of landlocked (fish living their whole life in freshwater) Arctic char from Zackenberg in 1999 was low (0.002 mg/kg ww).

## Hg/Se

Hg and Se concentrations were determined in muscle of landlocked populations from Isortoq, southwest Greenland, Zackenberg, northeast Greenland in 1999 and Ittoqqortoormiit, central east Greenland in 2000. Hg concentrations in Arctic char from Isortoq were higher than in fish from Zackenberg and especially Ittoqqortoormiit (Figure 3.3.1). Also in AMAP I the highest Hg concentrations in muscle of Arctic char were found in southwest Greenland (Riget et al. 2000b). The very low Hg levels found in the chars from Ittoqqortoormiit (10 times lower than in Isortoq) indicates that these chars may not be landlocked. Riget et al. (2000b) found that Hg levels in anadrome chars were 10-15 times lower than in landlocked char populations from the same area. Stable isotopes also indicated that these chars probably are anadrome (see chapter 3.2).

Hg concentrations in lake resident Arctic char populations in Greenland appear to be at the same levels as found in Arctic Canada and somewhat higher than in Finnish Lapland, Iceland, Norway, Russia and Sweden (Riget et al. 2000b).

#### Temporal trends

No time series of Cd concentrations in Arctic char exist.

Hg concentrations in Arctic char from Isortoq in 1999 can be compared with those found in 1994 and 95. No significant difference was found in Hg concentrations between the years (ANCOVA on log-transformed data, p=0.06).



Figure 3.3.1. Hg concentraions (mg/kg ww) in landlocked (except Ittoqqortoormiit 2000) Arctic char in Greenland (adjusted to 40cm length)

## 3.4 Organochlorines

In AMAP phase I, OCs were determined in four landlocked Arctic char from Avanersuaq, Nuuk, Isortoq (Qaqortoq) and Tasiilaq (Cleemann et al. 2000b). In general, the levels of  $\Sigma$ PCB,  $\Sigma$ DDT,  $\Sigma$ CHL and to a less extent HCB were higher in chars from east Greenland than in chars from west Greenland, whereas.  $\Sigma$ HCH levels were highest in chars from west Greenland. During AMAP phase II, OCs were analysed in chars from Isortoq and Zackenberg (east Greenland) sampled in 1999 and from Ittoqqortoormiit in 2000 (Appendix B). The OC analyses were conducted by NWOC.

## 3.4.1 Levels and spatial trends

The OC levels in landlocked Arctic char muscle were in the same range as found in muscle of marine fish species such as Atlantic cod, redfish, Atlantic salmon, capelin and Greenland halibut (Appendix B).

The OC levels in char from Isortoq (west), Zackenberg and Ittoqqortoormiit (east) sampled in 1999 and 2000 showed no large differences among locations, although chars from Ittoqqortoormiit tended to have higher levels of  $\Sigma$ PCB-10,  $\Sigma$ DDT,  $\Sigma$ CHL,  $\Sigma$ HCH, and HCB. Thus 1999 and 2000 results do not confirm higher OC levels in chars from east than from west Greenland as seen in 1994. Figure 3.4.1 shows length normalised  $\Sigma$ PCB-10 and  $\Sigma$ DDT concentrations in female char (expressed on lipid basis).



Figure 3.4.1. ΣPCB-10 (blue) and ΣDDT (red) in landlocked female Arctic char in Greenland (adjusted to 40 cm length).

Spatial comparisons of contaminant levels in Arctic char are complicated by the fact that char may be found in two or three co-existing forms which may differ in size, habitat use, diet, reproductive strategy and growth. The occurrence of sympatric forms is influenced by the availability of ecological niches, a parameter, which in turn is dependent on lake morphometry (Riget et al. 2000c). Despite these difficulties, the OCs levels in Arctic char in Greenland appear to be lower than found in Canada, but higher than found in Sweden and Finland (Cleemann et al. 2000b).

## 3.4.2 Temporal trends

The Arctic char population in Qaqortoq was also analysed for OCs in 1994 (Cleemann et al. 2000b). NERI performed the chemical analyses. Table 3.4.1 summarises the results of statistical tests of differences in mean OC levels between

1994 and 1999. Prior to the test, data were logarithmic transformed. If the log-OC concentrations were significantly dependent on fish length an analysis of covariance (ANCOVA) was performed, otherwise an analysis of variance (ANOVA) was performed.

All OC concentrations, except HCB in females, were higher in chars from 1994 than from 1999. For  $\Sigma$ HCH and  $\Sigma$ CHL both in females and males and for males  $\Sigma$ DDT, the difference was significant at the 1% level. In females, the difference in  $\Sigma$ DDT between years was significant at the 5% level.

Table 3.4.1. Results of statistical tests for difference in mean OC concentrations in Arctic chars sampled in Qaqortoq 1994 and 1999. \* denotes significance at 5% level and \*\* denotes significance at 1% level. The power of the test is given if no significant difference was found.

		Trend	Test	Significance (p)	Power (p)
НСВ	female	94<99	ANOVA	0.14	0.07
	male	94>99	ANOVA	0.50	0.15
THCH	female	94>99	ANOVA	<0.01**	-
	male	94>99	ANOVA	<0.01**	
ICHL	female	94>99	ANCOVA	<0.01**	
	male	94>99	ANOVA	<0.01**	
<b>I</b> DDT	female	94>99	ANCOVA	0.03*	
	male	94>99	ANCOVA	<0.01**	
<b>LPCB-10</b>	female	94>99	ANCOVA	0.10	0.64
	male	94>99	ANCOVA	0.05	0.82

 $\Sigma$ HCH = , , -HCH

 $\Sigma$ CHL = oxychlordane, trans-chlordane, cis-chlordane, cic-nonachlor, trans-nonachlor  $\Sigma$ DDT = p,p-DDE, p,p-DDD, p,p-DDT

 $\Sigma$ PCB-10 = congeners 28, 31, 52, 101, 105, 118, 138, 153, 156, 180

#### 3.5 RADIONUCLIDES

Table 3.5.1 and 3.5.2 and Figure 3.5.1 present average concentrations of <sup>137</sup>Cs and <sup>90</sup>Sr in fresh water sampled in 4 Greenland regions and the Faroe Islands and <sup>137</sup>Cs in Arctic char caught in northeast and southwest Greenland. The data indicate a large geographical variability, but reproduce the same trends as seen in the previous AMAP assessment. The highest concentrations of <sup>137</sup>Cs and <sup>90</sup>Sr in water are found in south and southwest Greenland, where the global fallout was highest. This is concurrent with the highest precipitation rates in these areas. The global fallout showed <sup>137</sup>Cs / <sup>90</sup>Sr activity ratios around 1.5. The lower ratios in fresh water are due to the larger mobility in the drainage area and the lower association to sedimenting particles of Sr. The present Greenlandic levels vary between 0.03 and 0.46 indicating a large variability in drainage area and lake characteristics.

By comparing <sup>137</sup>Cs concentrations in Arctic char and fresh water from the same sites, bioaccumulation factors around 2800, 37000 and 12000 Bq kg<sup>-1</sup> fresh char meat / Bq L<sup>-1</sup> water (or L kg<sup>-1</sup>) were calculated for Zackenberg, Isortoq and Itinnera, respectively. A relatively high bioaccumulation factor and a long environmental half life for radiocaesium is expected, (Ugedal et al. 1995, Rowan et al. 1998, Jonsson et al. 1999), but the extremely high bioaccumulation factors in south and southwest Greenland are noteworthy. Caesium is transferred preferentially via food and is biomagnified along food chains. The accumulation in fresh water fish is enhanced due to several ecological reasons, e.g. low ionic content, slow growth rates, food choice, age and size (Ugedal et al. 1995, Rowan et al. 1998).

The levels at Isortoq and Itinnera are similar to observations in the previous AMAP assessment (Aarkrog et al. 1997), where it could be concluded that only 10% of the Isortoq value was due to Chernobyl derived <sup>137</sup>Cs, i.e. the high levels are originating from global fallout in the 1950's and 1960's. As large variations between individuals and between different lakes can be expected, it is likely that other lakes in south Greenland will show even higher <sup>137</sup>Cs levels in Arctic char, especially clear-water, low-ionic oligotrophic lakes from areas with a high precipitation.

The concentrations of <sup>137</sup>Cs in fresh water fish are of no serious radiological concern. However, an annual consumption of 10 kg of the Isortoq char will cause an annual radiation dose of 10  $\mu$ Sv corresponding to a radiological risk which is considered to be at the limit of regulatory concern (EU, 1996).



Figure 3.5.1. <sup>137</sup>Cs and <sup>90</sup>Sr in lake water and <sup>137</sup>Cs in landlocked Arctic char.

REGIONS.							
Location	Region	Year	<sup>137</sup> Cs		9°Sr		
	-		Bq m⁻³	SD	Bq m <sup>-</sup> ³	SD	n
Faroe Islands	FR	1999	2.41	1.55	2.96	1.96	3
Zackenberg	NE	1999	0.27	0.07	1.62	0.17	3
Isortoq	SW	1999	2.10	0.16	4.57	0.45	4
ltinnera	CW	1999	1.73	0.14	5.02	0.11	3
Lake Crescent	NW	1999	0.16	0.01	5.17	0.38	3

Table 3.5.1. Average concentrations of  $^{\rm 137}\text{Cs}$  and  $^{90}\text{Sr}$  in fresh water sampled in the 5 regions.

IABLE 3.5.2. CS-137 (BQ / KG FRESH WEIGHT) IN LANDLOCKED ARCTIC CHAR							
Species	Location	Region	Year	<sup>137</sup> Cs Bq kg <sup>-1</sup> fr.w.	SD	n	
Arctic Char	Zackenberg	NE	1999	0.77	0.71	3	
Arctic Char	Isortoq	SW	1999	79	18	9	
Arctic Char	ltinnera	CW	1999	21	6	2	

Conclusions and recommendations

- <sup>137</sup>Cs / <sup>90</sup>Sr activity ratios in fresh waters have decreased from the fallout level around 1.5 to the present levels varying between 0.03 and 0.46. This indicates a large variability in drainage area and lake characteristics.
- Due to special environmental conditions, <sup>137</sup>Cs from global fallout is still transferred to landlocked Arctic char with extremely high efficiency in south Greenland.
- Radionuclide concentrations should be examined in landlocked Arctic char from a number of lakes in south Greenland preferentially oligotrophic, low-ionic lakes from areas with a high precipitation rate. In addition to <sup>137</sup>Cs, the natural radionuclides <sup>210</sup>Po and <sup>226</sup>Ra should be assessed in selected samples.

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## 4 Marine Environment

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#### 4.1 INTRODUCTION

This assessment includes a substantial amount of new heavy metals and OC data in Greenland marine biota, which were collected as part of the following AMAP projects: "Biological core programme", "Temporal time trend programme", "Contaminants in Greenland human diet", "Non-halogenated organic Substances in the Greenland Environment", "Population structure of west Greenland narwhals", "Population structure of Atlantic minke whales" and "Effects of Contaminants in the Greenland Sea Polar Bear". Radionuclides were collected in the projects: " Radionuclides, remaining phase 2 data, 2001","Radionuclides 2000","Anthropogenic radionuclides in Greenland and the Faroe Islands" and "Thuleundersøgelse-1997".

The description of contaminant levels, spatial trends and short-term temporal trends focuses on the heavy metals Cd and Hg (Se) and on the organochlorines  $\Sigma$ PCB,  $\Sigma$ DDT,  $\Sigma$ HCH, HCB and  $\Sigma$ CHL. Appendices A and B shows descriptive statistic of the new available data of heavy metals and organochlorines, respectively. Stable isotopes have been analysed in order to facilitate the interpretation of levels and trends. The radionuclides focus on <sup>137</sup>Cs, <sup>99</sup>Tc, <sup>90</sup>Sr and <sup>239,240</sup>Pu in components of the marine environment and one section deals with plutonium in Bylot Sound in the Thule area because of a nuclear accident here in 1968. Furthermore, one section deals with Pb contamination of seabirds from hunting with lead shot. One section summarizes the use of contaminant signatures beside other signatures (genetic, stable isotopes, fatty acids) to deduce population structure of minke whales and narwhals in Greenland waters.

#### 4.2 STABLE ISOTOPES

Stable-nitrogen and stable-carbon isotope ratios were measured in muscle of ringed seal (*Phoca hispida*) and black guillemot (*Cepphus grylle*) (see Table 4.2.1) according to Hobson et al. (1997) at the laboratory of Prairie and Northern Wildlife Research Center, US. Stable isotopes data can be informative about feeding preferences and trophic level (Hobson & Welch, 1995). The reason is that the abundance of  $\bullet^{15}$ 

(<sup>15</sup>N/<sup>14</sup>N) in the tissues of consumers is typically enriched over that in their prey owing to the preferential excretion of the lighter <sup>14</sup>N during protein transamination and deamination (Hobson & Welch ibid). Different feeding preferences among populations or between years may lead to different levels of bio-accumulating contaminants. Therefore information about stable isotopes is useful when interpretation contaminant levels.

Table 4.2.1. Stable-nitrogen and carbon values (mean  $\pm$  SD) of muscle from ringed seal and black guillemot.

Location	n	<sup>15</sup> N (‰)	<sup>13</sup> C (‰)
Ringed seal			
Qeqertarsuaq, 1994	38	14.2 ± 0.6	-18.7 ± 0.3
Qeqertarsuaq, 1999	20	$14.4 \pm 0.8$	$-19.2 \pm 0.4$
Qeqertarsuaq, 2000	20	14.2 ± 0.5	-19.1 ± 0.2
Avanersuaq, 1994	25	16.0 ± 0.9	-18.5 ± 0.4
Avanersuaq, 1998	21	16.6 ± 0.4	-18.9 ± 0.7
Ittoqqortoormiit, 1999	20	14.5 ± 1.7	-20.3 ± 0.3
Ittoqqortoormiit, 2000	19	15.9 ± 0.4	-20.2 ± 0.4
<u>Black guillemot</u>			
Qeqertarsuaq, 1999, juv	2	13.4 ± 1.3	-19.4 ± 0.0
Qeqertarsuaq, 1999, adult	7	14.2 ± 0.8	-19.6 ± 0.4
Qeqertarsuaq, 2000, adult	18	13.5 ± 0.4	-20.3 ± 0.4
lttoqqortoormiit, 2000, juv	8	13.7 ± 0.4	-22.8 ± 0.3
Ittoqqqortoormiit, 2000, adult	13	$13.9 \pm 0.3$	-22.1 ± 0.6

## Ringed seal

An analysis of covariance (factor: location combined with sampling year, covariate: age allowing different linear relationships between isotopes ( $\ddagger^{15}$ N and  $\ddagger^{13}$ C) and age among samples) revealed a complicated relationship between both  $\ddagger^{15}$ N and  $\ddagger^{13}$ C and age. In some samples, the relationship between isotopes values and age was negative while in others the relationship was positive. Because of this uncertainty of age dependency, the pairwise test of LSMEAN (least square mean) values was performed to test of differences in mean  $\ddagger^{15}$ N and  $\ddagger^{13}$ C among samples. The LSMEAN are estimated age adjusted values (SAS 1999-2001). The results of the statistical comparisons are shown in Table 4.2.2.

Table 4.2.2. Results of pair-wise comparisons (age adjusted values) between samples for <sup>15</sup>N and <sup>13</sup>C in ringed seal muscle. Samples are written in decreasing concentrations order and samples underlined were not significant different at the 5% level. Ava = Avanersuaq, Itt = Ittoqqortoormiit, Qeq = Qeqertarsuaq.

™N Ava98	Ava94	lttoo	Qeq99	ltt99	Qeq94	Qeqoo
<sup>13</sup> C Ava94	Qeq94_	Ava98	Qeq99	Qeqoo	Ittoo	ltt <u>9</u> 9

Both  $\Rightarrow^{15}$ N and  $\Rightarrow^{13}$ C values showed significant spatial and temporal differences. The ringed seals from Avanersuaq had higher  $\Rightarrow^{15}$ N that those from the other areas (especially in 1998) which indicate that these seals had fed at a relatively higher trophic level. One explanation may be the relatively high age (mean 9.2 years) of the seals from Avanersuaq in 1998. The ringed seals from Ittoqqortoormiit had lower  $\Rightarrow^{13}$ C values compared to those from the other areas. Carbon isotopes ratios can reflect input of dietary resources from inshore versus offshore areas (Hobson et al. 1997), and therefore indicate that the Ittoqqortoormiit seals had been relatively more

offshore. In both Avanersuaq and Ittoqqortoormiit significant differences in  $\div^{15}$ N values were seen between sampling years. This was also the case of  $\div^{13}$ C values in Avanersuaq and Qeqertarsuaq. These results have to be taken into account when evaluating spatial and temporal trends of heavy metals and OC levels.

#### Black guillemot

Analysis of variance was performed in order to test differences in mean  $\ddagger^{15}N$  and  $\ddagger^{13}C$  values among samples. The test was performed for juvenile and adult birds separately. Tukey's *post hoc* test was used to detect which samples differed from each other (Table 4.2.3).

Table 4.2.3. Results of Tukey's *post hoc* test between samples for  $^{15}N$  and  $^{13}C$  in black guillemot muscle. Samples are written in order of decreasing concentrations and samples underlined were not significantly different at the 5% level. Itt = Ittoqqortoormiit, Qeq = Qeqertarsuaq.

- <sup>15</sup> N		1.1.		,	
	Qeq99	<i>adult</i> Ittoo	Qeqoo	Juvenile Ittoo	Qeq99
<sup>13</sup> C					
-	Qeq99	Qeqoo	Ittoo	Qeq99	Ittoo

 $\downarrow$ <sup>15</sup>N values showed significant differences between 1999 and 2000 in black guillemot from Qeqertarsuaq indicating that the 1999 birds to have been feeding at a relatively higher trophic level. The  $\downarrow$ <sup>13</sup>C values were significantly different in all cases with the lowest values in Ittoqqortoormiit as were the case with ringed seal.

#### 4.3 HEAVY METALS

In AMAP phase I, heavy metals were determined in marine sediment, blue mussels (*Mytilus edulis*), shorthorn sculpin (*Myoxocephalus quadricornis*), polar cod (*Boreogadus saida*), glaucous gull (*Larus hyperboreus*), Icelandic gull (*Larus glaucoides*) and ringed seals at four locations in Greenland (Riget et al. 2000e). In general, lead levels were found to be low, whereas levels of cadmium, mercury and selenium in Greenland marine biota were high. Cadmium and mercury concentrations increase in higher trophic levels whereas this is not the case for lead and selenium (Dietz et. al. 1996). There was a tendency of higher mercury concentrations in east Greenland, whereas the highest cadmium concentrations were found in central west Greenland (Riget et al. ibid).

## 4.3.1 Levels and spatial trends

#### 4.3.1.1 Arsenic in marine sediments

The surface layer of Greenland sediments has been analyzed for arsenic. The background was that very high concentrations of arsenic had been found in some surface sediment from the Pechora Sea (Loring et al. 1995). At a station close to Guba Chernaya the concentration of arsenic was 308 mg/kg. The concentrations decreased seawards from this station to background values of less than 20 mg/kg. Although arsenic data were not available for the other circumpolar sediments, the Pechora Sea Arsenic concentrations were considerably higher than those reported (6 mg/kg) for the Gulf of St. Lawrence sediments. The data indicated that arsenic is enriched in the core samples either by natural and/or anthropogenic processes in the surface and near surface layers. The arsenic correlates with the plutonium derived from nuclear weapons under water tests performed at Guba Chernaya.

In a Norwegian AMAP study Maage et al. (unpubl.) found high arsenic concentrations at some locations in the Barents Sea near Svalbard far from nuclear weapon test sites. Concentrations between 50 and 80 mg/kg were regularly found just south of Svalbard. Maage et al. found a mean value of 22 ( $\pm$  22) mg/kg. Interestingly, looking at the As/Li ratio (mean 0.59  $\pm$  0.42), three of the stations closest to the south tip of Novaya Semlya showed relatively high values with two stations showing higher As/Li-ratios than 1.5. This suggests that a relatively large area around the Noveya Zemlya have elevated As sediment values. The other parts of the Barents Sea as such do not seem to have elevated arsenic in sediments even though high absolute values also were seen along King Carls Land east of Svalbard.

The sediment samples from Greenland were collected in the period 1985 to 1994. The top 1cm was analysed for total arsenic by NERI. Loring & Asmund (1996) have previously reported results for several other trace elements in these samples. Analytical results for arsenic and mercury are shown in Table 4.3.1. The average and standard deviation of the arsenic concentrations were 7.87 mg/kg and 5.68 mg/kg. This is much lower than reported by Maage et al. (unpubl.) for the Barents Sea, and comparable to the Gulf of St. Lawrence. The highest concentration found was 24.6 mg/kg. The conclusion is that Greenland marine sediments are not enriched in arsenic as reported for large areas of the Barents Sea.

ID-No	As	Ησ	ID-No	As	- Ησ
12 110	mg/kg	mg/kg		mg/kg	mg/kg
4001	1.02	0.0430	7/10	6.72	0.0176
4001	1.09	0.0512	7419	8.91	0.0207
4015	9.60	0.0463	7420	8.92	0.0235
4015	10.30	0.0472	7/22	17.29	0.1778
4016	10.72	0.0375	7/22	19.83	0.1071
4028	9.27	0.1082	7423	3.71	0.0219
4028	0.37	0.1071	7/23	4.58	0.0328
4029	9.36	0.0561	74-5	4.58	0.0200
4020	0.61	0.0510	7425	10.88	0.0456
4046	8 05	0.0200	7425	11.23	0.0481
4047	5.62	0.1035	7426	3 73	0.0700
4048	5.02	0.0204	7446	2 11	0.0562
4040	6 56	0.0568	7440	3.40	0.0563
4049	17 50	0.0215	7440	12 66	0.0012
4071	22 84	0.0515	7447	13.00	0.0915
4072	23.04	0.1525	7447	12.00	0.0935
4072	15.62	0.1511	7440	8 25	0.02/5
4073	15.02	0.0492	7400	8.25	0.0990
4073	0.51	0.0495	7400	0.53	0.0965
4074	2.62	0.0148	7407	5.30	0.2661
4074	3.12	0.0125	7469	4.05	0.0761
4075	2.01	0.0129	13824	8.21	0.0409
5046	9.02	0.0265	13832	5.60	0.0456
5047	11.12	0.0173	13832	6.76	0.0467
5047	12.54	0.0246	16964	3.38	0.0233
5063	2.27	0.0263	16964	3.58	0.0265
5079	1.83	0.0380	16970	2.60	0.0048
5081	1.26	0.0100	16970	2.61	0.0046
5081	1.53	0.0101	18890	2.07	0.0079
7321	18.43	0.3328	18890	2.96	0.0084
7417	5.09	0.0682	18891	2.40	0.0047
7418	5.50	0.0421	18891	2.87	0.0058

TABLE 4.3.1. MERCURY AND ARSENIC IN SURFACE SEDIMENTS FROM GREENLAND

## 4.3.1.2 Cd

#### Invertebrates

Cd concentrations have been determined in blue mussels (*Mytilus edulis*), Iceland scallop (*Chlamys islandica*) and queen crab (*Chionoetes opilo*) (Appendix A). Cd in blue mussels from Qeqertarsuaq ranged from 0.55 to 2.27 mg/kg ww increasing with length of the mussels as previously reported by Riget et al. (1996). Cd levels in blue mussels from Qeqertarsuaq are relative high compared to other locations in Greenland, however, it confirms the relative high Cd levels previously reported here in marine biota (Riget et al. 2000e). The concentration of 2.04 mg/kg ww found in Iceland scallop was lower than previously found in this species (Dietz et al. 1996). The Cd concentration in queen crab muscle was low (0.04 mg/kg ww), whereas it was high (5.1 mg/kg ww) in crab hepatopancreas.

## Marine fish

Cd concentrations have been determined in shorthorn sculpin, Atlantic cod (*Gadus morhua*), Atlantic salmon (*Salmo salar*), Greenland halibut (*Reinhardtius hippoglossoides*) and capelin (*Mallotus villosus*). In muscle, Cd concentrations in all species were low (below 0.003 mg/kg ww). In liver, Cd concentrations ranged from 0.05 mg/kg ww in Atlantic cod to 1.40 mg/kg in shorthorn sculpin. These values are in the range observed in 21 different marine fish species from Greenland (Riget et al. 1997). Cd concentrations in sculpin liver from Qeqertarsuaq were higher in both 1999 and 2000 than in sculpin from Ittoqqortoormiit. However, these differences were not significant at the 5% level (t-test on logarithmic transformed data, 1999: p=0.34, 2000-male: p=0.25, 2000-female: p=0.07).

## **Seabirds**

Cd concentrations have been determined in black guillemot (*Cepphus grylle*) liver and kidney from Qeqertarsuaq in 1999 and 2000 (only liver) and in black guillemot egg from Ittoqqortoormiit in 2000. In liver Cd concentrations ranged from 1.85 mg/kg ww in adults 1999 to 3.72 mg/kg ww in adults 2000. In kidney, Cd concentrations were higher than in liver (15-22 mg/kg ww). These values were within the range observed previously in that species (Dietz et al. 1996). In 1999, Cd concentrations in juvenile were surprisingly higher than in adults; usually the trend is opposite (Nielsen & Dietz 1989). In eggs, Cd concentrations were low (0.001 mg/kg ww). Cd concentrations in black guillemot liver from Greenland were similar to those observed in the Faroe Islands, Canada and the Barents Sea (AMAP 1998).

#### Marine mammals

Cd concentrations have been determined in ringed seal (*Phoca hispida*), narwhal (*Monodon monoceros*), beluga (*Delphinapterus leucas*), minke whale (*Balaenoptera acutorostrata*) and polar bear (*Ursus maritimus*) (Appendix A).

Cd concentrations in ringed seal liver were available from Qegertarsuag and Ittoqqortoormiit in 1999 and 2000, and from Avanersuaq 1998. In blubber, Cd concentrations were determined in seal blubber from Qegertarsuag in 2000. Cd concentrations in liver ranged from 8.22 mg/kg ww in seals from Qegertarsuag in 2000 to 16.8 mg/kg ww in seals from Qegertarsuag in 1999. Cd concentrations in seal blubber was low (0.011 mg/kg ww). These values are within the range observed previously in ringed seals (Dietz et al. 1996). Cd concentrations in ringed seals increase with age (Diet et al. 1998). Therefore, seals has been divided into age groups (0, 1-3, 4-6 and above 6 years old) before testing for differences in mean Cd concentrations between Qegertarsuag and Ittoggortoormiit in 1999 and 2000. Cd concentrations were higher for all age groups and both years in seals from Qegertarsuag than in seals from Ittoqqortoormiit. However, no significant (at 5% level) differences were found (t-test on logarithmic transformed data, t-test only performed if n>1). The Cd concentrations in seals from Avanersuag 1998 were similar to those from Ittoqqortoormiit, however, the relative high average age of Avanersuag seals should be noted. In general, Cd concentrations in ringed seals from west and east Greenland are similar to seals from the Canadian Eastern Arctic but higher than in Alaska and Svalbard.

Data of Cd concentrations in narwhals are available from Avanarsuaq, Balgoni Island (Melville Bay), Uummannaq, Kitsissuarsuit (Disko Bay) and Saqqaq (see also chapter 4.7.1).


Figure 4.3.1. Relationship between CD concentrations (mg/kg ww) and growth layer (age). Lines represent LOWESS smoother (from Riget et al. 2002)

Cd concentrations in muscle, liver and kidney tissue increase during the first 3 to 4 years of the narwhals life, after which a relatively constant Cd level is observed (a tendency of a slightly decrease can be seen) (Figure 4.3.1). In all tissues (muscle, liver and kidney) the Cd concentrations were significantly higher in females than in males (Riget et al. 2002). A consistent difference between Avanersuaq and Uummannaq was not found in any of the tissues (Figure 4.3.2). In muscle there was significant difference between the samples in 1993 and 1984 from Avanersuaq (Riget et al. 2002). However, the sample in 1985 was not different from the two others. In the sample from Uummannaq 1993, Cd concentrations, especially in females, were higher than in the other samples. Therefore, the year-to-year variation exceeded the geographical differences. In general, the Cd levels in the Greenland narwhals were within the range found in Arctic Canada (Wagemann et al. 1983, 1996).



Figure 4.3.2. Mean (mg/kg ww)  $\pm$  standard error of Cd concentrations in narwhals by area, year and sex (from Riget et al. 2002).

Cd concentrations in blubber of beluga were low (<0.005 mg/kg ww).

Cd concentrations in muscle, liver, kidney and baleen of minke whales from the North Atlantic and European Arctic were determined as a part of a multidisciplinary study of population structure of minke whales. Minke whales from west and east Greenland, Jan Mayen, North Sea, Vestfjorden/Lofoten, west Svalbard and the Barent Sea) were included (Born et al. submitted). Only few statistically significant differences among the above mentioned locations were found, however, there were a tendency of Cd concentrations in tissues of Greenland whales to be higher than in whales from the other locations (Born et al. submitted).

Cd concentrations in muscle, liver and kidney of polar bears (*Ursus maritimus*) from Ittoqqortoormiit in 1999 and 2000 have been determined (Appendix A). Cd concentrations in muscle were low (below 0.03 mg/kg ww). In liver, Cd concentrations ranged from 0.73 to 1.82 mg/kg ww) and in kidney from 20.1 to 36.7 mg/kg ww. The Cd levels in all tissues were in the range observed previously (Dietz et al. 2000a). Dietz et al. (ibid) compared Cd levels in polar bears from Avanersuaq with bears from Ittoqqortoormiit and found significantly higher concentrations in liver tissue from Avanersuaq, while no significant difference was found in kidney. Based on age normalised Cd concentrations, a trend could be seen of increasing Cd concentrations in polar bear liver from west Canada to east Canada and west Greenland and then lower Cd levels in east Greenland and Svalbard bears (Dietz et al. 2000a).

## 4.3.1.3 Hg and Se

In this chapter most focus is given to Hg levels. However, in most cases involving determination of Hg in biota, Se levels are also determined. In most Arctic samples, Se is present in a substantial surplus compared to Hg on a molar basis. However, in tissues of marine mammals from Greenland with high Hg concentrations (above approx. 10 nmol/g), a 1:1 molar ratio was found (Dietz et al. 2000b). Se is regarded as an antagonist to Hg and probably Se plays an important role with detoxification of Hg by formation of mercuric selenide complexes (Björkman et al. 1995, Wagemann et al. 1998).

#### Invertebrates

Hg and Se concentrations have been determined in the species blue mussel, Iceland scallop, queen crab and deep sea shrimp (*Pandalus borealis*) (Appendix A). Hg concentrations ranged from 0.011 mg/kg ww in blue mussels (4-5cm) to 0.096 mg/kg in queen crab. Se concentrations in muscle tissue ranged from 0.13 mg/kg ww in Iceland scallop to 0.60 mg/kg ww in queen crab. These values were within the range observed previously in invertebrates from Greenland (Dietz et al. 1996).

#### Marine fish

Hg and Se concentrations have been determined in shorthorn sculpin, Atlantic cod, Greenland cod, Atlantic salmon, Greenland halibut and capelin. In muscle, Hg concentrations ranged from 0.009 mg/kg ww in capelin to 0.154 mg/kg ww in Greenland halibut. In liver, Hg concentrations ranged from 0.007 mg/kg ww in Atlantic cod to 1.51 mg/kg in Greenland halibut. These values are in the range observed in 21 different marine fish species from Greenland (Riget et al. 1997). Shorthorn sculpin have been sampled in Qeqertarsuaq and Ittoqqortoormiit in both 1999 and 2000. In both years, Hg concentrations was significantly higher in Ittoqqortoormiit than in Qeqertarsuaq (t-test on logarithmic transformed data, separated by sex for year 2000, all cases p<0.01).

#### **Seabirds**

Hg and Se have been determined in black guillemot liver and kidney from Qeqertarsuaq in 1999 and 2000 (liver and egg) and in black guillemot eggs from Ittoqqortoormiit in 2000. In liver Hg concentrations ranged from 0.61 mg/kg ww in adults to 1.02 mg/kg ww in juveniles. In kidney, Hg concentrations were 0.54 and 0.51 mg/kg ww in juveniles and adults, respectively. These values were in the higher end of the range observed previously in that species (Dietz et al. 1996). In eggs, Hg and Se concentrations was significantly higher in Ittoqqortoormiit 2000 than in Qeqertarsuaq 1999 (t-test on logarithmic transformed data, Hg: p=0.01 and Se: p=0.008). Hg concentrations in black guillemot liver and eggs from Greenland were similar to those observed in the Faroe Islands, Canada and Franz Josef Land (AMAP 1998).

#### Marine mammals

Hg and Se concentrations have been determined in ringed seal, narwhal, beluga, minke whale and polar bear (Appendix A).

Hg and Se concentrations in ringed seal liver were available from Qegertarsuag and Ittoqqortoormiit in 1999 and 2000 and from Avanersuaq in 1998. In blubber, Hg and Se concentrations were determined in seals from Qegertarsuag in 2000. Hg concentrations in liver ranged from 1.78 mg/kg ww in seals from Qegertarsuag to 7.13 mg/kg ww in seals from Ittoqqortoormiit. Hg concentrations in seal blubber were very low (<0.005 mg/kg ww). These values are within the range observed previously in ringed seals (Dietz et al. 1996). Hg concentrations in ringed seals increase with age (Diet et al. 1998). Therefore, seals has been divided into age groups (0, 1-3, 4-6 and above 6 years old) before testing for differences in mean Hg concentrations between Qegertarsuag and Ittoggortoormiit in 1999 and 2000. In 1999 no significant (at 5% level) difference in Hg and Se concentrations were found between seals from Qegertarsuag and Ittogqortoormiit, however, for age groups 1-3 and 4-6 years the highest concentrations were found in Ittoqqortoormiit. In 2000, the Hg and Se concentrations were significantly (p < 0.01) higher in Ittoqqortoormiit than in Qeqertarsuaq for age group 1-3, which was the only age group allowing statistical testing (t-test on logarithmic transformed data, t-test only performed if n>1). The Hg and Se concentrations in seals from Avanersuag 1998 were high compared to previously findings in northwest Greenland (Dietz et al. 1996). However, the relative high average age (9.2 years) of Avanersuaq seals and the indication of feeding at a relatively higher trophic level (see chapter 4.2) should be noted. The circumpolar pattern of Hg levels in ringed seal showed the highest levels in Canadian Eastern Arctic, although with high local variability and lower levels in west and east Greenland, Alaska and Svalbard (AMAP unpublished).

Data of Hg and Se concentrations in narwhals are available from Avanarsuaq, Balgoni Island (Melville Bay), Uummannaq, Kitsissuarsuit (Disko Bay) and Saqqaq (see also chapter 4.7.1). Hg and Se concentrations in muscle, liver and kidney tissue showed the same relationship with age as shown in Figure 4.3.1 for Cd. In the first 3 to 4 years of the narwhals life the Hg and Se concentrations increase, after which a relatively constant level is observed. Both Hg and Se concentrations in liver were significantly higher in females than in males, while no sex differences were found in muscle and kidney (Riget et al. 2002). As was the case with Cd, no consistent difference between Avanersuaq and Uummannaq was found in either tissue. The between years variation at one location seem to be larger than the variation between location. In general, the Hg and Se levels in the Greenland narwhals were within the range found in Arctic Canada (Wagemann et al. 1983, 1996).

Hg and Se concentrations in muscle, liver, kidney and baleen (except Se) of minke whales from the North Atlantic and European Arctic were determined as a part of a multidisciplinary study of population structure of minke whales. Minke whales from west and east Greenland, Jan Mayen, West Svalbard, the Barents Sea, Vestfjorden/Lofoten and the North Sea) were included (Born et al. submitted). Irrespective of gender, Hg and Se concentrations in west Greenland whales were consistently low compared to the other areas (Table 4.3.2). Se and Hg concentrations were positively correlated in all tissues (p<0.001). No significant differences were found of the elements or tissues between west and east Greenland whales. The highest Hg and Se concentrations in most tissues were found in whales from the North Sea and Jan Mayen. Hg and Se concentrations in muscle, liver, kidney and hair (only Hg) of polar bears from Ittoqqortoormiit in 1999 and 2000 have been determined (Appendix A).

Table 4.3.2. Results of pair-wise comparisons (length adjusted values) between areas for Hg and Se in tissues of female and male minke whales. Areas underlined were not significant different at the 1% level. Abbreviations: WG = west Greenland, CG = central east Greenland, CM = Jan Mayen, EN = North Sea, EC = Vestfjord/Lofoten, ES = Svaldbard, EB = Barents Sea, EAST = CM+ES+EB (redrawn from Born et al. in press).

Hg		Male					Female	9			
Muscle	EN	EAST	EC	WG	CM	EN	EB	EC	CG	WG	ES
Liver	EN	EAST	EC	WG	СМ	EN	EC	WG	EB	ES	CG
Kidney	EN	EAST	EC	WG	СМ	CG	EN	EB	EC	WG	ES
Baleen	EAST	EN	WG.	-	ES	СМ	EB	EN	CG	WG	
Se											
Muscle	EN	EAST	EC	WG	EN	СМ	EB	ES	EC	WG	CG
Liver	EN	EC	EAST	WG	EN	EB	ES	WG	EC	СМ	CG
Kidney	<u>EN</u>	EAST	EC	WG	EN	EB	ES	EC	CM	WG	CG

Hg concentrations in muscle were lower than in liver and kidney. In liver, Hg concentrations ranged from 4.02 to 16.4 mg/kg ww and in kidney from 8.9 to 29.8 mg/kg ww, lowest in subadult bears. Both Hg and Se levels in muscle, liver and kidney were within the range observed previously (Dietz et al. 2000a). Dietz et al. (ibid) compared Hg and Se levels in polar bears from Avanersuaq with bears from Ittoqqortoormiit and found a tendency of higher Hg and Se concentrations in liver tissue from Avanersuaq. Based on age normalised Hg concentrations, a trend could be seen of increasing Hg concentrations in polar bear liver from Svalbard to east Greenland over west Greenland, peaking in bears from south-west Melville Island. Further eastward the Hg concentrations decreased and the lowest concentrations were found in the Chukchi Sea (Dietz et al. 2000a).

# 4.3.2 Temporal trend

Time series data of heavy metal concentrations in Arctic biota covering the last 20-30 years are scarce. From Greenland, Riget & Dietz (2000f) tried to assess trends of Cd and Hg in Greenland marine biota, however, only few time series were available and with only few "data points". They concluded that no overall temporal trends in Cd and Hg concentrations were found within the 20-years period. However, Cd concentrations in ringed seals tended to increase in the period late-1970s to mid-1980s and decrease again to the mid-1990s, whereas Hg concentrations tended to increase in the same period. Therefore Riget & Dietz (ibid) interpretated these changes as natural fluctuations caused by shift in feeding behaviour, rather than changes in anthropogenic exposure. During the Greenland AMAP programme

biological samples were collected in 1994 and 1999/2000, and in a few cases earlier comparable samples were available. However, data from only two or three years may not give evidence of temporal changes for several reasons, first of all because two or three "data points" are too few. Based on the results obtained during the Greenland AMAP programme phase I, Riget et al. (2000d) evaluated that a time series of 10-17 years with annual data is required to detect a linear trend of 10% per year with a significance of 5% and a power of 80%. Besides the large individual variability in heavy metal levels often observed in biota, a random year-to-year variability must also be expected. The year to year variability occurs because environmental factors such as temperature, production, prey availability etc. differ between years. Despite these difficulties, it has been useful to compare heavy metal levels obtained in 1994 (AMAP phase I) with those obtained in 1999/2000 and in a few cases even earlier results.

Heavy metal data were logarithmic transformed prior to the statistical analysis. Analysis of covariance was performed in cases were the metals increase with length/age of the animals. Otherwise an analysis of variance or t-test was performed. Pairwise t-test of LSMEAN (least square mean values meaning length adjusted values) or Turkey's *post hoc* test was performed to test for differences between years. In case where the statistical test showed no significant difference, the power of the test was estimated according to Cohen (1977). The statistical power is defined as the probability to detect a significant difference. In this case a significance level of 5% is used.

#### 4.3.2.1 Cd

#### Qegertarsuag

Table 4.3.3 gives an overview of the results of the statistical comparisons of Cd concentrations in Qeqertarsuaq 1994 and 1999/2000. Few statistically significant differences were found. Cd concentrations in blue mussels (7-8 cm) were significantly higher in 1999 than in 1994. In blue mussel significantly higher Cd concentrations were found in 1994 and 2000 than in 1999 indicating high year-to-year variation. This could also be seen in black guillemot where Cd concentrations were significantly higher in 2000 than in 1999. In ringed seals (1-3 years old), Cd concentrations were higher in 1994 than in 1999 and 2000.

Table 4.3.3. Results of statistical tests for difference in mean CD concentrations in marine biota from Qeqertarsuaq. Trend gives the years in the order of decreasing mean concentrations on a logarithmic scale. Years underlined are not significant different \* denotes significance at 5% level and \*\* denotes significance at 1% level. The power of the test is given if no significant difference was found (see text).

Qeqertarsuaq	Trend	Test	Significance	Power
Blue mussel (4-5 cm)	<u>94 99</u>	t-test	0.22	0.30
Blue mussel (5-6 cm)	<u>99 94</u>	t-test	0.66	0.67
Blue mussel (6-7 cm)	<u>99 94</u>	t-test	0.73	0.05
Blue mussel (7-8 cm)	<u>94 99</u>	t-test	0.68	0.07
Blue mussel (8-9 cm)	99 94	t-test	0.05*	
Shorthorn sculpin, liver	<u>94 oo</u> 99	ANCOVA	<0.01**	
Black guillemot, liver, adult	00 99	t-test	<0.01**	
Ringed seal, liver, o yrs	<u>94 00 99</u>	ANOVA	0.21	0.14
Ringed seal, liver, 1-3 yrs	94 <u>99 oo</u>	ANOVA	<0.01**	
Ringed seal, liver, 4-6 yrs	99 00 94	ANOVA	0.61	0.11

### Avanersuaq

Cd concentrations in ringed seals liver were higher for all age groups in 1984/85 than in 1994 and 1998 (Table 4.3.4). However, significant differences were only found for age group 1-3 years where the concentrations in 1984/85 and 1998 were significantly higher than in 1994.

Table 4.3.4. Results of statistical tests for difference in mean Cd concentrations in ringed seals from Avanersuaq. Trend gives the years in the order of decreasing mean concentrations on a logarithmic scale. Years underlined are not significantly different. \* denotes significance at 5% level and \*\* denotes significance at 1% level. The power of the test is given if no significant difference was found (see text).

Avanersuaq	Trend	Test	Significance	Power	
Ringed seal, liver, o yrs	84/85 98 94	ANOVA	0.25	0.30	
Ringed seal, liver, 1-3 yrs	<u>84/85 98</u> 94	ANOVA	<0.01**		
Ringed seal, liver, 4-6 yrs	84/85 94 98	ANOVA	0.71	0.12	
Ringed seal, liver, > 6 yr	84/85 94 98	ANOVA	0.96	0.05	

### Ittoqqortoormiit

Table 4.3.5 gives an overview of the results of the statistical comparisons of Cd concentrations in Ittoqqortoormiit 1986, 1994 and 1999/2000. Cd concentrations in ringed seals 1-3 and 4-6 years old were higher in 1996 than in the later years, however this was only significant from 1999 in case of age group 1-3 years and 1994 and 2000 in case of age group 4-6 years.

Table 4.3.5. Results of statistical tests for difference in mean CD concentrations in shorthorn sculpin and ringed seal from Itoqqortoormiit. Trend gives the years in the order of decreasing mean concentrations on a logarithmic scale. Years underlined are not significantly different. \* denotes significance at 5% level and \*\*

Ittoqqortoormiit	Trend	Test	Sign.	Power
Shorthorn sculpin, liver	<u>99 oo</u>	t-test	0.71	0.06
Ringed seal, liver, 0 yrs	00 99 86 94	ANOVA	0.49	0.22
Ringed seal, liver, 1-3 yrs	<u>86 94 00</u> 99	ANOVA	<0.01**	
Ringed seal, liver, 4-6 yrs	86 99 00 94	ANOVA	<0.01**	
Ringed seal, liver, > 6 yrs	94 86 00 99	ANOVA	0.89	0.10

DENOTES SIGNIFICANCE AT 1% LEVEL. THE POWER OF THE TEST IS GIVEN IF NO SIGNIFICANT DIFFERENCE WAS FOUND (SEE TEXT).

Samples of polar bears tissues have been collected in 5-7 years since 1983. Figure 4.3.3 and 4.3.4 shows mean Cd concentrations in subadult and adult bears, respectively. In both subadult and adult bears no temporal trend is appearent in any of the tissues.



Figure 4.3.3. Mean CD concentrations (+SD) in tissues of subadult polar bears from IttoqQortoormiit.



Figure 4.3.4. Mean CD concentrations (+SD) in tissues of adult polar bears from Ittoqqortoormiit.

# 4.3.2.2 Hg

### Qeqertarsuaq

Table 4.3.6 gives an overview of the results of the statistical comparisons of Hg concentrations in Qeqertarsuaq 1994 and 1999/2000. In blue mussels, Hg concentrations were higher in 1994 than in 1999 except for size group 7-8 cm. However, only for size group 6-7 cm the difference was significant. In shorthorn sculpin no temporal trend was found and in black guillemot no difference was found between 1999 and 2000. In ringed seals, Hg concentrations were higher in 1994 than in 1999 and 2000, however, this was only significant for age group 1-3 years.

Table 4.3.6. Results of statistical tests for difference in mean Hg concentrations in marine biota from Qeqertarsuaq. Trend gives the years in the order of decreasing mean concentrations on a logarithmic scale. Years underlined are not significantly different. \* denotes significance at 5% level and \*\* denotes significance at 1% level. The power of the test is given if no significant difference was found (see text).

Qeqertarsuaq	Tre	nd	Test	Significance	Power
Blue mussel (4-5 cm)		<u>94 99</u>	t-test	0.19	0.36
Blue mussel (5-6 cm)		<u>94 99</u>	t-test	0.31	0.21
Blue mussel (6-7 cm)		<u>94 99</u>	t-test	0.67	0.08
Blue mussel (7-8 cm)		94 99	t-test	0.0.1*	
Blue mussel (8-9 cm)		<u>99 94</u>	t-test	0.20	0.47
Shorthorn sculpin, liver	<u>00</u>	94 99	ANCOVA	<0.01**	
Black guillemot, liver, adult		00 99	t-test	0.70	0.10
Ringed seal, liver, o yrs	<u>94</u>	00 99	ANOVA	0.68	0.10
Ringed seal, liver, 1-3 yrs	94	99 00	ANOVA	<0.01**	
Ringed seal, liver, 4-6 yrs	<u>94</u>	00 99	ANOVA	0.18	0.15

### Avanersuaq

Hg concentrations in ringed seals liver age groups 4-6 and >6 years showed an increasing trend from 1984/85 to 94 and again to 1998, and for both age groups the concentrations in 1984/85 were significantly lower than in 1994 and 1998 (Table 4.3.7). For age group 1-3 years no significant difference was found between 1984/85 and 1994, but the concentrations in 1998 were significantly highest.

TABLE 4.3.7. RESULTS OF STATISTICAL TEST SFOR DIFFERENCE IN MEAN Hg CONCENTRATIONS IN RINGED SEALS FROM AVANERSUAQ. TREND GIVES THE YEARS IN THE ORDER OF DECREASING MEAN CONCENTRATIONS ON A LOGARITHMIC SCALE. YEARS UNDERLINED ARE NOT SIGNIFICANT DIFFERENTLY. \* DENOTES SIGNIFICANCE AT 5% LEVEL AND \*\* DENOTES SIGNIFICANCE AT 1% LEVEL. THE POWER OF THE TEST IS GIVEN IF NO SIGNIFICANT DIFFERENCE WAS FOUND (SEE TEXT).

Avanersuaq	Trend	Test	Significance	Power
Ringed seal, liver, o yrs	<u>98 94</u>	ANOVA	0.56	0.12
Ringed seal, liver, 1-3 yrs	98 <u>84/85 94</u>	ANOVA	<0.01**	
Ringed seal, liver, 4-6 yrs	<u>98 94</u> 84/85	ANOVA	<0.01**	
Ringed seal, liver, > 6 yr	<u>98 94</u> 84/85	ANOVA	<0.01**	

### **Ittoqqortoormiit**

Table 4.3.8 gives an overview of the results of the statistical comparisons of Hg concentrations in Ittoqqortoormiit 1986, 1994 and 1999/2000. Hg concentrations in ringed seals 0, 1-3 and 4-6 years were highest in 2000, however, this was only significant for age group 1-3 years.

Table 4.3.8 Results of statistical test for difference in mean hg concentrations in shorthorn sculpin and ringed seal from Ittoqqortoormiit. Trend gives the years in the order of decreasing mean concentrations on a logarithmic scale. Years underlined are not significantly different. \* denotes significance at 5% level and \*\* denotes significance at 1% level. The power of the test is given if no significant difference was found (see text).

Ittoqqortoormiit	Trend	Test	Sign.	Power
Shorthorn sculpin, liver	<u>00 99</u>	t-test	0.47	0.11
Ringed seal, liver, o yrs	00 99 86 94	ANOVA	0.37	0.20
Ringed seal, liver, 1-3 yrs	oo <u>94 86 99</u>	ANOVA	<0.01*	*
Ringed seal, liver, 4-6 yrs	<u>00 94 86 99</u>	ANOVA	0.10	0.47
Ringed seal, liver, > 6 yrs	<u>86 94 99 oo</u>	ANOVA	0.92	0.06

Samples of polar bears tissues have been collected in 5-7 years since 1983. Figure 4.3.5 and 4.3.6 shows mean Hg concentrations in subadult and adult bears, respectively. In both subadult and adult bears no temporal trends is appearent in any of the tissues.



Figure 4.3.5. Mean Hg concentrations (+SD) in tissues of subadult polar bears from IttoqQortoormiit.



Figure 4.3.6. Mean Hg concentrations (+SD) in tissues of adult polar bears from IttoqQortoormiit.

### 4.4 Organochlorines

In AMAP phase I, OCs were determined in marine sediments, blue mussels, shorthorn sculpin, polar cod, glaucous gull, Icelandic gull and ringed seals at four locations in Greenland (Cleemann et al. 2000a,c,d). In general, OC concentrations (except  $\Sigma$ HCH) were higher in the marine biota from east Greenland than from west Greenland. OCs bioaccumulate and the highest concentrations were found in species at the highest trophic levels.

## 4.4.1 Levels and spatial trend

## Invertebrates

OC concentrations have been determined in the following invertebrate species: blue mussel, shrimp and snow crab (muscle and liver). In general OC levels in invertebrate were lower than in marine fish, seabirds and marine mammals. The highest levels were found in snow crab liver (eg.  $\Sigma$ PCB-10 41 µg/kg ww) and the lowest in shrimp muscle (eg.  $\Sigma$ PCB-10 0.7 µg/kg ww) (Appendix B). Levels of  $\Sigma$ PCB-10,  $\Sigma$ DDT,  $\Sigma$ HCH and HCB) in soft tissue of blue mussels were comparable to levels reported from other Arctic areas as Canada, Iceland and Russia (Cleemann et al. 2000c).

## Fish

Data of OC levels in marine fish are available for Atlantic cod, capelin, Greenland halibut, starry ray (*Raja radiata*), spottet wollfish and shorthorn sculpin (Appendix B). Fish livers had relatively higher levels of OCs than fish muscle. The highest OC levels were found in Greenland halibut (eg.  $\Sigma$ PCB-10 in muscle and liver were 12 and 493 µg/kg ww, respectively). Greenland halibut is a bottom-feeding predator fish, long-lived and with a relatively high lipid content.

OCs have been determined in shorthorn sculpin liver from Qeqertarsuaq and Ittoqqortoormiit sampled in 1999 and 2000, and also from the Qaqortoq area in 2000. The relatively high PCB levels found in sculpins from Qaqortoq may be due to local contaminant sources (Vorkamp pers. com.). The  $\Sigma$ PCB-10,  $\Sigma$ DDT,  $\Sigma$ CHL,  $\Sigma$ HCH and HCB concentrations were higher in sculpins from east Greenland (Ittoqqortoormiit) than from west Greenland (Qeqerarsuaq) (Figure 4.4.1), similar to the pattern found during AMAP phase I (Cleemann et al. 2000c).

## **Seabirds**

OC concentrations have been determined in black guillemot, thick-billed murre (Uria lomvia), common eider (Somateria mollissima), king eider (Somateria spectabilis) and kittiwake (Rissa tridactyla) (Appendix B). Both feeding behaviour and wintering areas of Arctic seabirds may explain species differences in OC levels observed. The lowest levels were found in mussel eating birds as common eider and king eider (eg. king eider muscle  $\Sigma$  PCB-10 6.5 µg/kg ww and liver 8.7 µg/kg ww). Somewhat higher OC levels were found in fish-eating birds as black guillemot (eg. liver  $\sum$  PCB ranged between 27 and 113  $\mu$ g/kg ww). The highest OC levels were found in kittiwake (eg muscle  $\sum$  PCB-10 98 µg/kg ww.) when only including seabirds sampled in west Greenland. The reason probably is that the kittiwake winters in European and Amarican waters, thereby being more exposed to OCs than eiders, guillemot and murres wintering in the Arctic. Levels of  $\sum PCB-10$  in kittiwake liver were similar to east Baffin Island, Canada but lower than found at Bear Island and in Franz Josef Land (Muir & Johansen unpubl.). However, the OC levels were much higher in opportunistic feeders as glaucous and Icelandic gulls analysed during AMAP phase I (Cleemann et al. 2000d). A similar order of increasing OC levels of eider < kittiwake < glacous gull have been reported from the Barents Sea and partly from Arctic Canada (AMAP 1998).



Figure 4.4.1. OC concentrations in liver of shorthorn sculpin, black guillemot and ringed seal from west Greenland (Qeqertarsuaq – light grey) and east Greenland (Ittoqqortoormiit – dark grey).

Black guillemot liver and eggs collected in 1999 and 2000 in Qeqertarsuaq (west) and Ittoqqortoormiit (east) were analysed.  $\Sigma$ PCB-10,  $\Sigma$ DDT,  $\Sigma$ CHL, and to lesser extent HCB and HCH levels in birds from east Greenland were higher than in west Greenland (Figure 4.4.1) confirming the spatial trend found previously in glaucous gull (Cleemann et al. 2000d).

### Marine mammals

OC levels have been determined in ringed seal, narwhal, beluga and minke whales (Appendix B including data for walrus collected 1978 for comparative reasons).

Ringed seals are not generally considered to be a highly mobile species although some long migrations have been observed (Kapel et al. 1998). Data of OC in ringed seals are available from Qeqertarsuaq, Avanersuaq and Ittoqqortoormiit. In ringed seal, OC levels increase in tissues in the order kidney < liver < muscle << blubber. In general, OC concentrations are higher in male seals than in females, due to elimination of these lipophilic compounds via lactation. The dominant OCs in ringed seal were  $\Sigma$ PCB,  $\Sigma$ DDT and  $\Sigma$ CHL. The OC levels (except  $\Sigma$ HCH) in ringed seals generally were highest in seals from Ittoqqortoormiit, lowest at Qeqertarsuaq and intermediate at Avanersuaq (Appendix B). The higher OC levels in seals from east

Greenland than in seals from west Greenland confirms the previous results of AMAP phase I (Cleemann et al. 2000a). However, in that study no difference in OC levels between seals from Qeqertarsuaq and Avanersuaq were found, while in present study seals from Avanersuaq had higher OC levels than seals from Qeqertarsuaq.  $\Sigma$ PCB and  $\Sigma$ DDT showed a circumpolar trend of higher concentrations in ringed seals from The Yenisey Gulf (Russian Arctic), Svalbard and east Greenland than in west Greenland or the Canadian Arctic (Muir et al. 2000a).  $\Sigma$ HCH levels were higher in the Canadian Arctic than in west Greenland, east Greenland and Svalbard (Muir ibid).

Data of OC levels in narwhal are available from Avanarsuaq, Balgoni Island (Melville Bay), Uummannaq, Kitsissuarsuit (Disko Bay) and Saqqaq (see also chapter 4.5.1). The dominant OC was toxaphene followed by  $\sum DDT$ ,  $\sum PCB$  and HCB. In general, OC concentrations are higher in males than in females, due to elimination of these lipophilic compounds via lactation following the pattern shown in Figure 5.1.1 for total toxaphene. Based on age normalised OC data on a lipid basic (only males), Riget et al. (2002) found no statistically significant differences in  $\sum PCB$ , HCB, and  $\sum HCH$  among the locations mentioned above, except Saqqaq (analysis of covariance on logarithmic transformed data).  $\sum DDT$  showed significantly higher concentrations in narwhals from Balgoni Island, 1993 than all other location except Kitsissuarsuit, 1990 (Riget et al. (2002). Only few OC data of narwhals exist. Beck et al. (1994) cited in Muir et al. (1999) report on levels in 8 males from Lancaster Sound sampled in 1991. PCB appear to be at a little lower or at the same level in the Greenland samples than in the Canadian samples, whereas  $\sum HCH$  and  $\sum DDT$  appear to be higher.

OC levels in beluga from Saqqaq sampled in 2000 showed similar levels as found in narwhals (Appendix B).

As a part of a multidisciplinary study of population structure of minke whales in the North Atlantic and European Arctic (west and east Greenland, Jan Mayen, West Svalbard, the Barents Sea, Vestfjorden/Lofoten and the North Sea), OC levels were determined in blubber from 42 whales from west Greenland and 4 whales from east Greenland (Hobbs et al. in press). The dominant OC was  $\sum PCB$  (female mean 2290 µg/kg ww, sum of 102 congeners) followed by  $\sum DDT$  (female mean 650 µg/kg ww). Based on the total data available (155 minke whales),  $\sum PCB$  and  $\sum DDT$  showed significantly higher levels in males than in females, while no significant differences were observed between sex of  $\sum HCH$ ,  $\sum CHL$  and HCB (Hobbs et al. in press). Concentrations of OC groups as  $\sum PCB$ ,  $\sum DDT$  and  $\sum CHL$  generally increased from west to east, while  $\sum HCH$  showed the opposite trend. Proportions of OC in minke whales did not reveal any major difference among areas except those whales from Greenland waters and the North Sea differed significantly from those from other areas.

Blubber of 20 polar bears sampled in Ittoqqortoormiit in 1999-2000 were analysed for OCs.  $\Sigma$ PCB and  $\Sigma$ CHL were the major OCs in blubber of polar bear with mean values of 5983 µg/kg ww and 678 µg/kg ww in female bears (Appendix B).  $\Sigma$ DDT were lower, 282 µg/kg ww in female bears.

### 4.4.2 Temporal trend

Very few data exist to make an assessment of temporal trends of OCs in Greenland biota. In the Greenland AMAP programme biological samples from 1994 and 1999/2000 can be compared. However, data from only two or three years may not give evidence of temporal changes for several reasons, first of all because two or three "data points" are too few. On basis of the results obtained during the Greenland

AMAP programme phase I, Riget et al. (2000d) evaluated that a time series of 10-17 years was required to detect a linear trend of 10% per year with a significance of 5% and a power of 80%. Beside the large individual variability in OC levels often observed, a random year to year variability must also be expected. The year to year variability occurs because environmental factors such as temperature, production, prey availability etc. differ between years.

Despite these difficulties, it has been found useful to compare OC levels obtained in 1994 (AMAP phase I) with those obtained in 1999/2000. Three laboratories have been involved (NERI, NWOC, GWOC). Therefore it has been necessary to find groups of OCs, which could be compared. These OC groups were:  $\sum PCB10 = \text{sum of congeners 28, 31, 52, 101, 105, 118, 138, 153, 156, 180}$   $\sum DDT = \text{sum of p,p-DDE, p,p-DDD, p,p-DDT}$   $\sum HCH = \text{sum of or, }\beta$ -,  $\gamma$ -HCH HCB  $\sum CHL = \text{sum of oxychlordane, trans-chlordane, cis-chlordane, cic-nonachlor, trans-nonachlor}$ 

trans-nonachlor alone

OC data on a lipid basis were logarithmicly transformed prior to the statistical analysis. An analysis of covariance was performed in cases were the compounds increase with length/age of the animals. Otherwise an analysis of variance or t-test was performed. A pairwise t-test of LSMEAN (least square mean values) was performed to test for differences between years. The test was performed for each sex separately if data allowed. In case were the statistical test showed no significant difference, the power of the test was estimated according to Cohen (1977). The statistical power is defined as the probability to detect a significant difference. In this case a significance level of 5% is used.

### Qeqertarsuaq

Table 4.4.1 gives an overview of the results of the statistical comparisons of OC concentrations in Qegertarsuag 1994 and 1999/2000. In shorthorn sculpin, SPCB-10,  $\Sigma$ DDT,  $\Sigma$ HCH and trans-nonachlor showed a significant difference between years (Table 4.4.1 and Figure 4.4.2) with a decrease from 1994 to 1999, and then an increase to 2000). HCH concentrations showed a significant decrease from 1994 to 1999 and 2000. In ringed seal blubber, the temporal changes were more complicated.  $\Sigma$ PCB-10 concentrations showed no significant differences between years (Figure 4.4.2). The  $\sum$ DDT concentrations were significantly higher in 1999/2000 than in 1994, whereas  $\Sigma$ HCH and HCB concentrations in males were significant higher in 1994 than in 1999 and 2000. There was no indication of different feeding strategies (see 4.2). OC concentrations in black guillemot liver and  $\Sigma$ CHL in ringed seals were only available for year 1999 and 2000.  $\Sigma$ PCB-10 in males and females and  $\Sigma$ DDT,  $\Sigma$ HCH, HCB and  $\Sigma$ CHL concentrations in female black guillemot were significantly higher in 1999 than in 2000. The birds from 1999 had higher values of stable isotopes (see 4.2) indicating these to had been feeding at a relatively higher trophic level. No significant differences were observed in  $\bullet \Sigma$ CHL in ringed seal blubber between 1999 and 2000.

The OC concentrations in beluga tissues sampled in Saqqaq in 2000 can be compared with samples in Nuussuaq/Disko Bugt from 1989/90 reported by Stern et al. (1994). The comparison can only be indicative because age and sex are unknown for the beluga sampled in 2000. However, the levels of  $\Sigma$ PCB,  $\Sigma$ DDT and  $\Sigma$ CHL appear lower in the recent samples than in the samples from 1989/90.

Table 4.4.1. Results of statistical tests for difference in mean OC concentrations in marine biota from Qeqertarsuaq. Trend gives the years in the order of decreasing concentrations. Years underlined are not significantly different. \* denotes significance at 5% level and \*\* denotes significance at 1% level. The power of the test is given if no significant difference was found (see text).

Qeqertarsuaq	Sex	Trend	Test	Significance	Power
∑PCB-10 shorthorn sculpin, liver	f	<u>00 94</u> 99	ANCOVA	0.01*	
	m	oo <u>94 99</u>	ANVOVA	<0.01**	
black guillemot, liver	f	99 00	t-test	<0.01**	
	m	99 00	t-test	<0.01**	
ringed seal, blubber	f	<u>94 00 99</u>	ANCOVA	0.12	0.99
SDDT	m	<u>99 94 00</u>	ANCOVA	0.12	0.91
shorthorn sculpin, liver	f	94 <u>00 99</u>	ANCOVA	0.01**	
	m	<u>00 99</u> 94	ANCOVA	0.05*	
black guillemot, liver	f	99 00	t-test	<0.01*	
	m	<u>99 00</u>	t-test	0.16	0.21
ringed seal, blubber	f	<u>99 oo</u> 94	ANCOVA	<0.01**	
Such	m	99 00 94	ANCOVA	<0.01**	
shorthorn sculpin, liver	f	94 <u>99 oo</u>	ANCOVA	<0.01**	
	m	94 <u>00 99</u>	ANVOVA	<0.01**	
black guillemot, liver	f	99 00	t-test	<0.01**	
	m	<u>99 00</u>	t-test	0.89	0.05
ringed seal, blubber	f	94 <u>99 00</u>	ANCOVA	<0.01**	
	m	94 <u>99 oo</u>	ANCOVA	<0.01**	
HCB shorthorn sculpin, liver	f	94 <u>99 oo</u>	ANCOVA	<0.01**	
	m	<u>00 94 99</u>	ANVOVA	0.13	0.36
black guillemot, liver	f	99 00	t-test	<0.01**	
	m	<u>99 00</u>	t-test	0.86	0.05
ringed seal, blubber	f	<u>94 99 00</u>	ANCOVA	0.07 0.94	
	m	94 <u>00 99</u>	ANCOVA	<0.01**	

TABLE 4.4.1 CONTINUED Qeqertarsuaq	i continued iaq Sex Trend		nd	Test	Significance	Power
∑CHL black guillemot, liver	f		99 00	t-test	<0.01**	
	m		<u>99 00</u>	t-test	0.14	0.26
ringed seal, blubber	f		<u>00 99</u>	ANCOVA	0.21	0.40
	m		00 99	ANCOVA	0.31	0.21
shorthorn sculpin, liver	f	94	99 00	ANCOVA	<0.01**	
	m	00	<u>94 99</u>	ANCOVA	0.25	0.31
black guillemot, liver	f		99 00	t-test	0.06	0.45
	m		<u>99 oo</u>	t-test	0.40	0.18

 $\Sigma$ HCH = sum of i, j, HCH

 $\Sigma$ CHL = sum of oxychlordane, trans-chlordane, cis-chlordane, cic-nonachlor, trans-nonachlor  $\Sigma$ DDT = sum of p,p DDE, p,p DDD, p,p DDT

 $\Sigma$ PCB-10 = sum of congeners 28, 31, 52, 101, 105, 118, 138, 153, 156, 180







Figure 4.4.2.  $\sum$ PCB-10,  $\sum$ DDT and  $\sum$ HCH concentrations in shorthorn sculpin (length adjusted to male 25 cm and females 28cm) and ringed seals (adjusted to 5 years old) from Qeqertarsuaq sampled in 1994, 1999 and 2000. Males in blue, females in red.

### <u>Avanersuaq</u>

Table 4.4.2 gives an overview of the results of the statistical comparisons of OC concentrations in ringed seals from Avanersuaq 1994 and 1998. The only significant differences were observed for  $\Sigma$ HCH and trans-nonachlor in females with the highest concentrations in 1994.

Muir et al. (2000b) compared the OC levels in walrus (*Odobenus rosmarus*) from Avanersuaq sampled in 1978 and 1988. They found significant (p<0.05) increase for  $\Sigma$ HCH in females but no significantly differences for  $\Sigma$ CBz,  $\Sigma$ DDT,  $\Sigma$ PCB. OC levels in males showed no difference between 1978 and 1988 (Muir et al. ibid). A resampling of the Avanersuaq stock would be useful to examine long-term temporal trends of OCs.

TABLE 4.4.2. RESULTS OF STATISTICAL TESTS FOR DIFFERENCE IN MEAN OC CONCENTRATIONS IN RINGED SEAL BLUBBER FROM AVANERSUAQ. TREND GIVES THE YEARS IN THE ORDER OF DECREASING CONCENTRATIONS. YEARS UNDERLINED ARE NOT SIGNIFICANTLY DIFFERENT. \* DENOTES SIGNIFICANCE AT 5% LEVEL AND \*\* DENOTES SIGNIFICANCE AT 1% LEVEL. THE POWER OF THE TEST IS GIVEN IF NO SIGNIFICANT DIFFERENCE WAS FOUND (SEE TEXT).

Avanersuaq	Sex	Trend	statistic test	significance	power
∑PCB-10 ringed seal, blubber	f	<u>94 9</u> 8	ANCOVA	0.28	0.34
	m	<u>98 94</u>	ANCOVA	0.79	0.21
>DDI ringed seal, blubber	f	94 98	ANCOVA	0.74	0.07
<b>E</b> UCU	m	<u>94 98</u>	ANCOVA	0.80	0.06
ringed seal, blubber f m ∑HCH ringed seal, blubber f m	94 98	ANCOVA	<0.01**		
	m	<u>98 94</u>	ANCOVA	0.81	0.06
HCB ringed seal, blubber	f	94 98	ANCOVA	0.69	0.07
	m	<u>98 94</u>	ANCOVA	0.85	0.05
trans-nonachior ringed seal, blubber	f	94 98	ANCOVA	0.04*	
	m	<u>94 98</u>	ANCOVA	0.58	0.10

 $\Sigma$ HCH = sum of -, -, -HCH

 $\sum$ CHL = sum of oxychlordane, trans-chlordane, cis-chlordane, cic-nonachlor, transnonachlor

 $\sum$ DDT = sum of p,p-DDE, p,p-DDD, p,p-DDT

 $\Sigma$ PCB-10 = sum of congeners 28, 31, 52, 101, 105, 118, 138, 153, 156, 180

#### **Ittoqqortoormiit**

Table 4.4.3 gives an overview of the results of the statistical comparisons of OC concentrations in Ittoqqortoormiit 1994, 1999 and 2000 (see also Figure 4.4.3).  $\Sigma$ PCB-10 and  $\Sigma$ HCH concentrations in shorthorn sculpin were significantly lower in 1999/2000 than in 1994.  $\Sigma$ DDT, HCB and trans-nonachlor concentrations showed no significant differences between years. In ringed seal blubber all OC concentrations were lower in 1999/2000 than in 1994. This, however, was only significant for  $\Sigma$ HCH in males.

OC concentrations were determined in 20 polar bears from Ittoqqortoormiit sampled in 1999/2000. Norstrom et al. (1998) analysed OC concentrations in 18 polar bears

sampled in 1990 in Ittoqqortoormiit. The PCB congeners and  $\sum$ CHL compounds are not the same in the two studies but they both include the most important ones. In adult males and females levels of  $\sum$ PCB and  $\sum$ CHL appear to be much lower in 1999/2000 than in 1990 (20-40% of the levels in 1990). No differences were appearent in case of DDE and dieldrin.

TABLE 4.4.3. RESULTS OF STATISTICAL TESTS FOR DIFFERENCE IN MEAN OC CONCENTRATIONS IN MARINE BIOTA FROM ITTOQQORTOORMIIT. TREND GIVES THE YEARS IN THE ORDER OF DECREASING CONCENTRATIONS. YEARS UNDERLINED ARE NOT SIGNIFICANTLY DIFFERENT. \* DENOTES SIGNIFICANCE AT 5% LEVEL AND \*\* DENOTES SIGNIFICANCE AT 1% LEVEL. THE POWER OF THE TEST IS GIVEN IF NO SIGNIFICANT DIFFERENCE WAS FOUND (SEE TEXT).

Ittoqqortoormiit	Sex Tr	end	statistic test	significance	power
∑PCB-10 shorthorn sculpin, liver	both 94	00 99	ANOVA	<0.01**	
ringed seal, blubber	f <u>94</u>	00 99	ANCOVA	0.11	0.88
Foot	m 94	<u>00 99</u>	ANCOVA	0.02*	
∑DDT shorthorn sculpin, liver	both <u>99</u>	94 00	ANOVA	0.42	0.22
ringed seal, blubber	f <u>94</u>	<u> </u>	ANCOVA	0.02*	
	m <u>94</u>	00 99	ANCOVA	<0.01**	
∑HCH shorthorn sculpin, liver	both 94	99 00	ANOVA	<0.01**	
ringed seal, blubber	f <u>94</u>	99 00	ANCOVA	0.04	0.48
	m 94	<u>99 00</u>	ANCOVA	<0.01**	
HCB shorthorn sculpin, liver	both <u>99</u>	<u>94 00</u>	ANOVA	0.57	0.16
ringed seal, blubber	f <u>94</u>	00 99	ANCOVA	0.20	0.73
Four	m <u>94</u>	<u> </u>	ANCOVA	<0.01**	
•∑CHL ringed seal, blubber	f	<u>00 99</u>	ANCOVA	0.46	0.16
	m	<u>00 99</u>	ANCOVA	0.16	0.52
trans-nonachlor shorthorn sculpin, liver	both 99	94 00	ANOVA	0.29	0.19

 $\Sigma$ HCH = sum of  $\cdot \cdot$ ,  $\mu$ -,  $\cdot$ -HCH

 $\sum$ CHL = sum of oxychlordane, trans-chlordane, cis-chlordane, cic-nonachlor, trans-nonachlor

 $\sum$ DDT = sum of p,p-DDE, p,p-DDD, p,p-DDT

 $\Sigma$ PCB-10 = sum of congeners 28, 31, 52, 101, 105, 118, 138, 153, 156, 180



Figure 4.4.3.  $\Sigma$ PCB-10,  $\Sigma$ DDT and  $\Sigma$ HCH concentrations in shorthorn sculpin liver and ringed seals blubber (adjusted to 5 years old) from Ittoqqortootmiit from 1994, 1999 and 2000. Black – both sex, blue – males, red – females.

### 4.5 RADIONUCLIDES

Artificial radionuclides have been monitored in the Greenland environment since the 1960's. The Greenland data have been reviewed in the first Arctic Monitoring and Assessment (AMAP) reports, (Aarkrog et al. 1997; Strand et al.1998). Under the AMAP-II project 1999 – 2002, <sup>137</sup>Cs, <sup>90</sup>Sr, <sup>239,240</sup>Pu and <sup>99</sup>Tc have been monitored in selected components of the Greenland marine environment. Furthermore, results from a study in 1997 in Bylot Sound to investigate the fate of plutonium after the 1968 Thule accident is described in chapter 4.5.2.

## 4.5.1 Levels of <sup>137</sup>Cs, <sup>99</sup>Tc, <sup>90</sup>Sr and <sup>239,240</sup>Pu in components of the marine environment

Large seawater samples have been obtained by various means – mostly from ship pumps or with buckets from small boats. Biological samples were all from the NERI sampling, i.e. it is the same samples as used for metal and POP analysis.

Table 4.5.1 gives average radionuclide concentrations observed in surface seawater samples in 1999. These values and similar data from 2000 and 2001 are furthermore shown in Figures 4.5.1-4.5.4.

Region	<sup>137</sup> Cs			<sup>99</sup> Tc			⁰°Sr	<u>.</u>		Salinity			<sup>239,240</sup> Pu		
	Bq m⁻³	SD	n	Bq m³	SD	n	Bq m³	SD	n	‰	SD	n	mBq m³	SD	n
FR	1.7	0.1	2	0.020	0.000	2	1.1	0.1	2	34.8	0	2	4.6	0.4	2
IRM	1.7	-	1	<0.01	-	1	1.0	-	1	35.1	-	1			
lce	2.8	0.1	2	0.031	0.003	2	1.1	0.0	2	34.7	0.0	2			
NE	4.5	0.6	4	0.082	0.009	4	1.8	0.3	4	29.2	2.9	4	2.5	0.1	3
EGC	5.4	0.3	7	0.078	0.012	7	2.0	0.4	7	32.2	1.5	7			
SW	4.3	0.4	4	0.071	0.008	4	1.6	0.1	4	31.3	0.5	4	7.1	0.5	3
CW	2.8	0.8	3	0.052	0.017	3	1.5	0.1	3	31.8	2.0	3	2.1	0.8	3
NW	2.9	0.1	4	0.024	0.003	4	1.1	-	1	31.5	-	1			

TABLE 4.5.1 AVERAGE RADIONUCLIDE CONCENTRATIONS OBSERVED 1999 IN SURFACE SEAWATER SAMPLES

The region acronyms are FR: Faroe Islands; IRM: Irmiger current; Ice: Iceland Sea; EGC: the East Greenland Current in the Denmark Strait; NE: northeast Greenland at Scoresbysund and Zackenberg; SW: southwest Greenland; CW: central west Greenland; NW: northwest Greenland (cf. Figure 2.5.1).



Figure 4.5.1  $^{\scriptscriptstyle 137}\text{Cs},\,^{\scriptscriptstyle 99}\text{Tc}$  and  $^{\scriptscriptstyle 90}\text{Sr},\,\text{mBq}$  L', in surface seawater observed in 1999.



Figure 4.5.2.  $^{^{239.240}}\text{Pu}$  (µBq  $\text{L}^{\cdot}\text{)}$  and salinity (‰) in surface seawater observed in 1999.



Figure 4.5.3. TC-99 MBQ  $L^{1}$ , in surface seawater year 2000



Figure 4.5.4.  $^{^{137}}\text{Cs},\,^{^{99}}\text{Tc}$  and  $^{^{90}}\text{Sr},\,\text{mBq}$  L  $^{1},\,\text{in}$  surface seawater observed in 2001.

Table 4.5.2 gives average concentrations of <sup>137</sup>Cs and <sup>99</sup>Tc in seaweed taken 1999, 2000 and 2001 and Table 4.5.3 gives <sup>137</sup>Cs concentrations in various edible marine products sampled 1999. The concentrations of several radionuclides in seawater are decreasing in the order northeast Greenland and the coastal East Greenland Current > southwest Greenland > central west Greenland and northwest Greenland >

Irmiger Sea ~ Faroe Islands. The same tendency is seen for  $^{137}$ Cs and  $^{99}$ Tc in seaweed and for e.g.  $^{137}$ Cs in seal from east and west Greenland. This is in accordance with long-distance transport patterns from European coastal waters, which are responsible for most of the  $^{99}$ Tc and a large fraction of the  $^{137}$ Cs (Dahlgaard, 1994, Dahlgaard, 1995).

Table 4.5.2 Average concentrations of  $^{137}Cs$  and  $^{99}Tc, Bq \ kg^{\cdot1}$  dry weight in seaweed in 1999, 2000 and 2001

			'°′Cs			<sup>99</sup> Tc			dry
Location	Region	Year	Bq kg⁻¹ dw	SD	n	Bq kg ً' dw	SD	n	%
Faroe Islands	FR	1999	0.47	0.10	3	1.60	0.41	3	19.6
Scoresbysund	NE	1999	2.74	0.81	5	28.60	5.60	5	12.7
Scoresbysund	NE	2000	2.06	1.17	4				
Scoresbysund	NE	2001	1.42	0.56	3				21.0
Isortoq	SW	1999	1.83	0.35	3	5.50	0.30	3	19.6
South Greenland	SW	2000	0.29	0.12	3				
Godhavn	CW	1999	0.29	0.06	3	5.80	1.10	3	17.1
Kronprinsens Island	CW	2000	0.35	0.16	3	6.29	0.74	3	
Kronprinsens Island	CW	2001	0.34	0.05	2				26.0
Kronprinsens Island	CW	2001	0.23		1				29.0
Pittufik	NW	1999	1.23		1	3.80		1	16.0
Dundas	NW	2000	0.44	0.09	3	4.58	0.19	3	
Wolstenholme fjord	NW	2001	3.06	3.25	2				20.0
	Location Faroe Islands Scoresbysund Scoresbysund Scoresbysund Isortoq South Greenland Godhavn Kronprinsens Island Kronprinsens Island Kronprinsens Island Pittufik Dundas Wolstenholme fjord	LocationRegionFaroe IslandsFRScoresbysundNEScoresbysundNEScoresbysundNEIsortoqSWSouth GreenlandSWGodhavnCWKronprinsens IslandCWKronprinsens IslandCWPittufikNWDundasNWWolstenholme fjordNW	LocationRegionYearFaroe IslandsFR1999ScoresbysundNE1999ScoresbysundNE2000ScoresbysundNE2001IsortoqSW1999South GreenlandSW2000GodhavnCW1999Kronprinsens IslandCW2001Kronprinsens IslandCW2001PittufikNW1999DundasNW2000Wolstenholme fjordNW2001	Location   Region   Year   Bq kg <sup>-1</sup> dw     Faroe Islands   FR   1999   0.47     Scoresbysund   NE   1999   2.74     Scoresbysund   NE   2000   2.06     Scoresbysund   NE   2001   1.42     Isortoq   SW   1999   1.83     South Greenland   SW   2000   0.29     Godhavn   CW   1999   0.29     Kronprinsens Island   CW   2000   0.35     Kronprinsens Island   CW   2001   0.34     Pittufik   NW   1999   1.23     Dundas   NW   2000   0.44	Location   Region   Year   Bq kg <sup>-1</sup> dw   SD     Faroe Islands   FR   1999   0.47   0.10     Scoresbysund   NE   1999   2.74   0.81     Scoresbysund   NE   2000   2.060   1.17     Scoresbysund   NE   2001   1.42   0.56     Isortoq   SW   1999   1.83   0.35     South Greenland   SW   2000   0.29   0.12     Godhavn   CW   1999   0.29   0.06     Kronprinsens Island   CW   2000   0.35   0.16     Kronprinsens Island   CW   2001   0.34   0.05     Kronprinsens Island   CW   2001   0.23   -     Pittufik   NW   1999   1.23   -     Dundas   NW   2000   0.44   0.09	Location   Region   Year   Bq kg <sup>-1</sup> dw   SD   n     Faroe Islands   FR   1999   0.47   0.10   3     Scoresbysund   NE   1999   2.74   0.81   5     Scoresbysund   NE   2000   2.06   1.17   4     Scoresbysund   NE   2001   1.42   0.56   3     Isortoq   SW   1999   1.83   0.35   3     South Greenland   SW   2000   0.29   0.16   3     Kronprinsens Island   CW   2000   0.35   0.16   3     Kronprinsens Island   CW   2001   0.34   0.05   2     Kronprinsens Island   CW   2001   0.23   1   1     Pittufik   NW   1999   1.23   1   1     Dundas   NW   2000   0.44   0.09   3	Location Region Year Bq kg <sup>-1</sup> dw SD n Bq kg <sup>-1</sup> dw   Faroe Islands FR 1999 0.47 0.10 3 1.60   Scoresbysund NE 1999 2.74 0.81 5 28.60   Scoresbysund NE 2000 2.060 1.17 4 1.17   Scoresbysund NE 2001 1.42 0.56 3 1.17   Scoresbysund NE 2001 1.42 0.56 3 5.50   South Greenland SW 1999 1.83 0.35 3 5.50   South Greenland SW 2000 0.29 0.12 3 5.80   Kronprinsens Island CW 2000 0.35 0.16 3 6.29   Kronprinsens Island CW 2001 0.34 0.05 2 1   Pittufik NW 1999 1.23 1 3.80   Dundas NW 2000 0.44 0.09 3 4.58	Location   Region   Year   Bq kg <sup>3</sup> dw   SD   n   Bq kg <sup>3</sup> dw   SD     Faroe Islands   FR   1999   0.47   0.10   3   1.60   0.41     Scoresbysund   NE   1999   2.74   0.81   5   28.60   5.60     Scoresbysund   NE   2000   2.06   1.17   4	Location   Region   Year   Bq kg' dw   SD   n   Bq kg' dw   SD   n     Faroe Islands   FR   1999   0.47   0.10   3   1.60   0.41   3     Scoresbysund   NE   1999   2.74   0.81   5   28.60   5.60   5     Scoresbysund   NE   2000   2.06   1.17   4

Region acronyms: see Table 4.5.1. Species: Fu.ve: *Fucus vesiculosus*, Fu.di.: *F. disticus*, As.no.: *Ascophyllum nodosum* 

TABLE 4.5.3. CS-137 (BQ / KG WW) IN VARIOUS EDIBLE PRODUCTS. EXCEPT FOR SCULPIN	(WHOLE
FISH), THE VALUES ARE FOR MEAT.	

Species	Location	Region	Year	' <sup>o</sup> ′Cs			
		-		Bq kg <sup>-1</sup>	SD	n	
				W.W.			
Cod	Faroe Islands	FR	1999	0.22	0.05	2	
Haddock	Faroe Islands	FR	1999	0.10		1	
Mytilus, soft	Faroe Islands	FR	1999	0.05		1	
Sculpin total	Faroe Islands	FR	1999	0.05		1	
Shrimp	Faroe Islands	FR	1999	0.10	0.01	3	
Whale	Faroe Islands	FR	1999	0.23	0.08	3	
Black guillemot	Scoresbysund	NE	1999	0.35	0.01	3	
Sculpin total	Scoresbysund	NE	1999	0.47	0.10	3	
Seal	Scoresbysund	NE	1999	0.50	0.11	3	
Whale	Scoresbysund	NE	1999	0.47	0.17	3	
Black guillemot	Qeqertarsuaq	CW	1999	0.21	0.04	5	
Sculpin total	Qeqertarsuaq	CW	1999	0.26	0.06	3	
Seal	Qeqertarsuaq	CW	1999	0.19	0.08	3	

Region acronyms: see Table 4.5.1.

There has been some focus on the levels of <sup>99</sup>Tc in seawater and marine products because the British nuclear fuel reprocessing plant Sellafield increased its discharges from 1994 and onwards. From earlier studies (Aarkrog et al. 1983, Dahlgaard et al. 1986, Aarkrog et al. 1987; Dahlgaard, 1994), the 1994-1995 peak discharge may be expected off North East Greenland from year 2000 and onwards. Seawater data for 2000 actually indicated increased levels of <sup>99</sup>Tc off NE Greenland (Figure 4.5.3), whereas levels in 2001 seemed to be unchanged. The increased levels in year 2000 samples are probably caused by the increased discharges from Sellafield, but it should

be kept in mind that the sampled area is huge and it has not been possible to perform a systematic sampling of the various water masses in the East Greenland Current system. The samples from 1999, 2000 and 2001 are therefore not directly comparable. Shrimp meat samples from southwest Greenland were analysed in 2000, but all results were below detection limits. In normal oxygenated seawater, <sup>99</sup>Tc appears mainly as anionic pertechnetate with a low affinity to particles and to most marine organisms except brown macroalgae (*Fucus, Ascophyllum*) and certain crustaceans such as lobster and shrimp.

As a pilot study, liver, kidney and meat from 5 ringed seals caught in Disko Fjord (CW) under NERI's time-trend programme were analysed for <sup>210</sup>Po (Table 4.5.4). <sup>210</sup>Po is a naturally occurring alpha-emitter that appears in the <sup>238</sup>U decay series after <sup>226</sup>Ra, <sup>222</sup>Rn and <sup>210</sup>Pb, and it is bioaccumulated in aquatic organisms. The present levels are high compared to average global values of 2.4, 15 and 6 Bq <sup>210</sup>Po kg<sup>-1</sup> (wet weight) in fish, molluscs and crustaceans, respectively, found in an international study (Aarkrog et al., 1997b). That study concluded that <sup>210</sup>Po gives rise to a major component of the radiation dose to man from consumption of marine products, but the study did not include marine mammals and doses to Inuits. Consumption of 1 kg of kidney, 1 kg of liver and 4 kg of meat with the present average values would each give a radiation dose around 0.1 mSv. It is thus evident that consumption of fresh seal significantly enhances the natural radiation dose received by Inuits. Canadian caribou holds even higher concentrations in liver and kidney and similar concentrations in meat due to accumulation via lichen (Thomas et al. 1994).

		length	Bq <sup>210</sup> Po kg <sup>-1</sup>				
ID	Sex	cm	Kidney	Liver	Muscle		
24602	female	98	98	73	16		
24603	male	95	106	92	29		
24606	male	95	84	71	17		
24608	male	98	107	107	21		
24616	female	123	86	59	17		
Average			96	81	20		
SD			11	19	6		

TABLE 4.5.4. RINGED SEAL FROM DISKO FJORD (CW), <sup>210</sup>PO BQ KG<sup>-1</sup> WW. Decay corrected to time of catch: 6 May 2001

### 4.5.2 Plutonium in Bylot Sound – The Thule Accident 1968

On 21 January 1968, a B-52 aircraft from the US Strategic Air Command crashed on the sea ice of Bylot Sound 11 km west of the Thule Air Base in Greenland. The aircraft disintegrated on impact and an explosion and a fire ensued. The 4 nuclear weapons onboard were destroyed and fissionable material - plutonium and uranium - was dispersed. The benthic marine environment in the 180-230 m deep Bylot Sound was then contaminated with <sup>239,240</sup>Pu. The site was revisited August 1997, 29 years after the accident. The following is extracted from Dahlgaard et al. (2001) and Eriksson (2002).

### 4.5.2.1 Radioactive particles from the Thule accident.

The plutonium was present in an insoluble oxide form and mainly associated to particles with an average size of 2 micrometers (U.S.Air Force, 1970). During the months following the accident a clean up program was performed where most of the debris and the contaminated ice was removed from the area. The total amount of plutonium dispersed in the accident was 6 kg of which  $3.5 \pm 0.7$  kg was found on and in the sea ice. Except for an estimated amount of  $\sim 1$  TBq ( $\sim 0.4$  kg) remaining in the ice after cleaning, most of this plutonium was recovered and shipped to the US (U.S.Air Force, 1970; Strand et al. 1998), i.e.,  $\sim 3$  kg of plutonium may have entered

the environment. This amount may be reduced by an unknown amount attached to aircraft debris (Strand et al., 1998). After the accident, the amount of plutonium in the marine sediments in Bylot Sound have been estimated based on samples taken 1970, 1974, 1979, 1984, 1991 and 1997 (Aarkrog, 1971, Aarkrog, 1977, Aarkrog et al. 1984, Aarkrog et al., 1987, Aarkrog et al. 1994, Strand et al. 1998, Eriksson et al. 1999, Dahlgaard et al. 2001). These inventory estimates have been centred on 1 - 1.6 TBq or approximately 0.5 kg.

The inhomogeneous nature of the plutonium contamination (Figure 4.5.5) has been noted for many years, but it was earlier assumed not to influence significantly the inventory estimates. The earlier works are solely based on radiochemistry and alpha spectrometry. The hot particles may have been underestimated for two reasons: incomplete dissolution of the particles and in some cases inability to quantify very strong samples because insufficient energy resolution in the alpha spectrometry system used.

An improved method to determine the total inventory of a heterogeneously distributed contamination of marine sediments has been described (Eriksson, 2002). The estimate is based on gamma spectrometric screening of the <sup>241</sup>Am concentration in 450 one-gram aliquots from 6 sediment cores. The <sup>241</sup>Am activity is building up as a decay product of <sup>241</sup>Pu (half-life 14.4 yr.) which is present in weapons plutonium as an impurity. Based on radiochemical determination of the plutonium concentration in 20 of these subsamples, the <sup>241</sup>Am values are used to estimate the <sup>239,240</sup>Pu concentrations. A Monte Carlo programme then simulates a probable distribution of the activity, and based on that, a total inventory is estimated by integrating across the area to 100 km from the point of impact using a double exponential function. Results centre on a total inventory around 9.5 TBq or 3.5 kg<sup>239,240</sup>Pu, which is 7 times higher than earlier estimates (0.5 kg). The difference is partly explained by the full inclusion of hot particles in the present methodology. It should however be noted, that only 6 sediment cores are included in the present estimate, and that a large uncertainty is connected to the result. Thus the new result can at the present state not be considered as significantly different from the earlier, although it fits better to the estimate above of the missing 3 kg.



FIGURE 4.5.5. THULE-1997. SEDIMENT <sup>239,240</sup>PU CONCENTRATION (BQ KG<sup>-1</sup> DRY) PROFILES.

#### 4.5.2.2 Plutonium in water and seaweed.

The concentration of <sup>239,240</sup>Pu in *Fucus disticus* (a brown alga) around Thule and 750 km to the south near Uummannaq was measured. Concentrations in the range 0.15 - 1.14 Bq kg<sup>-1</sup> dry weight were observed. The source of most of this plutonium is global fallout – maybe except the highest value seen in a single sample near the accident site. With the exception of a near-bottom water sample taken at the point of impact, which shows a total concentration of 30 mBq <sup>239,240</sup>Pu m<sup>-3</sup>, no clear effect of the accident was seen in any of the water samples. 42% of this elevated level was particulate (McMahon et al. 2000, Dahlgaard et al. 2001) indicating that resuspended sediments containing accident plutonium is an important source. The general level inside, as well as far away from, Bylot Sound was 5 - 10 mBq <sup>239,240</sup>Pu m<sup>-3</sup> unfiltered surface water which may be regarded as global fallout background. The water and brown algae data thus indicate that plutonium from the contaminated sediments is not transported into surface waters in significant quantities.

### 4.5.2.3 Sediments

A set of plutonium sediment depth profiles are given in Figure 4.5.5 – for contaminated cores from Bylot Sound as well as for assumed background cores taken outside Bylot Sound (ny-3, 1412 and Schades Øer). In all cases, plutonium seems to be well mixed in the upper 3-5 cm sediment layers. It should be noted that the concentration axis in Fig. 4.5.5 is logarithmic. In spite of this, the large variation of

observed plutonium concentrations is obvious. This is caused by hot particles (cf. 4.5.2.1).

Plutonium concentrations in surface sediment are shown in Figure 4.5.6. The figure shows that the highest concentrations are centered on the accident site, and it indicates a fairly even distribution in the remaining deep part of Bylot sound, whereas almost fallout background concentrations prevail outside Bylot Sound. The accident site – around location V -with the highest concentrations is situated at water depths of 180 – 230 meters. The two assumed background sites outside Bylot Sound, Ny-3 and 1412, are at depths of 500 and 640 m, respectively. A surface 0-3 cm concentration of 0.12 Bq<sup>239,240</sup>Pu kg<sup>-1</sup> dry was observed 750 km further south. The surface concentrations outside Bylot sound, locations 1412 and ny-3, are an order of magnitude higher. It is not clear whether this is caused by accident plutonium or it is a natural perturbation caused by differences in sedimentological parameters. At other Arctic marine locations such as the waters south of Spitzbergen, similar levels of plutonium have been ascribed to global fallout.

### 4.5.2.4 Benthic biota

Where possible, plutonium concentrations in biota samples have been compared with concentrations in 0-3 cm surface sediments (Figure 4.5.6) to give a "concentration ratio", CR, Bq <sup>239,240</sup>Pu kg<sup>-1</sup> dry biota / Bq kg<sup>-1</sup> dry 0-3 cm sediment (Table 4.5.6). It is noted that although the analysed biota is living buried in the sediments or on the sediment surface, the CR values indicate that the bioavailability of the weapons plutonium is low. Most of the observed CR values are in the range 0.01 - 0.1, i.e. plutonium concentrations in benthic biota are in general 1-2 orders of magnitude lower than in surface sediments. Furthermore, a significant part of this plutonium is probably not metabolised but rather associated to particles in the guts and adhering to the surface structure of the animals. Higher transfer rates to benthic biota have been observed in the Irish Sea (Ryan et al. 1999), probably due to differences in physical and chemical forms of plutonium. One single bivalve sample showed a much higher level, which was probably due to a hot particle.

Class	Species	CR, Bq kgʻbiota / Bq kgʻsediment (0-3 cm)					
		Average	SD	n			
Mollusc	Bivalves	0.025	0.024	13			
Mollusc	Macoma calcarea	37		1			
Mollusc	Snails	0.0033	0.0018	9			
Mollusc	Squid, Rossia sp.	0.00036		1			
Echinoderm	Starfish	0.0094	0.0139	9			
Echinoderm	Brittle stars	0.013	0.0159	4			
Echinoderm	Feather stars	0.0070	0.0060	4			
Echinoderm	Sea Urchins	0.12	0.16	4			
Echinoderm	Sea cucumber	0.0080	0.0083	4			
Crustacea	Shrimp	0.0048	0.0088	4			
Crustacea	var.	0.038	0.039	4			
Annelida	Pectinaria	0.068	0.05234	4			
Annelida	var.	0.023	0.033	10			
Annelida	Tube	0.28	0.29	6			
Fish	Liparis sp.	0.00035		1			

Table 4.5.6. Thule-1997. Plutonium Concentration Ratios, CR, BQ  $^{239,240}$ Pu kG<sup>-1</sup> dry biota / BQ kG<sup>-1</sup> dry sediment between various groups of benthic biota and upper 3 cm of sediments.

\*: Outlier, probably caused by hot particle



Figure 4.5.6. Thule-1997. Plutonium concentrations in surface 0-3 cm layer of sediments, Bq <sup>239,240</sup>Pu kg<sup>-1</sup> dry. Location names in italics, concentrations in bold. The point of impact was on the sea ice at the location marked V2.

#### 4.5.2.5 Isotope ratios

A number of Thule sediment samples from the present 1997 sampling as well as a few stronger ones taken earlier have been analysed for <sup>240</sup>Pu/<sup>239</sup>Pu atom ratios by HR-ICPMS (Dahlgaard et al. 1999). These samples show <sup>240</sup>Pu/<sup>239</sup>Pu atom ratios in the range 0.027 - 0.057. The calculated uncertainties on most of the samples are 2 - 10 %. The samples with highest activity – which have all been identified as "hot particles" – show a significant variation in the <sup>240</sup>Pu/<sup>239</sup>Pu atom ratios, i.e. there is a variation in plutonium isotope ratios in the Thule debris significantly larger than measurement errors. This supports the earlier conclusion (Mitchell et al. 1997) that the Thule plutonium originates from at least two sources of different quality. Plutonium concentrations in the samples used for this work are dominated by the Thule weapons accident. Therefore, the higher <sup>240</sup>Pu/<sup>239</sup>Pu atom ratio observed in global fallout, approx. 0.18, will not affect the results. Any influence of the higher <sup>240</sup>Pu/<sup>239</sup>Pu atom ratios in Sellafield discharges, up to around 0.25 is even more unlikely, as the Sellafield contribution to the Arctic Ocean plutonium concentration is supposed to be less than global fallout.

Average isotope ratios, <sup>240</sup>Pu / <sup>239</sup>Pu atom ratios and <sup>238</sup>Pu / <sup>239,240</sup>Pu and <sup>241</sup>Am / <sup>239,240</sup>Pu activity ratios for sediment samples containing more than 20 Bq <sup>239,240</sup>Pu kg<sup>-1</sup>, i.e. at least an order of magnitude above the fallout background, are given in Table 4.5.7. The reference date is the sampling date, i.e. 1997. By comparison of the <sup>241</sup>Am / <sup>239,240</sup>Pu activity ratios for the sediments (Table 4.5.7) with data for the benthic biota samples (Table 4.5.8), it is seen that some of the biota groups seem to have a higher uptake of americium than of plutonium, especially molluscs and brittle stars (*Ophiuroids*). A higher affinity for americium than for plutonium in some biota groups is not new. Thus IAEA reported higher CF values for Am than for Pu in molluscs (IAEA, 1985).

Table 4.5.7. Thule-1997.Isotope ratios in sediment samples holding more than 20 Bq <sup>239:240</sup>Pu kg<sup>-1</sup>. Reference date: August 1997.

Sediments > 20 Bq/kg		Mean	SD%	n
<sup>240</sup> Pu / <sup>239</sup> Pu	atom ratio	0.045	15	30
<sup>238</sup> Pu / <sup>239,240</sup> Pu	activity ratio	0.014	53	223
<sup>241</sup> Am / <sup>239,240</sup> Pu	activity ratio	0.13	61	114

Table 4.5.8. Thule-1997.  $^{^{249}}\text{Am}$  /  $^{^{239,240}}\text{Pu}$  activity ratios in various groups of sediment dwelling benthic biota.

<sup>241</sup> Am / <sup>239,240</sup> Pu activity ratio							
Туре	sub-type	Mean	SD%	n			
Benthos	All	0.39	76	84			
Molluscs	All	0.63	62	24			
Polychaetes	All	0.28	77	16			
Crustaceans	All	0.22	36	5			
Echinoderms	Ophiuroidea	0.55	24	4			
Echinoderms	Asteroidea	0.41	34	11			
Echinoderms	Echinoidea	0.17	8	5			
Echinoderms	Holothurioidea	0.13	67	2			

Conclusions and recommendations

- In the plutonium contaminated Bylot Sound, biological activity has mixed accident plutonium efficiently into the 5-12 cm new sediment resulting in continued high surface sediment concentrations 3 decades after the accident.
- Plutonium from the contaminated sediments is not transported into the surface waters in significant quantities. This is deduced from analytical results of surface seawater and brown algae. However, plutonium-bearing sediments seem to be resuspended near the bottom.
- A recent Ph.D. thesis indicates that "hot particles" hold considerably more plutonium than previously anticipated and that the Bylot Sound sediments may be accounting for the major part of the un-recovered amount, i.e. around 3 kg.
- Transfer of plutonium to benthic biota is low and lower than observed in the Irish Sea. This is supposed to be caused by the physico-chemical form of the accident plutonium.
- A survey of the plutonium contamination in the Bylot Sound should be carried out in 2003 with special attention to be paid to the effect of hot particles and to possible changes in physico-chemical form that may increase bioavailability and mobility. The plutonium contamination in Bylot Sound should be monitored regularelly, e.g. every 5 years.

• A follow-up survey of plutonium levels in the terrestrial environment based on organic surface soil samples from areas where plutonium was detected after the Thule accident is suggested.

### 4.6 Lead contamination of Greenland seabirds hunted with lead shot

Southwest Greenland waters are important wintering grounds for seabirds, in particular thick-billed murre (*Uria lomvia*) and common eider (*Somateria mollissima*), and during winter substantial numbers, about three hundred thousands, of these two species are killed with lead shot in this region of Greenland. The study referred to here was initiated to assess human lead exposure from eating these birds.

Birds killed with lead shot were collected from winter hunting in the Nuuk region (64°N, 51°W), murres in 1998 and common eiders in 2000. Eiders not killed with lead shot were also collected. Each bird was x-rayed and shot pellets were located and counted. Wings, head, tarsus and toes were cut off, the bird was skinned and the viscera were removed. Then each skinned carcass without viscera was boiled according to a recipe often used in Greenland. After boiling, the right pectoral muscle was selected for chemical analysis. If the x-ray photos had shown presence of shot pellets in the muscle, visible pellets were located and removed. We used this procedure to simulate the human lead exposure from eating seabirds in Greenland.

After ashing of the entire pectoral muscle in a porcelain crucible, the ash was dissolved in suprapure nitic acid and analysed by AAS. Table 4.6.1 shows the results from the study. As the frequency distribution of data is very skewed, the "bootstrap method" (Efron & Tibshirani, 1993) using 1000 'resamples' was chosen to characterize data. 4 single high lead concentrations (above 1000  $\mu$ g/g ww) were omitted from data treatment, because it was suspected that a whole pellets or large pellet fractions were not detected and removed before analysis.

Table 4.6.1. Lead concentration ( $\mu$ G/G ww) in whole breasts from thick-billed murre and common eider. 95% confidence limits are computed from the "bootstrap method".

WEITIOD .					
Species	Killing method	n	Mean	St.dev.	95% conf. limit
Thick-billed murre	Lead shot	32	0.73	2.9	0.16-1.9
Common eider	Lead shot	25	6.1	13	2.1-12
Common eider	Drowned	24	0.14	0.13	0.09-0.19

The lead concentration is significantly higher (a factor of about 8) in eider than in murre, and it is much higher (a factor of 44) in eiders killed with lead shot than in drowned birds. But lead levels in drowned eiders are also elevated (a factor of about 3 above the detection limit), probably because the breast meat is contaminated by lead from being shot at earlier without being killed. In the drowned birds we found from 0 to 3 pellets in the breasts analyzed, and Falk & Merkel (2001) report that 24% of the common eiders in Greenland carry embedded lead shot.

Wingbones from eiders were also analysed, as the lead concentration in bone tissue is considered a good indicator for lead exposure over the lifetime of the individual. The lead level was low, indicating that the eiders only accumulate lead to a small degree and that lead has no toxic effect on the birds.

The mean lead concentration  $0.73 \ \mu g/g$  ww. in whole murre breasts is 3 to 4 times higher than we found when we analyzed 0.5-1 gram sub samples from the same birds,  $0.22 \ \mu g/g$  ww. (Johansen et al., 2001). The 95% confidence limits of the two

means overlap, but a contributing explanation of this difference could be that <u>all</u> nonvisible lead fragments will be included when the whole breast is analyzed, whereas only a fraction of these fragments is included in the sub sample.

Table 4.6.2 compares the Greenland data with similar Canadian and with residue guidelines for lead in Denmark ( $0.3 \mu g/g$  ww (Anon., 2002)) and Canada ( $0.5 \mu g/g$  ww (Scheuhammer et al. 1998)). In murres 11-17% of the observations exceed these residue guidelines, whereas in eiders this is the case for more than half of the birds analyzed.

Table 4.6.2. Comparison of data on birds hunted with lead shot. Greenland data are from this study and from Johansen et al. (2001). Canadian data are from Scheuhammer et al. (1998).

Species	Country	Sample type	Mean lead	St.dev.	% values	% values
			µg/g ww	µg/g	>0.3 µg/g	>0.5 µg/g
Several	Canada	Subsample	1.4	13		11
Murre	Greenland	Subsample	0.17	0.35	17	14
Murre	Greenland	Whole breast	0.73	3.0	11	11
Eider	Greenland	Whole breast	6.1	13	68	52

FAO/WHO have established a "Provisional Tolerable Weekly Intake" (PTWI) for lead of 25  $\mu$ g per kg bodyweight for both adults and children. In general lead levels in Greenland biota is very low, and consequently human lead intake from local food items is also estimated to be low, on average only 15  $\mu$ g per adult per week (Johansen et al. 2000). However, this estimate does not include any significant contribution from shot pellets, and the use of lead shot in Greenland may increase human lead intake considerably.

To illustrate the importance of birds as a dietary lead source we have calculated the lead intake from our analysis of whole breasts. If as an example we consider a meal being 200 gram bird meat, the resulting mean lead intake from such a meal will be 146  $\mu$ g for murre and 1220  $\mu$ g for eider. This implies that only one eider meal will result in a lead intake close to the PTWI. For murre the lead intake from one meal will be about 10% of the PTWI.

The actual lead intake from birds hunted with lead shot over longer periods will depend on 1) the amount of bird meat per meal, 2) the frequency of bird meals and 3) the lead concentration in the meals. There are not sufficient data to quantify this, but our calculation in the example illustrates that birds hunted with lead shot are a significant lead source and probably the most important single source. The example also indicates that the lead intake must be expected to exceed the PTWI in a number of cases, as both murre and eider are important in the diet, particular in southwest Greenland during winter.

## 4.7 CONTAMINANT SIGNATURES AS REFLECTING POPULATION STRUCTURE

## 4.7.1 West Greenland narwhals

Samples of muscle, liver, kidney, blubber and skin tissues of narwhals from West Greenland collected in the period 1983 to1994 have been analysed for heavy metals, organochlorines, stable isotopes and DNA (Figure 4.7.1) to test a hypothesis that different populations of narwhals in the West Greenland area exist. The obtained results of metal concentrations and DNA were included in the existing database,

whereas no previous data on organochlorines and stable isotopes in West Greenland narwhals existed. The results of this study are described in Riget et al. (2002).

### Metal analysis

In total, Cd, Hg, Se and Zn concentrations in muscle, liver and kidney tissues of app. 150 narwhals were analysed. Cd, Hg, Se concentrations were increasing in the first three to four years of the animals life, where after no dependence on age was observed. Females had significantly higher concentrations than males in case of Cd in all tissues and Hg and Se in liver. No consistence difference in metal levels between narwhals from Avanersuaq and Uummannaq was found. The between year variation at one location seem to be larger than the variation between the two location. The metal levels found were within the range of previous published results on narwhals from Arctic Canada and Avanersuaq, West Greenland.



FIGURE 4.7.1. MAP OF SAMPLING LOCALITIES

## Organochlorines

In total, organochlorines in blubber from 101 narwhals were analysed. OC concentrations were dependent on age and differences were found between males and females. Females showed decreasing OC concentration in the first 8 to 10 years, while males showed a slightly increase of  $\sum PCB$ ,  $\sum DDT$  and trans-nonachlor while  $\sum HCH$ , HCB,  $\sum CHL$  and toxaphene showed a slightly decrease in the first years and then rather independent of age. No or few statistical differences in mean OC concentrations were observed, however, the narwhals from Balgoni Island 1993 and Kitsissuarsuit 1990 showed the consistently highest levels and whales from Avanersuaq 1993 the lowest level. Also the pattern of PCB congeners showed some differences between samples. PCBs seem to be at a little lower or at the same level in the west Greenland samples as in the Canadian samples, whereas  $\sum HCH$  and  $\sum DDT$  seem to be higher. Total toxaphene was one of the dominanting OCs as previously observed in small Arctic toothed whales.

## Stable isotopes

Stable isotope ratios (<sup>15</sup>N/<sup>14</sup>N expressed as per mille is denoted  $\stackrel{15}{\sim}$ N and <sup>13</sup>C/<sup>12</sup>C denoted  $\delta^{13}$ C) in muscle of 150 narwhals were analysed. The ratios showed a decreasing trend in the first year when they live of mother's milk, hereafter the ratios were relative stable with age.  $\stackrel{15}{\sim}$ N was found to be significantly higher in samples from Uummannaq 1993 compared to the samples from Avanersuaq 1984 and 1985 indicating some difference in trophic levels of the narwhals.  $\stackrel{13}{\sim}$ C were also found to be significant higher in samples from Uummannaq 1984. No correlations were found between stable isotopes ratios and metal and OC concentrations.

### Genetic data

Genetic haplotypes in the skin of 426 narwhals were analysed from the same regions covered by the other analysis. Additionally 99 samples were analysed from Disko Bay, Upernavik, Eastern Canada and east Greenland. In general, the genetic variation was low relative to that found for other cetacean. However, the genetic data gave the strongest evidence for the existence of different populations in the West Greenland area expressed by the frequencies of haplotypes.

The population structure with two West Greenland populations suggested by the genetics study could not be supported by the metal and OC concentrations and stable isotopes.

## 4.7.2 North Atlantic minke whales

In 1998 samples of tissues of 159 minke whales were collected from: west and east Greenland, Jan Mayen, West Svalbard, the Barents Sea,, Vestfjorden/Lofoten and the North Sea (Figure 4.7.2). Tissues have been analysed for OCs (blubber), elements (muscle, liver, kidney and baleen), stable isotopes (muscle), caesium-137 (muscle), fatty acids (blubber) and genetic studies. The aim of the study was to deduce the population structure of minke whales in the northeast Atlantic and the North Sea. The results of each of the individual studies have been published for OCs (Hobbs et al. in press), element and stable isotopes (Born et al. sumitted, a), caesium-137 (Born et al. submitted, b), fatty acids (Møller et al. submitted) and genetics (Andersen et al. submitted).


Figure 4.7.2. Map of sampling locations of tissues of minke whales in 1998. Redrawn from Born et al. submitted

The individual studies revealed somewhat similar population structure of the minke whales in the northeast Atlantic and the North Sea. The difference in OC concentrations suggested that west and east Greenland minke whales constitute one group distint from whales from the other areas. However, the general similarity in mean values and proportions of OC compounds also suggested that the minke whales are quite mobile and may feed in multiple areas (Hobbs et al. in press).

The pattern of elements with relatively long biological half life suggested that minke whales have fidelity to certain summer feeding areas at least for several years and the following stocks was inferred: Greenland, Jan Mayen, a northern stock in the Barents Sea, Svalbard and coastal Norway and the North Sea (Born et al. submitted, a). Caesium-137 concentrations also showed differences among the areas, as the significantly highest levels were found in minke whales from the North Sea and the significantly lowest levels in whales from Svalbard (Born et al. submitted, b).

The fatty acid composition (a total 43 fatty acids) indicate differences between whales from Greenland (west and east), the Northeast Atlantic and the North Sea (Møller et al. submitted).

The genetic study including sequencing of the D-loop in mtDNA and 16 polymorhic nuclear microsatellite markers suggested 4 genetically different sub-populations: a west Greenland, central stock (north of Iceland), northeastern Atlantic and a North Sea sub-population (Andersen et al. submitted). This study also included previous collected samples, in total 306 whales.

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# 5 Other contaminants

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#### 5.1 INTRODUCTION

Numerous inorganic and organic pollutants occur in the industrial products of daily use, leading to a current emission into the environment, where they will be transported by the atmosphere and the sea. Former studies in the Arctic region have shown that long-range transport of compounds produced and emitted in industrialised countries to the remote regions of the Arctic takes place. Additionally, the use of imported industrial products in the Arctic has also been indicated to lead to a certain emission of pollutants.

Up to now the main focus in this context has been on strongly hydrophobic organic pollutants such as polychlorinated biphenyls (PCBs) and chlorinated pesticides. Due to the hydrophobic character of the compounds they will primarily be linked to organic matter of similar polarity and thus be likely to concentrate in sediment and/or to accumulate in animal lipids. The compounds have been found to bioaccumulate in animals and the highest levels are found in the top predators of the Arctic. As marine food, including tissues from the top predators, contributes significantly to the diet of many people in the Arctic, humans are exposed to a high intake of organochlorines and metals, which may affect their health.

However, other groups of organic chemicals could also be of concern in the Arctic. Brominated and fluorinated compounds are examples. These compounds have many physical and chemical properties in common with their chlorinated counterparts and can therefore be expected to increase in the Arctic environment in the same manner as the cloinated substances. Some compounds might be more persistence at higher latitudes than further south. This may be a problem if the compounds are toxic of very low concentrations.

In this chapter levels of a range of compounds not previously included in the Danish AMAP programme are discussed. The groups of contaminants considered are not *new* strictly speaking. The group of polycyclic aromatic hydrocarbons (PAHs) has for instance been analysed in environmental samples from the Temperate Zone for the last thirty years but data from the Arctic are sparse. Other compounds have not been analysed previously in samples from Greenland.

<sup>1)</sup> Chapter 5. Other contaminates.

<sup>2)</sup> AMAP Greenland and the Faroe Islands. Vol. 2: The Environment of Greenland.

# 5.2 TRIBUTYLTIN (TBT)

In the late 1960'ies tributyltin (TBT) replaced cupric oxides as the most used active component in antifouling paints. Already around 1970 the compound was discovered to cause morphological changes in non-target benthic fauna. First abnormal shell thickening in pacific oyster was observed and later the phenomenon called imposex in a range of neogastropods was seen. Endocrine disruption caused by organotins has also been observed in fish, birds and mammals. Organotins also show bioaccumulative properties. High levels (mean concentration: 1400 µg/kg ww) have e.g. been measured in livers of bottlenosed dolphins (*Tursiops truncatus*) stranded along US Atlantic and Gulf Coasts (Kannan et al. 1997). The atmospheric TBT deposition is generally negligible due to the physical-chemical properties of these compounds (Arnold et al. 1997, Fent 1996) and thus aquatic transport processes are considered to be the main pathways.

Jacobsen and Asmund (2000) have conducted a study at Nuuk in 1997, where concentrations of butyltin compounds were investigated in blue mussels (*Mytilus edulis*) (five sites) and marine sediments (three sites).



Figure 5.2.1. Map of the area around Nuuk, Greenland. The mussel sampling stations are marked ( $\star$ ) and the sediment stations by (•). The dotted line marks the main shipping route in the area.

Possible sources in the Nuuk area would mainly be shipping, but also wastewater and effluents from the shipyard should be taken into consideration. The sampling positions are described in Figure 5.2.1 and Table 5.2.1 and 5.2.2. Blue mussels were sampled at low tide by hand, while sediments were sampled with a HAPS gravity stainless steel box corer having an internal diameter of 13.4 cm, and the upper one-cm slice was collected by use of a stainless steel kitchen knife.

The samples were extracted and analysed by the NERI standard method described in detail by Jacobsen et al. (1997) and in the AMAP, Greenland 1996-2001, Data Report. The organotin concentrations were determined by GC-PFPD (Gas Chromatography – Pulsed Flame Photometric Detector). The limit of detection for TBT was around 0.1  $\mu$ g/kg ww for biota and 1  $\mu$ g/kg dw for sediments. In this section all concentrations are presented as tin (Sn) in order to facilitate the comparison between TBT and degradation products.

#### Results and Discussion

The measured organotin concentrations in the collected bivalves are shown in Table 5.2.1, which also includes background information as distance to Nuuk, number of blue mussles collected and the mean shell length.

Table 5.2.1. Positions and data for the blue mussels (*Mytilus edulis*) sampled around Nuuk in November 1997. Concentration levels of organotin and tin (IV) in blue mussels in  $\mu g/kg^{2}$  (all as Sn), monobutyltin was not detected (< 0.1  $\mu G/kG$  ww as Sn). The L.O.D. was estimated to be at less than 0.1  $\mu G/kG$  ww (as Sn). The water content in mussel tissue was (80.2  $\pm$  1.1) % (5 individual determinations)

Station	Lat.	Long.	Distance to Nuuk harbour	No of collected bivalves	Mean shell length	ТВТ	DBT	Sn⁴⁺
	Ν	W	km	i	ст	µg/kg ww	µg/kg ww	µg/kg ww
Hundeøen	64°08.1	51°47.5	4	10	4.76	0.5 ± 0.01	0.8±0.06	1.3 ± 0.29
Nordlandet	64°09.2	51°57.1	13	17	5.19	0.2 ± 0.03	0.5 ± 0.23	0.6 ± 0.22
Qasigiaguit	64°11.8	51°43.5	5	6	4.45	0.4	0.5	1.1
Kaqeq	64°06.5	52°03.4	20	11	3.77	1.2	0.8	0.8
Kook Islands	64°02.6	52°04,8	23	20	4.68	0.7 ± 0.09	0.6±0.04	0.8 ± 0.18

The blue mussels all contained TBT levels between 0.2 and 1.2  $\mu$ g/kg ww and DBT levels between 0.5 and 0.8  $\mu$ g/kg. It was noteworthy that blue mussels 20 km from Nuuk harbour had higher levels of TBT compared to blue mussels closer to Nuuk. This is suggested to relate to the shipping route in the vicinity of the sampling stations and thus TBT is very well distributed in this particular area.

In Iceland Skarphedinsdottir et al. (1996) found a body burden of  $5.9 \pm 5.3 \ \mu g/kg$  ww (as Sn) in blue mussels far from the Icelandic capital Reykjavik. This concentration represents a seasonal maximum in June / August. Near Reykjavik the concentration increased to  $49 \pm 37 \ \mu g/kg$  ww. Thus the concentrations found near Nuuk are 40 to 70 times lower than the concentrations found near Reykjavik.

A TBT study around the Faeroe Islands by Følsvik et al. (1998) showed concentrations ranging from 55  $\mu$ g/kg ww near the capital Thorshavn to 8 - 12  $\mu$ g/kg ww in remote places. These concentrations are comparable to findings in Iceland in autumn, but higher than found in spring when the concentrations near Reykjavik were app. 4  $\mu$ g/kg ww. In comparison, the concentration of TBT in sediments in Danish waters were found to range from 1  $\mu$ g/kg dw in open waters to 16 000  $\mu$ g/kg in highly polluted harbour sediments (Mortensen et al.1996; Jacobsen et al.1998). The organic content of the sediment samples was characterised by determining the loss of ignition at 550 °C. Station 1 and 2 are inside the harbour of Nuuk whereas station 3 is approximately 4 km from the harbour (Figure 5.2.1 and Table 5.2.2). The highest concentration of TBT was  $171 \pm 32 \,\mu$ g/kg dw found in the harbour of Nuuk at station 2, where also the organic content was highest (9.3 %). At station 1 within the port, the TBT level was  $9.7 \pm 3.4 \,\mu$ g/kg dw and the organic content 1.3 % (sandy sediment). At station 3 (Hundeøen) the levels were below 1  $\mu$ g/kg dw.

Recently a second study of TBT concentrations in blue mussels from the westcoast of Greenland was conducted (Strand & Asmund, 2002). The focus of this study was on the difference in organotin concentrations between locations inside and outside harbours. Levels outside Nuuk in this study were comparable to those found before, while the TBT level in mussels inside the habour of Nuuk were about 20 times higher. This pattern with relatively high TBT levels inside harbours and low levels outside harbours and in open water stations was shown at all six areas investigated along the west coast. TBT levels inside Greenland harbours were comparable to levels found in coastal waters in more urbanized parts of the world. The TBT levels measured in blue mussels were compared to levels of imposex detected in neogastropods at the same stations. This revealed TBT levels inside harbours to be high enough to induce imposex in neogastropods, while the levels in open waters are generally below levels where such effects can be found.

Table 5.2.2. Positions and data for the sediment sampling stations collected in November 1997. Concentration levels of butylitn in sediment, N.D.: not detected (less than 1  $\mu$ g/kg dw (as Sn)

Station	Lat.	Long.	Depth	Distance to Nuuk Harbour.	ТВТ	DBT	MBT	Organic content	TBT ratio to organic
	Ν	W	т	km	µg/kg dw	µg/kg dw	µg/kg dw	in %	
S1 Sandkaj (Sand quay)	64°10.2	51°43.5	32	0	9.7 ± 3.4	3.9 ± 1.0	N.D.	1.3	746
S2 Havnen (The harbour)	64°10.5	51°43.5	21	0	171 ±32	9.6 ± 1.1	N.D.	9.3	1839
S <sub>3</sub> Hundeøen	64°09. 0	51°47.2	182	4	N.D.	N.D.	N.D.	3.1	-

More samples are needed to elucidate the TBT contamination level in more remote areas of Greenland, especially also including samples from the east coast. A major drawback in the reviewed studies is that sediment and mussels sampling stations are not coherent. The concentrations of degradation products (such as DBT) in the samples from Greenland were low possibly due to slow degradation rates at the low temperatures in the Arctic.

#### Conclusions and recommendations

TBT and degradation products were detected in the marine Greenland environment. The concentrations inside harbours along the westcoast were comparable to concentrations measured elsewhere in the world, and likely to cause adverse biological effects. Concentrations measured outside the harbour area at Nuuk both in blue mussels and in sediments were much lower than found in Iceland and on the Faroe Islands.

Further screening of TBT baseline levels away from point sources is recommended, possibly in combination with effect studies, and including stations at the east coast. Considering the potential for bioaccumulation of TBT, the occurrence of TBT in the

low trophic levels emphasises the importance of investigating other biological samples in the Arctic food web, especially top predators such as marine mammals.

#### 5.3 TOXAPHENE

Toxaphene is a chlorinated pesticide consisting of a complex mixture of polychlorobornanes. Theoretically, there are over 30 000 possible chlorobornane isomers. Technical toxaphene, which mainly consists of  $C_7 - C_9$  chlorobornanes could contain at least 6840 congeners (Muir & de Boer, 1996). Analysis of toxaphene is difficult because of the mixture's complexity. Toxaphene is very persistent in the environment and is globally dispersed via atmospheric transport, as are several other chlorinated pesticides.

Appendix C shows the data available of toxaphene in the Greenland environment. Data are derived from the following AMAP projects: "Contaminants in Greenland human diet", "Biological core programme", "Temporal trend programme" and "Population structure of West Greenland narwhals, a multidisciplinary approach". Data of toxaphene in walrus published in Muir et al. (2000b) is also shown for comparative reasons. Several analytical laboratories have been involved. In some cases total toxaphene has been determined, while others are based on selected toxaphene congeners. Analysis of single congeners is the most precise method.

#### Levels

Toxaphene concentrations in biota from the terrestrial environment (ptarmigan, hare, lamb and musk ox) were low (range  $<0.1 - 2.6 \mu g/kg ww$ ). In the marine environment the highest total toxaphene concentrations were found in narwhals (range in blubber 2033 to 8825 µg/kg ww). In monodontiids (beluga and narwhal) toxaphene is reported to be the most dominant OC (Muir et al. 1999). This was also detected in samples from Greenland. In minke whale, walrus and ringed seal blubber, the total toxaphene concentration ranged between 219 and 369  $\mu$ g/kg ww, lowest in ringed seal and highest in minke whales (Appendix C). In seabird liver the total toxaphene concentrations ranged between 13.5 µg/kg ww in common and king eider and 53.0 µg/kg ww in thick-billed murre. Total toxaphene was not determined in black guillemot, only single congeners. Based on the concentrations of these congeners, the highest concentrations in seabirds were found in black guillemot (Appendix C). A few livers of marine fish sampled in southwest Greenland were analysed for some toxaphene congeners (Appendix C). The highest concentrations of CHB-50 (the dominant congener) was found in liver of Atlantic cod (62.9 µg/kg ww) and the lowest in liver of shorthorn sculpin (14.2  $\mu$ g/kg ww). The concentration of CHB-50 in marine fish was in the same order of magnitude as found in seabirds. The lowest concentration of toxaphene congeners in the marine biota was found in blue mussels (Appendix C).

Compared to other Arctic regions, the toxaphene concentrations in blubber of ringed seals from Greenland were comparable to the concentrations found in the Canadian Arctic, but higher than concentrations in seals from Svalbard (Cleemann et al. 2000a). Toxaphene concentrations in walrus from Avanersuaq were at the same level as found in the Canadian Arctic (Muir et al. 1999). In walrus from Ittoqqortoormiit the toxaphene concentrations were higher (also the case for other persistent organochlorines) than in Avanersuaq, but at a similar level as walrus from Inukjuak (east Hudson Bay, Canada) (Muir et al. 1999).

# Sex differences

Possible differences between toxaphene concentrations in males and females were tested in cases of adult black guillemot sampled in Qeqertarsuaq 1999 and 2000 and in Ittoqqortoormiit in 2000 and of ringed seals sampled in Qeqertarsuaq and Ittoqqqortoormiit in 2000. The test was performed as a t-test on logarithmic transformed lipid normalised data for each toxaphene congener separately (CHB-26, 40, 41, 44 (only black guillemot), CHB-50 and 62). No differences between males and females were found in the case of black guillemot from Qeqertarsuaq 1999 and 2000 and for ringed seals from Qeqertarsuaq and Ittoqqortoormiit 2000, except for CHB-62, which was significantly higher in females. In black guillemot from Ittoqqortoormiit 2000 the concentrations of all congeners except CHB-41 were significantly (p<0.05) higher in females than in males.

Figure 5.3.1 shows the relationship between total toxaphene and age, represented by number of growth layers, in narwhals from west Greenland. The relationship of toxaphene with age was also typical for other OCs such as  $\sum$ PCB, HCB,  $\sum$ HCH and DDT (Riget et al. 2002). Toxaphene concentrations in females showed a decreasing trend from the yearlings to an age of about 8 to 10 years. Animals between 10 to 15 years showed an increasing concentration. In males toxaphene showed a decrease in the first few years of life followed by a gradual increase with increasing age. The lower levels of toxaphene in adult females compared to younger females and adult males are common in cetaceans and pinnipeds because of elimination of these lipophilic compounds via lactation (e.g. Addison & Smith, 1974). The increase from 10 years to 15 years was therefore unexpected. However, high levels in only 3-4 individuals created this pattern.



Figure 5.3.1. Relationships between total toxapene concentrations ( $\mu$ G/kg l.w.) and age (Growth Layer Groups) in narwhals from west Greenland. Lines represent LOWESS smoother. F=females, M=males

#### Area differences

Possible differences between toxaphene concentrations in west (Qeqertarsuaq) and east (Ittoqqortoormiit) were tested for black guillemot and ringed seal sampled in 2000. The test was performed as a t-test on logarithmic transformed lipid normalised data. The test was done for each toxaphene congener and sex separately (CHB-26, 40, 41, 44 (only black guillemot), CHB-50 and 62). No significant (p<0.05) differences were found in case of female black guillemot and female ringed seal between west and east. But in male black guillemot the concentration of toxaphene congeners CHB-26, 40, 41 and 50 and in male ringed seal the concentrations of all congeners except CHB-40 were significantly higher in east Greenland than in west Greenland.

The somewhat higher toxaphene concentrations in east Greenland than in west Greenland found in this study confirmed the previous findings in AMAP phase I of higher toxaphene concentrations in blubber of ringed seal and muscle of Arctic char from east Greenland than in the same species from west Greenland (Cleemann et al. 2000a, 2000b). A similar geographical pattern has been reported in walrus from east and west Greenland (Muir et al. 2000b)

In the study "Population structure of West Greenland narwhals", no geographical differences in total toxaphene concentrations among four locations in west Greenland were found (Riget et al. 2002).

#### Conclusions and recommendations

Toxaphene concentrations in the Greenland marine biota were within the range observed in other Arctic areas. Toxaphene levels in Greenland terrestrial biota were lower than in marine biota. The highest toxaphene levels were found in marine mammals especially narwhal and beluga. Only few data exist to form the basis of an assessment of temporal trends of toxaphene levels in Greenland biota. Trend studies in single key-species could reveal if the ban of toxaphene at lower latitudes leads to a decrease in toxaphene levels in the Greenland environment

#### 5.4 DIOXINES AND FURANES (PCDD/Fs)

Polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) are formed as by-products in industrial processes or by incinerations and are highly toxic, especially the 2,3,7,8-TCDD congener. Most PCDD/F congeners are extremely hydrophobic and resistant to biodegradation. Some congeners are known to bioaccumulate, while vertebrates readily degrade others (AMAP, 1998).

Dioxines and furans have been analysed in liver and blubber of polar bears sampled in Ittoqqortoormiit in the project "Effects of Contaminants in the Greenland Sea Polar Bear". The National Water Research Institute, Canada conducted the chemical analyses. The following congeners were measured:

dioxins	furans
2,3,7,8 TCDD	2,3,7,8 TCDF
1,2,3,7,8 PCDD	1,2,4,6,8 PCDF
1,2,3,4,7,8 HxCDD	1,2,4,7,8 PCDF
1,2,3,6,7,8 HxCDD	1,2,3,7,8 PCDF
1,2,3,7,8,9 HxCDD	2,3,4,7,8 PCDF
1,2,3,4,6,7,9 HpCDD	1,2,3,4,7,8 HxCDF
1,2,3,4,6,7,8 HpCDD	1,2,3,6,7,8 HxCDF
1,2,3,4,6,7,8,9 OCDD	1,2,3,7,8,9 HxCDF
	1,2,3,4,6,7,8 HpCDF
	1,2,3,4,7,8,9 HpCDF
	1,2,3,4,6,7,8,9 OCDF

The total dioxins and furans levels were at the same level as found in polar bears from Arctic Canada (Norstrom & Muir, 1994). The dominant dioxin congener was HxCDD (Table 5.4.1), while in the Canadian polar bears TCDD and OCDD dominated (AMAP 1998).

Total	n	n Lipid (%)		PCDDs	PCDFs
Fat	5	5 88.0 ± 6.7		7.25 ± 1.66	3.29 ± 0.92
Liver	5	5 10.9 ± 2.3		12.2 ± 6.6	13.9 ± 3.4
Congeners	n TCI	DD PCDD	HxCDD	HpCDD	OCDD
Fat	5 0.55±0.2	8 1.80±0.81	2.62 ± 0.90	0.71 ± 0.34	1.57 ± 1.53
Liver	5 0.48±0.3	7 2.74±1.76	7.57 ± 4.22	0.87 ± 0.45	0.55 ± 0.09
Fat Liver	n TC 5 0.40 ± 0.3 5 0.05 ± 0.1	DF PCDF 9 1.73 ± 0.79 1 12.7 ± 3.6	HxCDF ND 1.14 ± 0.45	HpCDF 0.36 ± 0.40 0.05 ± 011	OCDF 0.80 ± 0.38 ND

Table 5.4.1. Total dioxins (PCDDs) and furans (PCDFs) concentrations (Ng/kg ww) and cogeners in five polar bears sampled in IttoqQortoormiit 1999/2000.

The levels of dioxins and furans in polar bears from east Greenland were low, measured as WHO toxicity equivalents 2.85 ng/kg ww in fat and 4.33 ng/kg ww in liver. However, it should be noted that only few data are avilable from Greenland.

## Conclusions and recommendations

Dioxins and furans were detected in polar bears. Compared to marine mammals in other Arctic regions the concentrations were relatively low. Further investigations regarding sources of these compounds and concentrations at lower levels in the foodchain is recommended, taking the high potential for long-term detrimental effects of these compounds into account.

## 5.5 COPLANAR PCBs (NPCB)

Coplanar PCBs are PCB congeners with 3,3',4,4' chlorine substitutions. The lack of chlorine substituents in the 2 and 6 positions permits nPCBs to form planar configurations similar to that of polychlorinated dibenzo-p-dioxins and dibenzofurans. The coplanar PCBs are the most toxic PCB congeners and exhibit biochemical and activity much comparable to the activity of the dioxin conger TCDD.

Coplanar PCBs (PCB 77, 126 and 169) were analysed in muscle and blubber of ringed seal and liver and blubber of polar bears. The samples were from Ittoqqortoormiit, measured as part of the projects "Effects of Contaminants in the Greenland Sea Polar Bear" and "Contaminants in Greenland human diet". The National Water Research Institute, Canada conducted the chemical analyses.

Very low concentrations of PCB 77, 126 and 169 were found in ringed seal muscle (mean toxic equivalents 0.13 ng/kg ww, n=5 (Muir & Johansen, unpubl.)) and in blubber (mean toxic equivalents 5.6 ng/kg ww, n=10 (Muir & Johansen, unpubl.)).

The concentrations of coplanar PCBs congener in polar bears (as WHO TEQ) were higher (6.33 ng/kg ww for fat and 5.67 ng/kg ww in liver) than the concentrations of dioxin congeners indicating that coplanar PCBs are more important than dioxins and furans from a toxicological point of view. Compared to ringed seals and cetaceans from Arctic Canada, the concentrations in polar bears from East Greenland were lower (AMAP, 1998).

TABLE 5.5.1. COPLANAR PCBs CONCENTRATION	(NG/KG WW) IN	N FIVE POLAR	BEARS SAM	IPLED IN
Ittoqqortoormiit 1999/2000.				

Congeners	n	CB77	CB126	CB169
Fat	5	9.78±5.95	54.6±26.5	86.7±57.7
Liver	5	12.3±0.3	53.2±31.7	35.4±19.9

Conclusions and recommendations

Coplanar PCBs were detected in ringed seal and polar bears from east Greenland. The coplanar PCBs contributed relatively more to total toxicity, measured as WHO TEQ, than dioxins and furans (PCDD/F). Compared to marine mammals in other Arctic regions the concentrations were relatively low. Taking the high potential for long-term detrimental effects of these compounds into account further monitoring in key species is recommended.

## 5.6 CHLOROBENZENE (CBZ)

Chlorobenzenes are cyclic aromatic compounds formed by the addition of 1-6 atoms of chlorine to the benzene ring. Chlorobenzenes are used as intermediates in the synthesis of pesticides and other chemicals. 1,4-DCB is used in industrial odor control and as a moth repellant. The higher chlorinated benzenes (TCBz and 1,2,3,4-TeCBzs) have been used as dielectric fluents. Hexachlorobenzene, HCB was used as a fungicide on grains, especially wheat. The release of chlorobenzenes to the environment occurs primarily during manufacture and through the dispersive nature of their uses. In general the water solubility of chlorobenzene compounds is medium to low decreasing from 293 to 0.83 mg/L with increased chlorination.

Chlorobenzenes released to the aquatic environment will evaporate (boiling points in the range 132 - 277 °C), deposite in the sediment or metabolize. Chlorobenzenes are transformed mainly by photodegradation or microbial degradation, which takes place under aerobic conditions. Chlorobenzenes tend to accumulate in tissues with a high fat content due to the lipophilic nature of the compounds expressed by log K<sub>ow</sub> in the range 2.98 – 5.03. They are generally only moderately toxic to wildlife and man, but effects on the liver, kidneys, adrenal glands, mucous membranes, brain ganglion cells and metabolising enzymes have been observed following acute exposure to non-lethal doses. Some chlorobenzenes have carcinogenic and teratogenic properties (reviewed in WHO 1991a).

Data are derived from the following AMAP projects: "Contaminants in Greenland human diet", "Biological core programme"and "Temporal trend programme". The National Water Research Institute, Canada conducted the chemical analyses of chlorobenzenes (1,2 DCB, 1,3 DCB, 1,4 DCB, 1,3,5 TCB, 1,2,4 TCB, 1,2,3 TCB, 1,2,3,4 TTCB, PeCB, HCB).

Appendix D shows the concentrations of higher chlorinated benzene (tetra-, penta and hexachlorobenzene) in the Greenland environment. In the terrestrial environment sCBz (sum of tetra- and penta and hexachlorobenzene) concentrations ranged from 0.17 ng/g ww in lamb muscle to 16.5 ng/g ww in musk ox muscle. The dominant chlorobenzene was HCB constituing 80-90%, except in ptarmigan liver where TeCB dominated (53%). In landlocked Arctic char muscle sCBz were low (range 0.38-0.91 ng/g ww) with HCB as the dominating chorobenzene (app. 94%).

In marine invertebrate (snow crab and shrimp), sCBz concentrations were also low (maximum 3 ng/g ww in crab hepatopancreas) and the dominating chlorobenzene was HCB, except in shrimp muscle where TeCB dominated. In marine fish, the highest sCBz concentrations were found in liver of Greenland halibut (45 ng/g ww) and in liver of shorthorn sculpin (13 ng/g). In shorthorn sculpin, higher levels were found in fish from east Greenland (Ittoqqortoormiit) than in fish from west Greenland (Qeqertarsuaq). HCB was also here the dominating chlorobenzene (81-90%). No bioaccumulation of chlorobenzene from fish to seabirds was observed, the

highest sCBz concentrations were found in liver of Greenland halibut (45 ng/g ww) and in liver of shorthorn sculpin (13 ng/g). In shorthorn sculpin, higher levels were found in fish from east Greenland (Ittoqqortoormiit) than in fish from west Greenland (Qeqertarsuaq). HCB was also here the dominating chlorobenzene (81-90%). No bioaccumulation of chlorobenzene from fish to seabirds was observed, the highest levels were found in liver of thick-billed murre liver (6.5 ng/g ww). In marine mammals, the highest sCBz concentrations were found in blubber of marine mammals, especially narwhal and beluga (mean 462 and 260 ng/g ww, respectively). HCB was the dominating chlorobenzene (53% in ringed seal kidney - 96% in narwhal blubber).

In general, the CBz levels in terrestrial Greenland species appear higher than in similar species from Canada, whereas the levels in freshwater and marine Greenland species appear lower than in similar species from Canada (AMAP, 1998).

## Conclusions and recommendations

The highest chlorobenzene concentrations were found in blubber of narwhal and beluga. The far dominating chlorobezene in Greenland biota is hexachlorobenzene (HCB).

Continued monitoring of the levels of this compound in top predators in Greenland are recommended in order to evaluate the time trend of concentration levels.

#### 5.7 New chlorinated pesticides

This section deals with heptachlor and heptachlor epoxide, dieldrin, aldrin, endrin, endosulfan, metoxyclor and mirex. These compounds are not used in Greenland and are found mainly due to long-range transport from lower latitudes. The pesticides heptachlor, aldrin, dieldrin and endrin together with mirex are banned worldwide but are still found in considerable concentrations due to high persistence in the environment. Endosulfan and methoxychlor belong to a newer class of less persistent chlorinated pesticides. Information about their use, chemical proporties, environmental fate and toxicity are shown in Box 5.7.1.

Data are derived from the following AMAP projects: "Contaminants in Greenland human diet", "Biological core programme" and "Temporal trend programme". The National Water Research Institute, Canada conducted the chemical analyses of these compounds, except for ringed seals from Avanersuaq in 1998, which was conducted by the National Wildlife Research Center, Canada.

#### Aldrin and Dieldrin

Aldrin is readily metabolised to dieldrin in plants and animals. As their mode of action and their acute and chronic toxicity also is similar, national and international regulatory bodies usually consider them together. Aldrin and dieldrin are organochlorine insecticides, which were used from the 1950s to the early 1970s to control soil pests and to treat seeds. Since the 1970s, a number of countries have severely restricted or banned aldrin and dieldrin from use in agriculture (WHO, 1989).

Both compounds are stable unless attacked by oxidising agents and concentrated acids. Dieldrin is more resistant to biodegradation than aldrin (WHO 1989). Aldrin and dieldrin are highly toxic for aquatic organisms, with 96-h  $LC_{50}$ -values below 50 µg/L for crustaceans and about 1-40 µg/L for fish (WHO ,1989). Both aldrin and dieldrin are described as "possibly carcinogenic to humans" on the US-EPA's list of chemicals evaluated for carcinogenic potential, and they are both identified as endocrine disrupters.

Both compounds are virtually insoluble in water. Their log  $K_{ow}$  values are 7.2 and 6.2 for aldrin and dieldrin, respectively, indicating high lipophilicity (Verschueren, 1996). Volatilisation appears to be the main route of loss from soil, though atmospheric levels of dieldrin and aldrin are low (WHO, 1989). Aldrin bioaccumulates mainly as its degradation products. The bioconcentration of dieldrin in aquatic organisms is principally from the water rather than by ingestion of food (WHO, 1989).

#### <u>Endrin</u>

Endrin is an organochlorine insecticide of high acute toxicity and chemically related to aldrin and dieldrin, being the stereoisomer to dieldrin. It has been produced since 1950 and was used throughout the world up to the early 1970s, when it was restricted or even banned in several countries (WHO, 1991b). In the USA, production and sale of endrin stopped in 1986 (ATSDR, 1997). Endrin was used to control a range of pests, particularly Lepidoptera on cotton (WHO, 1991b).

Endrin is practically insoluble in water and is retained in soils with a high organic matter content. Its persistence can reach up to 12 years. Volatilisation, photodegradation and microbial transformation can take place to reduce endrin residues in soils. It is mainly transported into the aquatic environment by run-off processes. Aquatic invertebrates and fish will rapidly take it up. Endrin is metabolised by animals, and the accumulation in lipids is low (WHO, 1991b).

Endrin has a high acute toxicity. It affects the liver and the central nervous system and causes neurotoxic effects. A number of metabolites have even higher acute toxicity, for instance 12-ketoendrin (about 1 mg/kg body weight) (WHO, 1991b).

#### Endosulfan

Endosulfan is an organochlorine insecticide of the cyclodiene group. It has been used in all branches of agriculture since 1954 (Gupta & Gupta, 1979). Today, its application is prohibited in a number of countries, but is still in use in e.g. Spain and the United States (Aguilera-del Real et al. 1997, Antonius & Byers, 1997).

The technical product is comprised of 70 % alpha-endosulfan and 30 % beta-endosulfan, with alpha being more toxic than beta. The high acute toxicity are directed towards the central nervous system. In spite of its hydrophobicity (log  $K_{ow}$ =4.7), endosulfan does not accumulate in organisms. However, it is very toxic to fish and other aquatic organisms and caused a massive fish killing in the river Rhine as the consequence of an accidental discharge (Greve & Wit, 1979; Gill et al. 1991).

Endosulfan is readily hydrolysed to endosulfan-diol or oxidised to endosulfan-sulphate in the environment. The metabolites, endosulfan-sulphate, was found to be more toxic than the parent compounds (Dubey et al. 1984).

#### Metoxychlor

Methoxychlor is an organochlorine insecticide still in use to protect vegetables, fruits, trees, farm animals and pets against a variety of pests (US-EPA, 1988). It has a low solubility in water (0.1 mg/L at 25°C) and a log  $K_{ow}$  around 3-4.3. In water, methoxychlor is adsorbed onto suspended solids and sediments. It may be ingested and bioaccumulated by some aquatic organisms, but significant and persistent accumulation has not been shown. In soil it is mainly degraded anaerobically, with half-lives from 1 week to 2 months, while the aerobic degradation results in half-lives of more than 3 months. Animal tests indicated reproductive toxicity and a carcinogenic potential of methoxychlor.

#### **Heptachlor**

Heptachlor is an organochlorine cyclodiene insecticide. During the 1960s and 1970s, it was used primarily by farmers to kill termites, ants, and soil insects in seed grains and on crops, as well as by exterminators and home owners to kill termites. Heptachlor about 10% of the pesticide formulation chlordane, discussed in preceeding chapters. The half-life of heptachlor in the environment is in the range of days to a few weeks. An important metabolite of heptachlor is heptachlor epoxide, which is an oxidation product formed from heptachlor by bacteria and many plant and animal species.

Heptachlor is a moderately toxic compound in EPA toxicity class II. In 1988, the EPA canceled all uses of heptachlor in the U.S. The only commercial use still permitted is for fire ant control in power transformers. Heptachlor is still available outside the U.S.

#### Mirex

Mirex was used as an insecticide and fire retardant, mainly in the United States and Canada, until 1978. Mirex is considered to be one of the most stable and persistent pesticides in soil, sediment, and water, with a half life in soil of up to 10 years. A log  $K_{ow}$  of 7,4 indicates mirex will strongly adsorb to organic materials. For most part mirex is resistant to biological and chemical degradation. Photolysis of mirex may occur, especially as mirex is relatively volatile. Mirex is highly fat-soluble and has a high acute toxicity to aquatic organisms, exemplified by a  $LC_{50}$  of 0,1-1,0 ppb for chrustaceans. There is indication of cancerogenic and reproductive effects in laboratory animals.

## Results and discussion

Table 5.7.1 summarises levels of organochlorine pesticides in various terrestrial animals from different places in west Greenland. Higher concentrations were found in liver and kidney, compared to fat and muscle tissues. Levels are furthermore much lower than found in marine organisms. This phenomenon might be due to the lower trophic level of the terrestrial species analyzed.

Heptachlor epoxide, dieldrin and mirex concentrations were below detection limits for musk ox and hare. Levels of dieldrin and mirex in ptarmigan were at the same level as reported for orther Arctic regions in AMAP phase I. Levels of methoxychlor and endosulfan have not been reported in terrestrial animals from other places in the Arctic. Even though levels are generally low, the occurrence of these substances in the Greenland environment is noteworthy as these chemicals have not been used in Greenland, but are transported from lower latitudes - even endosulfan and methoxychlor which are much less persistant than the "old" OCs,

TABLE 5.7.1 LEVELS OF ORGANOCHLORINE PESTICIDES (NG/G LIPID) IN TERRESTRIAL ORGANI	SMS
from Greenland, 1999. $\Sigma$ Drine = Aldrin+Dieldrin+Endrin, Heptachlor = Heptach	lor +
Heptachlor epoxide, $\Sigma$ Endosulfan=alfa+beta endosulfan, n=5 for all matrices	

Species	Tissue	Av. lipid (%)	$\Sigma$ Heptachlor	$\Sigma$ Drine	$\Sigma$ Endosulf an	Methoxy- chlor	Mirex
Ptarmigan, Nuuk	Muscle	3.8	0.18 ±0.41	3.17 ±0.68	0.66 ±0.38	n.d.	0.09 ±0.20
	Liver	6.8	5.82 ±4.78	14.6 ±13.09	1.85 ±0.87	n.d.	0.08 ±0.18
Hare, Qeqertarsuaq	Kidney	32.5 etc.	0.99 ±0.49	2.82 ±1.04	0.13 ±0.15	0.02 ±0.02	0.13 ±0.09
	Liver	4.1	40.1 ±29.3	66.3 ±56.5	0.52 ±0.10	n.d.	1.50 ±0.44
	Muscle	3.8	3.50 ±4.69	9.89 ±9.98	0.38 ±0.42	0.25	0.02 ±0.04
Lamb, Narsaq	Fat	90.2	0.05 ±0.02	0.07 ±0.04	n.d.	0.25 ±0.56	0.03 ±0.04
·	Kidney	4.2	0.34 ±0.27	3.83 ±3.23	0.08 ±0.07	3.07 ±6.65	0.07 ±0.10
	Liver	9.6	0.15 ±0.06	0.38 ±0.35	0.14 ±0.28	0.56 ±1.25	0.18 ±0.19
	Muscle	12.3	0.27 ±0.23	0.75 ±0.54	n.d.	0.23 ±0.41	0.19 ±0.14
Musk ox, Kangerlussuaq	Fat	72.1	0.02 ±0.04	0.31 ±0.45	0.37 ±0.80	5.03 ±11.2	0.02 ±0.02
	Kidney	3.2	0.10 ±0.10	4.12 ±1.17	0.04 ±0.08	n.d.	0.38 ±0.47
	Liver	10.3	0.08 ±0.17	1.51 ±0.58	n.d.	0.01 ±0.03	0.23 ±0.04
	Muscle	15.3	0.07 ±0.12	1.26 ±0.59	0.05 ±0.12	0.72 ±0.54	0.07 ±0.13

In Table 5.7.2 levels of chlorinated pesticides in whales from west Greenland are presented. Levels of mirex in beluga from the Canadian Arctic were higher than seen from Greenland, while the opposite was the case for dieldrin and heptachlorepoxide, the latter were approximately 5 times lower in this study than in belugas from the Canadian Arctic (Metcalfe et al. 1999, Muir et al. 1996). In an earlier study by Metcalfe et al. (1999), the distribution of mirex in beluga from the Canadian Arctic was somewhat different from the pattern seen in this study. Metcalfe (ibid) found higher concentrations in liver than in muscle tissue, the opposite pattern seen in Greenland.

Table 5.7.2 Levels of organochlorine pesticides (ng/g lipid) in whales from Nuuk, west Greenland 1999.  $\Sigma$ Drine = Aldrin+Dieldrine+Endrin,

ΣΗερτάςμ	$\Sigma$ Heptachlor=Heptachlor+Heptachlor epoxide, $\Sigma$ Endosulfan=alfa+beta endosulfan						
Species	Tissue	Av.	$\Sigma$ Heptachlor	$\Sigma$ Drine	$\Sigma$ Endosulfane	Methoxy-	Mirex
		lipid	·			chlor	
		(%)					
Beluga	Blubber(10)	87.9	118 ±63.8	489 ±258	n.d.	n.d	10.8 ±4.15
	Kidney (5)	4.4	59.3 ±29.5	269 ±133	14.6 ±7.86	2.66 ±2.69	6.43 ±3.73
	Liver (5)	6.8	38.9±24.3	183 ±119	10.1 ±6.22	2.54 ±2.78	4.36 ±2.44
		etc.					
	Muscle (16)	2.3	105 ±70.9	488 ±350	33.4 ±19.1	1.04 ±1.93	17.3 ±14.9
	Skin (5)	3.6	99.7 ±62.5	391 ±253	43.5 ±28.7	n.d.	13.8 ±7.29
Narwhal	Blubber (3)	78.6	167 ±94.9	554 ±316	72.9 ±24.3	10.9 ±4.11	14.3 ±5.90

In Table 5.7.3 pesticide levels in ringed seals from Greenland regions are summarized. As earlier reported for other OCs, levels were generally higher on the east coast compared to the west coast and levels in males are generally higher than in females (cf. Figure 5.7.1). This pattern is often reported for bioaccumulating contaminants as females excrete a part of their body load to their offspring.

Mirex was in the same range as reported for female seals in Canada 6.7  $\mu$ g/kg ww and 22.9  $\mu$ g/kg ww for female and male, respectively. Dieldrin was not measured in the

present study and therefore the sums of drine in Table 5.7.3 includes only the sum of aldrin and endrin. For dieldrin mean values found in the Canadian Arctic were 36.5 and 34.9 in female and male seals, respectively – these values were twice as high in male seals from Avernarsuaq (Cameron et al. 1997). Levels of dieldrin and mirex were also measured in different areas of the Arctic during AMAP phase I. Dieldrin levels in blubber were in the range 13.6 to 187  $\mu$ g/kg, while mirex was found in concentrations of 3.43 to 26.1  $\mu$ g/kg.



Figure 5.7.1 Levels of chlorinated pesticides in seals from Qeqertarsuaq, west and ittoqqortoormiit, east Greenland. F and M denotes female and males, respectively

Table 5.7.3 Levels of organochlorine pesticides (ng/g lipid) ringed seals from Greenland.  $\Sigma Drine = Aldrin+Dieldrin+Endrin$ ,

 $\Sigma$ Heptachlor=Heptachlor+Heptachlor epoxide,  $\Sigma$ Endosulfan=alfa+beta endosulfan. Itt=Ittoqoortoormiit, Qeq=Qeqertarsuaq, Ava=Avannersuaq.

Area, Year	Sex	Organ	$\Sigma$ Heptachlor	$\Sigma$ Drine	$\Sigma$ Endosulfan	Methoxy- chlor	Mirex
ltt., 1999	F	blubber	26.7 ±14.9	2.00 ±2.54	2.13 ±1.85	0.30 ±0.85	7.13 ±4.95
ltt., 1999	М	-	50.4 ±49.9	6.70 ±12.1	4.03 ±5.76	0.80 ±2.35	8.80 ±12.34
ltt., 1999	F	liver	51.1 ±8.29	6.36 ±6.03	3.95 ±2.00	n.d.	12.4 ±9.80
ltt., 1999	М	-	83.6 ±37.2	4.96 ±7.00	4.26 ±3.42	n.d.	24.4 ±14.7
ltt., 1999	F	muscle	31.8 ±13.7	8.03 ±5.97	2.66 ±2.87	0.09 ±0.25	13.1 ±9.41
ltt., 1999	М	-	41.3 ±34.1	5.83 ±7.95	3.80 ±7.37	1.37 ±2.47	10.8 ±10.2
Qeq., 1999	F+M	blubber	24.2 ±9.51	5.31 ±1.75	4.13 ±3.12	0.42 ±0.93	3.11 ±1.78
Qeq., 1999	F+M	liver	2.38 ±0.46	5.10 ±3.79	6.40 ±2.93	0.98 ±2.20	2.20 ±1.18
Qeq., 1999	F+M	kidney	0.40 ±0.14	6.26 ±5.32	2.31 ±2.64	n.d.	0.79 ±0.35
Qeq., 1999	F+M	muscle	1.13 ±1.66	5.89 ±3.70	3.41 ±2.10	0.06 ±0.26	2.47 ±3.26
Ava, 1998	F	blubber	n.a.	38.8 ±14.4	n.a.	n.a.	5.80 ±4.58
Ava, 1998	М	blubber	n.a.	84.5 ±64.7	n.a.	n.a.	11.5 ±11.3

In Table 5.7.4 levels in birds from the Nuuk area are shown. The most interesting result is probably the higher levels of endosulfan and mirex found in kittiwake compared to the other species in the area, which probably is a reflection of migration patterns but could also reflect interspecific differences in metabolic capacities.

Table 5.7.4 Levels of organochlorine pesticides (ng/g lipid) in seabirds from Nuuk, western Greenland, 1999.  $\Sigma$ Drine = Aldrin+Dieldrin+Endrin,  $\Sigma$ Heptachlor=Heptachlor+Heptachlor epoxide,  $\Sigma$ Endosulfan=Alfa+beta endosulfan, N=5 for all matrices

N-5 FOR ALL MATRICES								
Species	Tissue	$\Sigma$ Heptachlor	$\Sigma$ Drine	$\Sigma$ Endosul-	Methoxy-	Mirex		
				fan	chlor			
Common eider	Liver	83.1 ±20.7	137 ±21.1	5.3 ±1.9	n.d	2.4 ±1.4		
	Muscle	24.3 ±6.4	52.8 ±16.4	3.3 ±1.3	n.d	3.2 ±1.2		
King eider	Liver	109 ±70.7	140 ±47.4	4.1 ±1.3	n.d	5.1 ±1.9		
	Muscle	21.2 ±6.7	36.7 ±17.4	4.2 ±2.9	n.d	3.9 ±1.1		
Kittiwake	Liver	30.9 ±42.5	58.8 ±49.5	15.1 ±18.2	0.14 ±0.19	30.4 ±35.43		
	Muscle	41.0 ±9.7	90.3 ±19.8	58.3 ±17.0	2.3 ±1.9	22.5 ±25.5		
Thick-billed murre	Liver	17.3 ±3.6	68.1 ±14.7	10.1 ±2.9	2.4 ±1.6	5.6 ±1.9		
	Muscle	35.7 ±46.4	76.6 ±71.8	5.5 ±3.3	2.6 ±8.7	4.4 ±4.0		

Only few data are available of concentrations of these chlorinated pesticides in adult birds from the Arctic as well as from lower latitudes. In AMAP phase I, levels of dieldrin, mirex and heptachlor epoxide were reported for a few liver samples of kittiwake, king eider and thickbilled murre from the Russian Arctic. Dieldrin was not found in any of these samples while levels of mirex were 0.21, <0.01-0.07, <0.01-0.67 µg/kg ww for kittiwake, king eider and thickbilled murre, respectively. For the last two species this is in the same range as measured in the Nuuk area, while kittiwake from Nuuk shows concentrations of mirex up to 20 times the level reported from Russia. Heptachlor epoxide was not detected in king eider from Russia while levels in thick billed murre were in the range 0.44-1.49 µg/kg ww which is in the same range as reported in this study. Levels in kittiwake were 3.36 µg/kg, which is similar to levels in kittiwake from Nuuk (AMAP, 1998).

Mirex has later been analysed in muscle tissue from glaucous gulls (*Larus hyperboreus*) from Bjørnoya, Norway, and concentrations were  $1.162 \pm 0.931 \,\mu$ g/kg lw (Skagerup et al. 2002). This is lower than found in the area of Nuuk. Of all birds analysed during AMAP phase I only two cases were higher for mirex than reported here, namely levels of 253 and 40.8  $\mu$ g/kg ww found in glaucous gulls and northern fulmar (*Fulmaris glacialis*) from the Russian Arctic (AMAP, 1998).

Table 5.7.4 Levels of organochlorine pesticides (NG/G lipid) in seabirds from Nuuk, western Greenland, 1999.  $\Sigma$ Drine = Aldrin+Dieldrin+Endrin,

$\Sigma$ Heptachlor=Heptachlor+Heptachlor epoxide,	∑Endosulfan=alfa+beta	ENDOSULFAN,
N=5 FOR ALL MATRICES		

Species	Tissue	$\Sigma$ Heptachlor	$\Sigma$ Drine	$\Sigma$ Endosul-fan	Methoxy- chlor	Mirex
Common eider	Liver	83.1 ±20.7	137 ±21.1	5.3 ±1.9	n.d	2.4 ±1.4
	Muscle	24.3 ±6.4	52.8 ±16.4	3.3 ±1.3	n.d	3.2 ±1.2
King eider	Liver	109 ±70.7	140 ±47.4	4.1 ±1.3	n.d	5.1 ±1.9
	Muscle	21.2 ±6.7	36.7 ±17.4	4.2 ±2.9	n.d	3.9 ±1.1
Kittiwake	Liver	30.9 ±42.5	58.8 ±49.5	15.1 ±18.2	0.14 ±0.19	30.4 ±35.43
	Muscle	41.0 ±9.7	90.3 ±19.8	58.3 ±17.0	2.3 ±1.9	22.5 ±25.5
Thick-billed murre	Liver	17.3 ±3.6	68.1 ±14.7	10.1 ±2.9	2.4 ±1.6	5.6 ±1.9
	Muscle	35.7 ±46.4	76.6 ±71.8	5.5 ±3.3	2.6 ±8.7	4.4 ±4.0

In Table 5.7.5 the levels of organochlorine pesticides in various fish species are summarized. In AMAP phase I, levels of dieldrin, mirex and heptachlor epoxide were measured in muscle tissue of Arctic char from the Canadian Arctic – levels of dieldrin found here were generally one order of magnitude higher than found in this study while heptachlor epoxide and mirex were in the same range. Levels of mirex and dieldrin earlier measured in the Canadian Arctic in the marine species Greenland halibut and sculpin were higher or in the same range as the data presented here.

Table 5.7.5 Levels of organochlorine pesticides (ng/g lipid) in fish from Nuuk, western Greenland, 2000.  $\Sigma$ Drine = Aldrin+Dieldrin+Endrin,

 $\Sigma$ Heptachlor=Heptachlor+Heptachlor epoxide,  $\Sigma$ Endosulfan=alfa+beta endosulfan. Nuu=Nuuk, Itt=Ittoqqortoormiit, Iso=Isortoq, Zac=Zackenbergt.

Species		Organ	$\Sigma$ Heptachlor	$\Sigma$ Drine	$\Sigma$ Endo- sulfan	Methoxy- chlor	Mirex
Atlantic cod	Nuu 2000	liver	6.92±0.57	52.5 ±4.42	14.3±3.28	1.65±0.69	0.90 ±0.13
		muscle	6.55±3.78	50.5 ±38.9	115±252	8.42±11.3	0.68 ±0.26
Redfish	Nuu 2000	muscle	6.96±2.17	41.6 ±17.4	18.9±5.93	n.d.	1.39 ±1.42
Atlantic salmon	Nuu 2000	muscle	5.35±0.84	24.1 ±8.16	11.6±1.99	n.d.	0.65 ±0.25
Greenland halibut	Nuu 2000	muscle	7.09±3.01	69.2 ±68.0	105±214	n.d.	23.8 ±70.1
Capelin	Nuu 2000	muscle	13.4±1.99	81.7 ±14.4	56.8±18.4	10.6±22.4	0.45 ±0.35
Deep sea shrimp	Nuu 2000	whole organism	5.07±1.05	23.5 ±4.98	3.21±1.20	7.87±10.8	3.18 ±2.09
Snow crab	Nuu 2000	hepato- pancreas (5)	10.2±2.13	19.0 ±3.98	25.6±38.3	25.2±34.3	6.04 ±3.98
		muscle (5)	61.5±20.6	70.9 ±56.6	22.5±16.4	29.4±13.7	9.44 ±4.58
Sculpin	ltt 1999	liver	15.7±5.74	82.3 ±31.5	20.3±12.0	7.28±5.81	5.57 ±3.02
Sculpin	ltt 2000	liver	13.0±3.41	52.4 ±18.9	18.6±8.63	0.64±1.11	4.22 ±2.48
Sculpin	Qeq 1999	liver	4.83±1.84	23.4 ±10.7	3.74±2.13	1.02±4.00	0.82 ±0.82
Arctic char	lso 1999	muscle	5.83±2.52	45·3 ±59·4	15.6±6.74	n.d.	22.1 ±19.2
Arctic char	Zac, 1999	muscle	8.58±4.41	33.7 ±14.9	18.2±12.5	0.52±2.14	5.96 ±6.70
Arctic char	ltt., 2000	muscle	8.73±2.26	53.7 ±19.1	29.8±21.8	1.53±3.75	2.88 ±3.11

The levels in both sculpin and char show higher levels in east than in west Greenland (c.f. Figure 5.7.1), a tendency that is well described for the "old" OCs. Furthermore there is a tendency of higher levels in male fish compared to female, a picture often seen in mammals.

Figure 5.7.2 levels of chlorinated pesticides ( $\mu$ G/kg lw + std) in sculpin from



QEQERTARSUAQ (WEST GREENLAND) AND ITTOQQORTOORMIIT (GREENLAND).

#### Conclusions and recommendations

Except for methoxychlor all chlorinated pesticides analysed were found in all types of organisms included in this study, showing a tendency of bioaccumulation in the same manner as seen for the OCs traditionally analysed in the Arctic. This is in accordance with results from other parts of the Arctic. The chlorinated pesticides described here can be transported to Greenland only by long range transport. The highest levels of aldrin, dieldrin, endrin, heptaclor, endosulfan, methoxychlor and mirex were comparable to levels detected elsewhere in the Arctic. Data on levels of endosulfan and methoxychlor, two chlorinated pesticides still in use, in Arctic biota are sparse. The concentrations were lower than found in more industrialized parts of the world.

Very few data exist to make an assessment of temporal trends of chlorinated pesticides in Greenland biota, therefore it is recommended that levels are continuously monitored in key species of higher trophic level.

## 5.8 POLYBROMINATED DIPHENYL ETHERS (PBDE)

Brominated flame retardants (BFRs) are a chemically diverse group of brominated organic compounds used in plastics, textiles, electronic circuity and other materials to prevent fire. Some BFRs like polybrominated diphenyl ethers (PBDEs) are additives mixed into polymers, not chemically bound to the matrix and can therefore leach from the surfaces of the products into the environment. PBDEs are insoluble in water  $(9x10^{-7} \text{ mg/L at } 20^{\circ}\text{C})$ , highly lipophilic (log K<sub>ow</sub> 6,64-6,97) and have some structural similarities to PCB and PCDD/F. Annual worldwide production is 40 000 t. Bromkal 70-5DE is one of several technical products that contains lower brominated PBDEs such as 2,2'4,4'-TeBDE (BDE-47) and 2,2',4,4',5-PeBDE (BDE-99). Among the PBDE congeners found in the environment BDE-47, BDE-99 and BDE-100 usually make up approximately 90 % of the total level of PBDEs in aquatic biota (Janson et al. 1993; Asplund et al. 1999) and BDE-47 constitute more than 60% of the total level (Jansson et al, 1993).

Several time trend studies exist of PBDE levels in various environmental compartments: sediments, fish, beluga and human samples indicate a rapid increase in PBDE levels during the last 20 years (Nylund et al. 1992, Luross et al. 2000, Ikonomou et al. 2002, Norén & Meironyté, 2000). In the study by Norén & Meironyté (2000) a nearly exponential increase in PBDE concentration in human milk was observed for the period 1972 to 1997, with a doubling time of 5 years.

Lucross et al. (2000) reported PBDEs in marine mammals from the Canadian Arctic for the first time, suggesting that PBDEs are ubiquitous pollutants in the Arctic environment (Aspelund et al. 1999, Lucross et al. 2000). The samples presented in this section were from the projects: "Effects of Contaminants in the Greenland Sea Polar Bear", "Contaminants in Greenland human diet" and "Non-halogenated Organic Substances in the Greenland Environment", representing the first investigations of PBDEs in Greenland. Chemical analyses were performed by The National Water Research Institute, Canada and by NERI, Denmark.

#### Results and discussion

Table 5.8.1 summarises PBDE concentrations measured in various sample types and areas of Greenland.

The spatial trend for PBDEs has earlier been reported to be much like that for PCBs and DDT with a decreasing trend in concentration levels going from south to north (Selström et al. 1993). As different sample types were collected at different latitudes of Greenland this trend could not be investigated through these data. Spatial

differences were seen in PBDE levels in black guillemot. Levels are highest on the east coast compared to the west coast, the same pattern earlier seen for a range of chlorinated compounds.

This difference between east and west was also seen for ringed seals. The relatively low level of PBDEs discovered in blubber of ringed seal from Qeqertarsuaq (4 ng/g ww) agrees well with earlier findings of much lower levels of PBDEs in Arctic ringed seal (58 ng/g ww) compared to e.g. the Baltic Sea (344 ng/g ww, Hagelund et al. 1997).

In the study from southern Greenland samples were collected in areas with different degree of urbanisation, Qaqortoq a town of 3200 inhabitants, Igaliko a settlement with 40 inhabitants and a background area with no human population. Total PBDE levels were positively correlated with degree of urbanisation in the sampling area indicating the importance of local sources of PBDEs (Christensen et al. 2002).

BDE-47 was the dominating congener in all marine mammals studied (de Wit, 2002). This was also consistent with the data for all samples of mussels, fish and mammals presented in Table 5.8.1.

Higher concentrations were observed in males compared to females of black guillemot. For polar bears no difference in overall PBDE level in the two sexes were seen. This is in contrast to the general trend for many other halogenated substances. The level of PBDEs in polar bears from Ittoqqortoormiit was in the same range as seen for ringed seals from the same area, in other words there were no signs of biomagnification at this trophic level. However, the proportion of BDE-47 was higher in polar bear than the other organisms studied, which agrees well with earlier findings that this congeneer shows the highest tendency of biomagnification (Jansson et al. 1993). The concentrations of PBDEs at lower trophic levels, in fish and mussels from south Greenland revealed signs of biomagnification for total PBDEs and the congener BDE-47 in particular. Table 5.8.1 PBDE concentrations (NG/G WW) in various samples from Greenland. \* denotes samples analysed by NWOC, all other samples were analysed by NERI. F: female, M: male and juv.: juvenile. # sex was not determined for two samples.WG=west Greenland, SG=south Greenland, EG=east Greenland

Species	Area	Organ	Sex	n	BDE-47	BDE-99	$\frac{BDE-47}{BDE-99}$	ΣPBDE
Atlantic cod*	Nuuk-WG	Muscle	-	9	1.03	0.21	5	3.35
Atlantic cod*	Nuuk-WG	Liver	-	3	1.79±0.2	0.32±0.07	6	5.13 ±0.85
Greenland	Nuuk-WG	Liver	-	5	1.04±0.58	0.18±0.07	6	2.71±0.99
halibut*								
Black guillemot	Qeqertarsuaq-WG	Egg	-	7	1.45±0.25	0.38±0.10	4	2.64±0.45
Black guillemot	Qeqertarsuaq-WG	Liver	М	9	0.70±0.37	0.17±0.21	4	1.05±0.71
Black guillemot	Qeqertarsuaq-WG	Liver	F	10	0.58±0.44	0.11±0.14	5	0.77±0.73
Ringed seal*	Qeqertarsuaq-WG	Blubber	-	9	2.4±0.7	0.4±02	6	3.6 ±1.1
Ringed seal*	Ittoqqortoormiit-EG	Blubber	-	8	40.6±15.5	4.6±1.2	9	58.0±22.6
Black guillemot	Ittoqqortoormiit-EG	Liver	M, adult	8	1.83±0.71	0.28±0.21	7	2.76±1.35
Black guillemot	lttoqqortoormiit-EG	Liver	F, adult	3	3.36±2.37	0.54±0.32	6	5.56±4.25
Black guillemot	Ittoqqortoormiit-EG	Liver	juv.	8	0.49±0.30	0.09±0.06	6	0.70±0.44
Thick-billed murre*	Nuuk-WG	Liver	-	5	0.36±0.11	0.26±0.10	1	1.71±1.55
Shorthorn	Qaqortoq-SG	Liver	F	5	7.81	<0.13	-	8.2
sculpin								
Shorthorn	Igaliko-SG	Liver	F	5	2.90	0.05	58	3.1
sculpin								
Shorthorn sculpin	Igaliko-SG	Liver	М	5	2.90	0.06	48	3.1
Shorthorn	Usuk-SG	Liver	F	5	1.66	<0.12	-	1.8
sculpin								
Shorthorn	Usuk-SG	Liver	М	4	2.17	0.12	18	2.3
sculpin								
Greenland cod	Usuk-SG	Liver	F	5	5.42	0.57	10	7.1
Greenland cod	Usuk-SG	Liver	М	5	9.58	0.59	16	12.0
Spotted wolffish	Usuk-SG	Liver	М	1	1.22	<0.13	-	1.2
Starry ray	Usuk-SG	Liver	М	1	1.10	0.08	14	1.4
Blue mussel	Usuk-SG	Soft	-	20	0.10	0.02	5	0.11
		tissues						
Polar bear*	Ittoqqortoormiit-EG	Fat	М	9	36.4	2.9	1258	55.0
Polar bear*	Ittoqqortoormiit-EG	Fat	F	8	34.7	3.3	11	54.1
Polar bear*	Ittoqqortoormiit-EG	Fat	F+M	19#	34.8	3.0	12	53.1

Conclusions and recommendations

PBDEs are found in all matrices analysed from Greenland, showing a tendency of bioaccumulation in the same manner as seen for the OCs traditionally analysed in the Arctic. This is in accordance with results from other parts of the Arctic. PBDEs are transported to Greenland by long-range transport, but local sources of contamination are also of importance.

In the Arctic PBDE levels are low and it seems unlikely that they will affect any species here. However, the levels of PBDEs have elsewhere been seen to increase at a nearly exponential rate. Continued monitoring of PBDEs in the Greenland environment can therefore be recommended.

## 5.9 POLYCYCLIC AROMATIC HYDROCARBONS (PAH)

In the present study, the term PAHs is used for the compounds consisting of two or more fused aromatic rings. These are planar structures, consisting of carbon and hydrogen atoms. Additionally the heterocyclic (sulfur containing) PAH analogue dibenzothiophene is included. The general physical characteristics common to the class are high melting- and boiling points, low vapour pressure and low water solubility (Sims & Overcash, 1983, Kjeldsen & Larsen, 1988), which tend to decrease with increasing molecular mass.

PAHs are emitted to the environment primarily from pyrogenic and petrogenic sources. PAH molecules with several rings are cancerogenic. The compounds also have endocrine, mutagenic, terratogenic and immunosupressive effects (e.g. Neff, 1979). PAH have proven toxicity to aquatic organisms at very low concentrations. Aqueous PAH concentrations of 0.7  $\mu$ g/L can cause malformations and genetic damage in fish larvae, while sublethal effects, such as premature hatching, were observed at concentrations of 0.4  $\mu$ g/L (Carls et al., 1999). Early development of flatfish was also afflicted at benzo(a)pyrene concentrations of 0.1  $\mu$ g/L in the water phase (Hose et al., 1982).

For PAHs, there is little knowledge of the degree of long-range transportation into the Arctic. PAHs are more likely to have an impact in regions with direct inputs like power plants, waste incinerator, heavy traffic, oil wells and refineries. Petroleum production however now takes place in many parts of the Arctic and exploration has also taken place in Greenland. Furthermore natural oil seeps can lead to substantial elevations of PAH levels in the environment.

The survey described in this section was part of the project "Non-halogenated organic substances in the Greenland Environment" (NOSGE) carried out in Southern Greenland in 1999-2000. As little information was available on PAH levels in Greenland, the main objective of this project was a screening for PAH in the Greenland environment, including biotic and abiotic matrices. Three main sampling sites were chosen, representing different degrees of human population: Usuk (no population), Igaliko (population 40) and Qaqortoq (population 3200) (Figure 5.9.1). Thus, samples available from the three sites might also give information on the effect of human population on the PAH levels in the environment. All analyses were performed at the NERI laboratory, Denmark. The list of PAHs analysed is shown in Table 5.9.1.



Figure 5.9.1 Sampling locations. Marine samples were collected at Usuk (B), a reference area with low degree of human activity, Igaliko (C), a settlement with approximately 40 inhabitants, and Qaqortoq (D), a village with approximately 3200 inhabitants. Freshwater samples were taken in the Lake (A) close to Igaliko. Pricipitation was collected at the locations A, B, and D.

Compound	Group
Naphthalene	2-3 rings
2-methylnaphthalene	Alkylated
1-methylnaphthalene	Alkylated
Dimethylnaphthalene	Alkylated
Trimethylnaphthalenes	Alkylated
Acenaphthylene	2-3 rings
Acenaphthene	2-3 rings
Fluorene	2-3 rings
Dibenzothiophene	2-3 rings
C1-dibenzothiophene	Alkylated
Phenanthrene	2-3 rings
2-methylphenanthrene	Alkylated
3,6-dimethylphenanthrene	Alkylated
Antracene	2-3 rings
Fluoranthene	4-7rings
Pyrene	4-7rings
1-methylpyrene	Alkylated
Benz(a)fluorene	4-7rings
Benz(a)anthracene	4-7rings
Triphenylene/Chrysene	4-7rings
Benz(b+j+k)fluoranthene	4-7rings
Benz(e)pyrene	4-7rings
Benz(a)pyrene	4-7rings
Perylene	4-7rings
Indeno(1,2,3-cd)pyrene	4-7rings
Benz(ghi)perylene	4-7rings

TABLE 5.9.1 PAHs monitored in the present study.

In the calculation of sum concentrations, the parameter  $\Sigma$  higher PAH was introduced, summing all compounds from Fluorene to Benz(ghi)perylene from Table 5.9.1. This parameter was chosen to account for incomplete data sets, which sometimes lacked the smaller PAH molecules due to analytical errors. Thus, sum concentrations based on the same number of compounds could be used for comparisons between matrices.

## 5.9.1 Precipitation

Precipitation samples of 2.5-10 L were collected in the background area (Usuk), near Igaliko (a settlement with 40 people) and at the town Qaqortoq with about 3200 inhabitants. The data set consists of single samples collected over a period of approximately 5 months. Therefore, variation between samples is expected to be large.

During summer 2001 the PAH concentration in precipitation at Igaliko was at the same level as at Usuk (the background site). The concentration at Qaqortoq was almost nine times higher than the background concentrations, thus indicating the influence of local activities.

During winter 2001, PAH concentrations were similar to summer 2001 at Usuk, while the concentration in precipitation collected at Igaliko was 2.5 times higher than summer 2001. The somewhat higher concentrations at Igaliko could be caused by local emissions from heating during winter. Interestingly, the sum PAH concentration at Qaqortoq was somewhat lower during winter than during summer. This could indicate that the activities giving rise to the elevated PAH levels at Qaqortoq are somewhat reduced in winter. The sum of PAH in precipitation at Qaqortoq in winter is still 5.5 times higher than at Usuk. The difference in PAH levels at Qaqortoq is mainly caused by much lower concentrations of acenaphtylene (8 times lower) and fluorene (10 times lower) in winter compared to summer 2001. Interestingly, benzo(ghi)perylene is higher in winter compared to summer (25 times), while other PAHs are at the same levels in both samples from Qaqortoq. Automobile exhaust has previously been identified as a source to benzo(ghi)perylene (Masclet et al., 1986).



Figure 5.9.2 Concentrations of sum of PAH (ng/L) in precipitation samples from Southern Greenland.

TABLE 5.9.2 RELATIVE CONCENTRATIONS OF PAHS IN PRECIPITATION FROM SOUTHERN GREENLAND SUMMER AND WINTER 2001. LMW/HMW: RATIO OF SUM 2-3 RINGED COMPOUNDS TO 4-7 RINGED. ALKYLATED/SUM: RATIO OF ALKYLATED COMPOUNDS TO TOTAL SUM PAHS.

Location	LMW/HM	LMW/HM	Alkylated/sum	Alkylated/sum						
	W	W	Summer	Winter						
	Summer	Winter								
Usuk (B)	0.7	-	0.17	0.15						
Igaliko (Lake) (A)	0.4	0.8	0.15	0.18						
Qaqortoq (D)	1.7	0.4	0.04	0.14						

The PAH concentrations of 14 compounds in precipitation at Igaliko are comparable to PAH concentrations in rainwater observed during summer at background sites in France (Garban et al., 2002). Surprisingly, the PAH concentration in both summer and winter precipitation from Qaqortoq was about 2-3 times higher than average PAH concentrations at background sites in France during summer. This indicates that local pollution sources are present at Qaqortoq.

## 5.9.2 Terrestrial environment

PAH concentrations found in soil and lichens (*Cetraria nivalis*) are presented in Table 5.9.4 and Figure 5.9.3. The suitability of the lichen species *C. nivalis* for biomonitoring of atmospheric deposition of elements in Greenland has previously been investigated (Riget et al., 2000). The results indicate that the lichen was well suited for this purpose.

Table 5.9.3 Sum PAH in soil (µg/kg dw) and lichens (µg/kg wv	✗) FROM SOUTHERN
Greenland. Sampling locations are shown in Figure 5.9.1.	

Sample type	Location	Sum all	Sum higher	Sum all	Sum higher
		PAH 1999	PAH 1999	PAH 2000	PAH 2000
Soil	Usuk (B)	-	-	106	41
	Igaliko (A)	-	-	105	42
	Igaliko (C)	-	-	128	44
Lichens	Usuk (B)	74	31	79	25
	Igaliko (A)	-	33	93	36
	Igaliko (C)	-	39	-	31

Generally the PAH levels in both soil and lichens are within the same range. Concentrations of PAH in soil vary only slightly among the sites, the only noteworthy difference being the somewhat higher concentration of sum of all PAH at Igaliko – farm (site C). This slightly higher concentration is mainly due to higher levels of trimetylnaphtalene, acenaphtylene and fluorene in this sample. The PAH levels in lichen samples from two consecutive years indicate that the interannual variability in PAH concentrations is low and that *C. nivalis* is suited for biomonitoring of atmospheric deposition of PAHs.



Figure 5.9.3 Concentrations of sum of higher PAHs in lichens ( $\mu$ g/kg ww) and soil ( $\mu$ g/kg dw) sampled in 2000.

## 5.9.3 Freshwater environment

The results are summarised in Table 5.9.4. Arctic chars from the two lakes have similar PAH levels. Male samples show similar ratios of alkylated to sum PAHs. PAH concentrations in Arctic char are significantly lower than levels in shorthorn sculpin.

Table 5.9.4 Sum PAH in lake sediment ( $\mu$ G/kG) and Arctic char livers ( $\mu$ G/kG ww) from Southern Greenland. LMW/HMW: Ratio of sum 2-3 ringed compounds to 4-7 ringed. Perylene/Sum Penta PAH: Ratio of Perylene to sum 5 ringed PAHs. Alkylated/Sum: Ratio of alkylated compounds to total sum of PAHs. M: Male. F: Female. Sampling locations are shown in Figure 5.9.1

Sample type	Location	Year	$\Sigma PAH$	$\Sigma$ higher	LMW/	Alkylated/	Perylene/
				PAH	HMW	$\Sigma PAH$	$\Sigma$ Penta-PAH
Sediment	Lake (A)	2000	120	40	7.4	0.2	-
Arctic char	Lake (A) M	2000	290	150	-	0.5	-
	Lake (A) F	2000	-	120	-	-	-
	Itilleq (F) M	2000	250	140	-	0.6	-
	Itilleq (F) F	2000	-	190	-	-	-

#### 5.9.4 Marine environment

PAH concentrations have been analysed in bladder wrack (*Fucus vesiculosus*), blue mussels (*Mytilus edulis*), shorthorn sculpin (*Myoxocephalus scorpius*) livers and sediments. All samples originate from the three sampling locations with different numbers of population in Southern Greenland and were collected in 1999 and 2000. Usuk is regarded as a background station without any potential influence from human activity. The matrices analysed are not always consistent: Sediment samples are available from Igaliko only. Bladder wrack was only sampled in 2000, as well as shorthorn sculpins and blue mussels from Qaqortoq. Besides, data are available for several other invertebrates and macroalgae collected at either Usuk or Igaliko (Table 5.9.5).

The macroalgea summarised in Table 5.9.5 can accumulate organic pollutants from seawater. The PAH levels in bladder wrack, Arctic wrack, sea lettuce and sweet tangle are similar to the levels in blue mussels from 1999, while the sum PAH concentration in Enteromorpha are about two times lower. It has to be noted, however, that all results except for periwinkle are based on single samples. The concentrations are higher in sand hopper and particularly in lugworm, indicating either an accumulation of the compounds or a stronger exposure. Lugworms are likely to take PAH up from the sediment. Thus, the exposure is higher, in particular to higher molecular weight PAH associated with the organic matter of the sediment. This might contribute to the lower LMW/HMW ratio than observed for sand hopper and algae.

Table 5.9.5: Sum concentrations of PAH ( $\mu$ G/kg ww) in invertebrates and macroalgae from three locations in Southern Greenland. Sand hopper: *Gammarus sp.* Periwinkle: *Littorina saxatilis*. Arctic wrack: *Fucus distichus*. Sweet tangle: *Laminaria saccarina*. Sea lettuce: *Ulva lactuca*. LMW/HMW: Ratio of sum 2-3 ringed compounds to 4-7 ringed. Perylene/ $\Sigma$ Penta-PAH: Ratio of perylene to sum 5 ringed PAH. n=2 for periwinkle, others n=1.

Species	Station	Year	Σ	$\Sigma$ higher	LMW/	Alkylated	Perylene/
			PAH	PĂH	HMW	$/\Sigma PAH$	$\Sigma$ Penta-PAH
Sand hopper	В	1999	98	57	4.1	0.5	0.2
Lugworm	С	1999	370	320	1.1	0.2	0.2
Periwinkle	С	1999	45	22	2.8	0.4	0.2
Bladder wrack	В	2000	66	37	1.9	0.6	0.5
Bladder wrack	С	2000	66	34	2.1	0.6	0.8
Bladder wrack	D	2000	41	34	-	0.4	0.9
Arctic wrack	В	2000	43	32	-	0.3	0.9
Sweet tangle	В	2000	43	8.8	3.4	0.6	0.3
Sea lettuce	В	2000	52	17	2.0	0.6	0.3
Enteromorpha	В	2000	24	6.9	2.7	0.6	0.1

Differences between the sampling sites, which might be related to the different degrees of human activity, can be observed for blue mussels. Furthermore, an increase in sum PAH can be noticed for the samples taken at Usuk and Igaliko in 1999 and 2000 (Table 5.9.6), but not for shorthorn sculpins or sediments. Apparently, the year-to-year variation is more pronounced for blue mussels, which primarily accumulate organic compounds from seawater.

Blue mussels from 1999 include the background station Usuk and two sampling sites at Igaliko inside and outside the harbour (Table 5.9.6). The low molecular weight PAHs are omitted from the data set for most samples due to low recovery rates for these compounds in the chemical analysis of the blue mussels. The samples are divided into three groups of different sizes of mussels, which do not correlate with the sum PAH concentration. The concentrations of the samples from the inner harbour tend to be slightly higher than those from outside the harbour. The levels from Igaliko exceed the concentrations at Usuk, but due to the large variation within the Igaliko samples, this difference cannot be quantified.

Blue mussels collected in 2000 are divided into two groups, ranging from 30-50 mm and from 50-70 mm. No obvious difference in the sum PAH concentrations can be seen between the two size groups. The sum PAH concentrations in blue mussels from Igaliko exceed the concentrations from Usuk. Results from Qaqortoq, the site with the largest number of inhabitants, are about 50 % higher than concentrations at Igaliko. The LMW/HMW ratio as well as the perylene/ΣPenta-PAH ratio also reflect different PAH patterns, possible caused by different local impacts. However, the LMW/HMW ratio is not consistent: Samples from Qaqortoq, the location with the highest number of human activity had the highest percentage of low molecular weight compounds, while Igaliko has the lowest LMW/HMW ratio. This inconsistency might reflect different influences from pyrogenic and petrogenic sources. The concentrations in the mussels from 2000 are similar to levels found for blue mussels from the Baltic Sea (Baumard et al., 1999).

Station	Year	Size	$\Sigma PAH$	$\Sigma$ higher	LMW/	Alkylated/	Perylene/	
		(mm)		PAH	HMW	$\Sigma PAH$	$\Sigma$ Penta-PAH	
Usuk (B)	1999	20-39	32	28	-	0.03	0.2	
Usuk (B)	1999	40-59	36	35	-	0.05	0.3	
Usuk (B)	1999	> 60	58	38	-	0.2	0.3	
Igaliko (C) H	1999	20-39	69	69	-	0.06	0.2	
Igaliko (C) H	1999	40-59	87	52	1.2	0.3	0.3	
Igaliko (C) H	1999	> 60	71	71	-	0.07	0.3	
Igaliko (C) OH	1999	20-39	112	68	0.7	0.4	0.2	
Igaliko (C) OH	1999	40-59	47	43	-	0.1	0.2	
Igaliko (C) OH	1999	> 60	42	35	-	0.1	0.3	
Usuk (B)	2000	30-50	130	58	1.8	0.3	0.6	
Usuk (B)	2000	50-70	100	53	1.8	0.4	0.7	
Igaliko (C)	2000	30-50	130	72	0.8	0.5	0.5	
Igaliko (C)	2000	50-70	130	80	0.8	0.5	0.4	
Qaqortoq (D)	2000	50-70	210	120	3.6	0.5	-	

Table 5.9.6: Sum concentrations of PAH ( $\mu$ G/kg ww) in blue mussels from three locations in Southern Greenland. LMW/HMW: Ratio of sum 2-3 ringed compounds to 4-7 ringed. Perylene/ $\Sigma$ Penta-PAH: Ratio of perylene to sum 5 ringed PAH. H: Harbour. OH: Outside the harbour N=2 for Usuk (1999). Others N=1

The degree of urbanisation was found to correlate with the concentrations of brominated flame retardants in shorthorn sculpins from the three sampling sites (Christensen et al., 2002), indicating local sources of these contaminants in Greenland. Shorthorn sculpins are stationary fish and can therefore be assumed to reflect the actual concentrations in the sampling area. The increasing sum PAH concentrations in blue mussels from stations with increasing numbers of population might indicate the same phenomenon. Local sources of PAH might include combustion processes such as waste incineration and boat or vehicle engines as well as direct losses of petrol and oil to the environment.

However, the trend found in blue mussels was not confirmed for bladder wrack or shorthorn sculpins (Table 5.9.7). Being a stationary fish species, shorthorn sculpin was found to reflect local sources of brominated flame retardants from the three sampling locations. Different metabolisation processes might occur for PAH in shorthorn sculpins, but they are unlikely to even out potential differences caused by local sources. However, even though the absolute concentrations do not differ between the three sampling sites, the LMW/HMW ratio for samples from Qaqortoq tends to be higher than for the samples from the less populated stations. No difference is observed for Igaliko and Usuk. The higher percentage of low molecular weight PAH might indicate local impacts, which are different from the exposure at Igaliko and Usuk.

As other factors such as age and nutritional status might influence the concentrations in shorthorn sculpins, samples were analysed separately for small (young) and large (old) as well as for female and male fish (Table 5.9.7). No trend can be established for this differentiation. While female, large fish from Usuk have higher concentrations than the small fish, the opposite can be seen for the female fish from Igaliko. For male fish, the concentrations are highest in the small fish in three out of four cases. For persistent organic pollutants, higher concentrations in male marine animals than in female have been described in the literature (AMAP, 1998), which are explained by an excretion of the pollutants to the offspring. This observation cannot be confirmed for the PAH data

collected on shorthorn sculpins from Southern Greenland, possibly due to more complex metabolisation processes.

RINGED PAH	. N=1, E	ACH SA	MPLE IS	POOLED O	f 4-5 INDIVI	DUALS.		
Station	Year	Sex	Size	$\Sigma PAH$	$\varSigma$ higher	LMW/	Alkylated/	Perylene/ $\varSigma$
					PAH	HMW	$\Sigma PAH$	Penta-PAH
Usuk (B)	1999	F	small	460	200	2.8	0.4	0.3
Usuk (B)	1999	F	large	510	340	1.4	0.3	0.2
Usuk (B)	1999	Μ	small	440	270	1.8	0.4	0.3
Usuk (B)	1999	Μ	large	380	180	2.6	0.4	0.2
Igaliko (C)	1999	F	small	600	380	1.1	0.4	0.3
Igaliko (C)	1999	F	large	340	280	-	0.3	0.3
Igaliko (C)	1999	Μ	small	470	370	1.3	0.6	0.3
Igaliko (C)	1999	Μ	large	430	190	2.8	0.5	0.2
Usuk (B)	2000	F	small	270	240	-	-	-
Usuk (B)	2000	F	large	450	330	1.4	0.4	0.2
Usuk (B)	2000	Μ	small	380	230	1.7	0.5	0.3
Igaliko (C)	2000	F	small	430	270	1.8	0.6	0.2
Igaliko (C)	2000	F	large	370	220	2.2	0.5	0.2
Igaliko (C)	2000	Μ	small	320	200	2.1	0.5	-
Igaliko (C)	2000	Μ	large	520	410	0.6	0.4	0.3
Qaqortoq (D)	2000	F	small	440	270	3.5	0.5	0.2
Qaqortoq (D)	2000	F	large	440	260	1.4	0.4	-
Qaqortoq (D)	2000	М	small	430	300	2.5	0.5	0.2
Qaqortoq (D)	2000	Μ	large	370	260	2.0	0.5	0.2

Table 5.9.7: Sum concentrations of PAH (NG/G ww) in shorthorn sculpin livers from three locations in Southern Greenland.  $\Sigma$  higher PAH excludes Naphthalene, methyl Naphthalenes, acenaphthylene and acenaphthene. LMW/HMW: Ratio of sum 2-3 ringed compounds to 4-7 ringed. Perylene/ $\Sigma$ Penta-PAH: Ratio of perylene to sum 5 pinced PAH. N=1 each sample is pooled of 4-5 individuals.

The PAH concentrations in the matrices analysed from Usuk, Igaliko and Qaqortoq are summarised in Figure 5.9.4, which illustrates the increasing concentrations in blue mussels with increasing number of population in the sampling area. The concentrations in biota are exceeded by the levels in sediment, which vary considerably between 1999 and 2000. However, the sediment concentrations are related to dry weight, while the biota concentrations are based on wet weight. These levels indicate the occurrence of PAH in Arctic sediments, which is likely to be a source of contaminant uptake by aquatic organisms.



Figure 5.9.4: Sum concentrations of higher PAH in biota (ng/g ww) and sediment (ng/g dw) from three locations in southern Greenland and two sampling periods.  $\Sigma$  higher PAH excludes naphthalene, methyl naphthalenes, acenaphthylene and acenaphthene. n.a.: not analysed.

For all sampling locations and both years studied, the concentrations increase from bladder wrack to blue mussels and shorthorn sculpins, which indicates bioaccumulation of PAH at low trophic levels in the marine food chain. However, it has to be noted that the concentrations are not normalised to dry weight. PAH have the potential to bioaccumulate in aquatic organisms, which lack efficient mixed-function oxidase detoxification mechanism (Law et al., 1997). Unlike the biomagnification of halogenated compounds in the Arctic marine food chain (e.g. Cleemann et al., 2000a), the main route of exposure for sediment dwelling fish is uptake from the water which includes dissolved and particular bound PAH (Law et al., 1997).

#### Conclusions and recommendations

This study shows the occurrence of PAH in various compartments of the Greenland environment. The precipitation and blue mussel data indicate an existence of local antropogenic sources in Greenland as the sum PAH concentration correlates with the number of population at the sampling location. More research is needed to study the extent of this phenomenon. Data available on seawater, blue mussels and shorthorn sculpins show increasing PAH concentrations with higher trophic levels, possibly reflecting bioaccumulation of PAH. However, the complex pattern of exposure, accumulation and metabolisation was not subject of this study. Hence, conclusions on the fate of PAH in the Greenland environment will require further research.

#### 5.10 CONTAMINANTS OF FUTURE CONCERN

The contaminants described in the preceeding sections are all contaminants that have just recently been discovered in the Arctic environment or compounds that are not included in the traditional monitoring programs in the Arctic. The data presented here illustrates the fact that previously unknown or disregarded organic pollutants are likely to be emitted to the environment and transported to remote regions in a similar way as shown for PCBs and other organohalogens, or emitted from local sources in the Arctic. Recognizing this, and recognizing the vast amount of new chemicals taken into use each year, it seems obvious that some of these could be expected to become *future contaminants* in the Arctic. Examples of such chemicals are briefly described in this section.

# 5.10.1 Perfluorooctane sulfonate (PFOS)

Fluorinated organic compounds (FOCs) have been manufactured for more than 50 years, but have except for the CFC-gasses received less attention than brominated and chlorinated compounds, primarily perhaps because their measurement is more challenging. Some perfluorinated compounds are very stable in the environment. Among these fluorinated organic compounds, sulfonyl-based fluorochemicals have been produced and used for over 40 years as surface protectors in carpets, leather, paper and packaging, fabric and upholstery. It has been hypothesised that the fluorine-containing products could degrade to other fluorochemicals including perfluoroctane sulfonate (PFOS). According to UNEP the total production of PFOS-compounds is about 5000 tons a year worldwide (cited in Havelund, 2002).

Surface-water concentrations of 25-144 ng PFOS/L have been detected near to perfluorinated surfactant related manufacturing facilities (Hansen et al. 2002). PFOS is relatively soluble in water with a max. solubility of 460 mg/L (estimated on the basis of critical micelle concentration). The compound is very persistent in the aquatic environment (Sanderson et al. 2002). Giesy and Kannan (2001) recently reported PFOS levels in a number of wildlife species from all over the world. PFOS were present in most samples also from remote marine areas. However, concentrations of PFOS in these regions were several times lower than those from more industrialized areas. In the Baltic Sea levels of PFOS in the range 14-230 ng/mL were detected in blood from gray seals and ringed seals. In the same species from the Canadian and Norwegian Arctic the levels were 3-50 ng/mL. Livers of polar bears from Alaska contained 180-680 µg/kg ww. Fish-eating, predatory animals contained PFOS in concentrations higher than their diet, indicating bioaccumulation of PFOS (Giesy & Kannan, 2001). Under laboratory conditions the biomagnification factor based on the concentrations of PFOS in liver of mink was approximately 22. The level of PFOS in the general human population of the U.S. is 30-44 ng/m serum. The mean elimination half life in humans is about 4 years (U.S. EPA 2000 cited in Sanderson et al. 2002)

Sanderson et al. (2002) reported significant influence on zooplankton communities at a concentration of 10 mg PFOS/L and 96-hour acute toxicity tests with rainbow trout determined  $LC_{50}$  values of 1250-2500 mg/L (Conducted by the 3M Company, http://www.chemicalindustryarchives.org/dirtysecrets/scotchgard/1.asp). Little information is available on possible long-term toxic effects of PFOS to wildlife. PFOS and related perfluorinated compounds have been shown to affect e.g. cell-cell communication and membrane transport processes. In a recent study by Seacat et al. (2002) the effect of PFOS was measured in cynomolgus monkeys. Significant adverse affects measured one year after ended treatment were observed in animals receiving 0.75 mg/kg/day, these animals showing decreased bodyweight, increased liverweights, lowered serum cholesterol, lowered triiodothyronine and lowered estradiol levels.

## 5.10.2 Synthetic musks

Synthetic musks are of great industrial importance. They impart desirable musk-like odours and are used on a grand scale as fragrance fixatives and materials in personal care and household products, such as cosmetics, soaps, laundry detergents, fabric softeners, household cleaning products, air fresheners etc. In 1996 the worldwide production of synthetic musk compounds amounted 8000 tons, of this production of nitro musks accounted for 25 % (mainly musk ketone and musk xylene), polycyclic musks made up 70 % (mainly HHCB and AHTN) and macrocyclic musks accounted for 5 % (Rimkus, 1999).

The synthetic musks enter the environment mainly via wastewater or household waste when dumped directly in the environment. Nitro musks have been detected in a broad range of environmental compartments: marine and fresh water as well as fish, mussels and shrimps (Rimkus & Wolf 1995, Gatermann et al. 1995) and in human addipose tissue and breast milk (Liebl & Ehrenstorfer 1993, Müller et al. 1996) Due to the high potential for bioaccumulation (log K<sub>ow</sub> = 4.31 and 4.45 for musk ketone and musk xylene respectively) musk xylene was banned in Japan in the 1980ies and was in 1998 included in the third list of chemicals for priority action of the EU and OSPAR commision. Nitro musks are highly persistent in the environment and accumulate in aquatic biota. High acute toxicity of nitro musks has been reported for several aquatic species and the compounds have been related to reproductive toxicity and endocrine effects in animals and humans (e.g. Eisenhart et al. 2001).

Polycyclic musks are now increasingly substituting the nitro musk compounds. In Europe HHCB and AHTN are being classified as high volume chemicals with an average use per capita in 1995 of about 15.5 mg/day (in Gatermann et al. 2002). In various environmental compartments the polycyclic musks exceed the concentration of the nitromusks. Biodegradation of polycyclic musks is relatively slow (half-life in soils of aprox. 180 days), and due to their lipophilic properties (log  $K_{ow} = 5.7$  and 5.9 for AHTN and HHCB) as conciderable bioconcentration is recorded (Balk and Ford, 1999). Polycyclic musks have been found in most environmental compartments and have also been detected in human addipose tissue and human milk (Müller et al. 1996, Rimkus & Wolf 1996). High acute toxicity have been reported for polycyclic musks (LC<sub>50</sub> <1 mg/L) for several aquatic species (Balk & Ford, 1999).

## 5.10.3 Polychlorinated naphthalenes

Polychlorinated naphthalenes (PCNs) have mainly been used as dielectric fluids, flame retardants and fungicides and occur as impurities in technical PCB formulations. They are also by-products of human activities such as copper-roasting, degradation of polychlorinated alkenes and combustion processes. Total global production has been estimated to 150 000 tons (in Falandysz, 1998). PCNs have never been banned but have to a large extent been replaced by less toxic compounds.

PCNs are a mixture of 75 congeners – all planar compounds that can affect the aryl hydrocarbon (Ah) receptor and thereby elict dioxin like responses – including immunotoxicity, embryotoxicity, terratogenicity and carcinogenicity (reviewed in Hayward, 1998). TCDD equivalency factors (TEFs) for PCN congeners are reported to range from  $7x10^{-6}$  to  $2x10^{-3}$  (Hanberg et al., 1991). Evidence exists that these substances are widespread pollutants in the environment that co-occur with PCBs and other organohalogens (e.g. Giesy et al. 1997, Kanan et al. 2000). Results from plankton analysis in the Baltic Sea and sediment and biota in Sweden indicate long-range transportation of these pollutants (Falandysz & Rappe, 1996). PCNs are very lipophilic with log K<sub>ow</sub> from 3.9 to 8.3

(http://www.es.lancs.ac.uk/kcjgroup/6.html) and therefore tend to accumulate in sediments and biota. Signs of biomagnification have also been documented (Falandysz & Rappe, 1996, Falandysz et al. 1997) PCNs have also been measured in low concentrations in the Arctic. Levels of  $\Sigma$ PCN (3-7 Cl) in blubber ranged from 35.9 to 383 ng/kg lw in beluga whales and from 35.4 to 71.3 ng/kg lw in ringed seals from the Canadian Arctic. The PCN concentrations were less than 1 % of the coplanar PCBs – but as their toxic potential measured as TCDD-TEQ is 11 times higher they contributed significantly to the total toxicity (Helm et al. 1998).

## 5.10.4 Brominated flame retardants

Beside the polybrominated diphenylethers other compound groups of brominated flame retardants can possibly present an increasing problem in the Arctic. Little knowledge regarding concentrations and fate in the environment is available of hexabromocyclododecane (HBCD), tetrabromobisphenol A (TBBPA) and polybrominated biphenyls (PBBs). The estimated world market demand for HBCD is 15 900 t annually in 1999 (de Wit, 2002). HBCD is used as an additive in foams and expanded polystyrene. Sellström et al. (1998) detected levels of 7600 ng/g carbon in sediments and up to abot 8000 ng/g lw in pike in a river receiving wastewater from several industries. Ratios of HBCD in fish and sediments from 0.6 to 15 show that the compound is bioavailable and can potentially bioaccumulate.

TBBPA is the flame retardant produced in the highest amount globally: 60 000 t pr. year. TBBPA is incorporated in polymers as a reactive flame retardant covalently bound to the polymer. Where detected in the environment, TBBPA is mainly found in soil and sediment samples. A relatively high bioconcentration factor seems to be balanced by rapid excretion and the compound has not normally been found in environmental biological samples. The phenolic groups of TBBPA may however be methylated in the environment and the resulting Me<sub>2</sub>-TBBPA is more lipophilic. This compound has also been found in sediment, fish and shellfish (reviewed in WHO, 1995).

PBBs are a group of manufactured chemicals that may contain up to 209 individual compounds. In the United States, the production of PBB products was banned in 1977. PBBs were used mainly to prevent fires in plastic parts used in electronic products, such as radios and televisions. PBBs were also used in plastics for business machine housings and other industrial products, such as motor housings. In many ways, PBBs are similar to polychlorinated biphenyls (PCBs), they are highly persistent in the environment and are shown to bioaccumulate (reviewed in WHO, 1994). The detection of PBBs and PBDEs in sperm whales, wich feed in deep ocean waters, shows that these compounds can be considered as global pollutants (Soni et al. 1998).

## 5.10.5 PBDD/F

Polybrominated dibenzodioxins and dibenzofurans (PBDD/F) are formed as byproducts in chemical processes. They have been found in traces in organic chemicals such as tribromophenol and brominated flame retardants. The main source of formation is the thermal decomposition of brominated precursor compounds, for instance polybrominated diphenylethers. Thus, PBDD/F have been detected in emissions from municipal waste incineration, but to a clearly less extent than the chlorinated dioxins and furans (PCDD/F). The detection of chloro-bromocontaining dioxins or furans has been reported more frequently. These mixed halogenated species are primarily in the form of monobromo-PCDD/PCDF (Hardy, 1997). However, corresponding to the formation of PCDD/F, highest concentrations of PBDD/F and dibromoPCDD/F were found in fly ashes, which might increase with larger amounts of bromine-containing material being incinerated (Huang et al. 1992; Weber et al. 2002).

Theoretically, 75 PBDD and 135 PBDF congeners can exist. Like the chlorinated compounds, the 2,3,7,8 substituted congeners have the highest toxicity. The effects are assumed to be similar to the chlorinated compounds, but the acute toxicity has been found to be 5-10 times weaker compared to the PCDD/F (Mennear & Lee, 1994). Occupational exposure is possible in industrial branches producing and processing brominated flame retardants. Apart from studies connected to municipal
waste incineration, information on environmental levels of PBDD/F is sparse, possibly due to the very sensitive analytical methods required.

#### 5.10.6 Triclosan

Triclosan is a diphenyl ether (bis-phenyl) derivative, known as either 2,4,4'-trichloro-2'-hydroxydiphenyl ether or 5-chloro-2-(2,4-dichlorophenoxy) phenol. Triclosan is manufactured in the U.S. under the trade name Irgasan DP-300, and by several other manufacturers outside of the U.S. Triclosan inhibits the enzyme ENR involved in the bacterial lipid biosynthesis and is therefore inhibitory against both gram-negative and gram-positive bacteria (Levy et al. 1999, McMurry et al. 1998). It has found increasing use in personal care products, i.e. toothpaste, deodorant soaps, deodorants, antiperspirants and body washes, detergents, dish washing liquids, cosmetics and anti-microbial creams, lotions and hand soaps. It is also used as an additive in plastics, polymers and textiles to give these materials antibacterial properties. In Sweden for example 25 % of the total amount of toothpaste sold in 1998 contained triclosan, corresponding to about 2 tons of active ingredient (from Lindström et al. 2002)

Triclosan is moderately watersolube (10 mg/L at 20 °C) and has a vapour pressure of  $6,45 \times 10^{-7}$  mm Hg. It is relatively persistent in the sediment with half-lives of about 3 weeks (Vershueren, 1996). Triclosan is lipophilic with a log K<sub>ow</sub> of 4.76. Methylated derivatives can furthermore be formed in the environment, possibly by biological methylation of triclosan (Lindström et al. 2002). Laboratory experiments showed that triclosan in the dissociated form was rapidly decomposed in lake water when exposed to sunlight (half-life less than 1 h in August at 47degrees latitude). Methyl triclosan and nondissociated triclosan, however, were relatively stable to photodegradation (Lindström et al. 2002).

Triclosan has not been shown toxic to mammals but it is toxic to water-living organisms such as fish (LOEC, rainbow trout early lifestages = 71.3 µg/L) and *Daphnia magna* (EC<sub>50</sub> = 390 µg/L) and especially to algae (*Scenedesmus sp.* EC<sub>50</sub> = 1.4 µg/L) (Orvos et al. 2002) and, of course, to bacteria. Bioacumulation factors are reported in the range 2500 to 4100 (Orvos et al. 2002). Of further concern is the transformation of triclosan into clorinated dioxins upon incineration and influence of sunlight (Kanetoshi et al. 1988a, b).

The environmental occurrence of triclosan has been reported in wastewater and surface waters from Europe and the US in a range of 2-2300 ng/L (Paxéus 1996, Lindström et al. 2002, Kolpin et al. 2002) Triclosan and its methylated derivative has also been detected in wildlife fish (Miyazaki et al. 1984, Adolfsson-Erici et al. 2002). In the survey by Adolfsson-Erici et al. 2002 triclosan was furthermore found in samples of human milk.

Due to its widespread use local sources of triclosan pollution will most likely occur in the Arctic, and due to the lipophilic properties of the compound bioaccumulation is likely to occur.

#### 5.10.7 Aromatic amines

Monocyclic aromatic amines (MAA) are potential environmental pollutants. They contain a single aromatic ring and at least one amine function to the ring. Many of these compounds originate from azo dyes which are widely used in textiles, food and drink, pharmaceuticals, cosmetics, plastics, paper, leather, printing ink, paints, varnishes, lacquer and wood staining (Øllgaard et al. 1998). The total input of azo dyes in Denmark is 2400 t/year (Øllgaard et al. 1998). When azo dyes enter the human gastrointestinal tract through ingestion of food or drink, aromatic amines are

produced by azoreductases of intestinal microorganisms and, to a lesser extent by intestinal enzymes. MAAs are also released into the environment when azo dyes are discharged into the rivers from the textile industry, the dyestuff manufacturing industry and other industries or by municipal waste. MAAs are potentially toxic, mutagenic and/or carcinogenic to humans and animals (in Chung et al. 1997).

#### 5.10.8 Conclusions and recommendations

The compounds PFOS, synthetic musks, polychlorinated naphthalenes, brominated flame retardants (HBCD, TBBPA and PBB) other than PBDE, polybrominated dibenzodioxins and dibenzofurans, aromatic amines and the biocide triclosan are examples of high volume chemicals of high international concern found in the environment in lower latitudes. Some of these compounds have already been detected in Arctic samples. A screening of the Greenland environment for these compounds is therefore recommended. If the screening reveals abundance of the chemicals mentioned, further studies regarding baseline levels and bioaccumulation are recommended.

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## 6 Effects

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#### 6.1 CADMIUM TOXICITY TO RINGED SEALS

A total of 100 ringed seals from 1998 sampled in Qaanaaq, North West Greenland were examined to detect cadmium induced nephropathy and osteodystrophy. Cadmium concentrations in the kidneys were determined and histological examination of the kidneys and DXA scanning of the sceletal system (lumbal vertebraes) were conducted as described in Sonne-Hansen et al. (2000, 2002).

The background of the study is that the Greenland marine food chains contain high levels of cadmium, mercury and selenium. Concentrations of cadmium in the kidney of ringed seals from the municipalities of Qaanaaq and Upernavik (northwest Greenland) are among the highest recorded in the Arctic and therefore selected for the study.

The purpose of the study was to determine whether cadmium induced damage in the kidneys and the skeletal system could be detected among 100 ringed seals from Northwest Greenland.

The cadmium concentrations in the kidney cortex ranged from 0 to 248  $\mu$ g/g ww (mean = 44.5  $\mu$ g/g ww) in the 99 kidneys examined. Experience from cadmium poisoned humans and laboratory mammals indicate that concentrations above 50-200  $\mu$ g/g ww may induce histopathological changes (Friberg, 1986; WHO, 1992; Elinder & Järup, 1996). Overall, 31 of the ringed seals had cadmium concentrations in the kidney cortex above 50  $\mu$ g/g ww, 11 had concentrations above 100 and 1 had concentrations above 200  $\mu$ g/g ww (see Figure 6.1.9). Obvious histopathological changes (categorized mainly as glomerulonephritis) were found in 10 of the seals, however, none of these changes could specifically be atributed to cadmium induced renal damage (mainly tobulopathy) as described for other species (see Table 6.1.1 and Figure 6.1.7).

Damage to the proximal kidney tubules is known to induce demineralisation of the skeletal system (Fanconi's syndrom). Therefore the three lowest lumbar vertebrae were scanned in 91 seals to measure the content of calcium. The 10 cases of nephropathy could neither be linked to the degree of mineralisation of the skeleton or to the cadmium concentrations (see Figure 6.1.8 and 6.1.9). Furthermore, the degree of mineralisation of the skeleton was not correlated with the cadmium concentration or sex (p=0.68), but was highly significant correlated to age (p<0.001).

TABLE 6.1.1. CLASSIFICATION OF THE HISTOPATHOLOGICAL FINDINGS INTO FOUR GROUPS.

<u>Group 1:</u> No apparent histopathological changes (N = 75). Lesser PAS positive deposits focally spread in the mesangial matrix (see Figure 6.1.1).

<u>Group 2:</u> Minimal changes (N = 14). Focally spread PAS positive matrix deposits in the mesangium and a limited segmental thickening of the glomerular basement membrane (see Figure 6.1.2).

<u>Group 3:</u> Obvious histopathological changes (N = 6). Generalized distinct PAS positive deposits in the mesangium leading to a thickening of the hilus. Segmental distinct thickening of the glomerular basement membrane with PAS positive deposits (humps). Varying degrees of arteriosclerotic changes in the efferent and afferent arterioles (see Figure 6.1.3).

<u>Group 4:</u> Intense histopathological changes (N = 4). Generalized distinct PAS positive deposits in the mesangium leading to an obvious thickening of the hilus. Segmental distinct thickening of the glomerular basement membrane with PAS postive deposits (humps). Arteriosclerotic changes in the afferent and efferent arterioles leading to sclerosis (atrophy and fibrosis) of the glomeruli. Fibrous peritubular necrotic tubules (see Figure 6.1.4).

Figure 6.1.1 Histological findings in Group 1. No changes are seen neither in the mesangium nor in the basement membranes, the glomeruli or the tubules. Abbreviations used: Glo: glomerulus, Me: mesangium, Pt: proximale tubules, Hi: hilus, Dt: distale tubules, Gb: glomerulare basale membrane, Bb:Bowmann's basale membrane (PAS, 250x).

FIGURE 6.1.2. HISTOLOGICAL FINDINGS IN GROUP 2. NOTE THE MINOR PAS-POSITIVE DEPOSIT IN THE GLOMERULAR BASEMENT MEMBRANE ON THE RIGHT (ARROW) (PAS, 400X).

FIGURE 6.1.3. HISTOPATHOLOGICAL FINDINGS IN GROUP 3. NOTE THE OBVIOUS PAS-POSITIVE DEPOSITS IN THE HILUS (ARROW) (PAS, 400X).

Figure 6.1.4. Histopathological findings in Group 4. Note the intense PAS-positive deposits in Bowmann's basale membrane (humps) (arrows). Deposits are also seen in the mesangium (PAS, 400X).

Figure. 6.1.5. Histopathological findings in Group 3 and 4. Note the glomerular fibrosis (1), the infiltration of mononuclear cells (2), the necrotic tubules (3) and the segmental thickening of the basement membrane (4) (PAS, 250x).











Figure 6.1.6 An example of obvious thickening of the basement membrane (black) (PASM, 1000x).



Figure 6.1.7. Histopathologic findings in group 4. Interstitial fibrosis (coloured red), dilatation and atrophy of the proximale tubules with luminal hyaline deposits (1) and glomerular sclerosis (atrophy and fibrosis) (2) (Van Gieson, 100x).









Figure 6.1.9. The kidney cortex concentration of cadmium (CdK,  $\mu$ g/g ww) as a function of the age (years). Presence of histopathological changes are indicated by: yes (•) and if not present by: no (0).

It can be concluded that 10% of the ringed seals showed renale histopathological changes. Despite high levels of cadmium it cannot be concluded whether the ringed seals showed cadmium-induced nephropathy or osteodystrophy. This might be explained by the composition of the ringed seals diet, which contains high levels of vitamin D, calcium, phosphorus, zinc, selenium and protein. These elements are all likely to counteract cadmium-induced damage. It is speculated that ringed seal are not particularly vulnerable to osteodystrophy, due to their continuous growth (bone mineralisation) throughout life and the female estrogen hormonal activity throughout life.

#### 6.2 Effects of contaminants in the Greenland Sea Polar bear

Recently, there has been an increased focus on the negative effects on Arctic organisms of organochlorines (OCs) that originate in the industrialized parts of the world. Long-lived and persistent substances such as DDT and PCB become concentrated in food webs, from lower to higher trophic levels. As apex predator in the Arctic marine ecosystem, polar bears acquire relatively large burdens of OCs because their diet consists primarily of seal blubber and meat. Bears in Svalbard, the western Russian Arctic and East Greenland have relatively high concentrations of OCs, and their levels are high enough to raise concern about effects on health and reproductive performance. Propably 17 cases of female polar bears with deformities in their external sex organs (*pseudohermaphrodites*) have been recorded at Svalbard since 1990 (Derocher pers. comm.). These deformities are suspected of being caused by high levels of OCs (Wiig et al. 1998).

In 1999 the NERI and the Greenland Institute of Natural Resources (Nuuk) initiated a study to assess the effects of OCs on internal and external organs of polar bears in east Greenland. The study involves:

- (1) obtaining information from the Greenland polar bear hunters concerning their observations of bears with aberrant organs or behavior,
- (2) analyzing skulls, histopathology of internal organs and levels of anthropogenic pollutants (OCs a.o.) from 100 polar bears killed by hunters from the municipality of Scoresby Sound in central east Greenland and
- (3) comparing frequencies of morphological anomalies in a historic and the recent sample of polar bear skulls from east Greenland.

The project is ongoing and still awaits the ageing of the individuals, results from additional chemical analysis and histological examinations. Therefore, the results presented below are regarded as preliminary and no confirm conclusions should be made.

#### Aberrant polar bears in east Greenland

Dietz et al. (2001) investigated the frequence of macroscopic pathological changes detected by local hunters - in polar bears in east Greenland in 1999. 52 local east Greenland hunters from Scoresby Sound and Ammassalik were interviewed and they covered at least 1110 polar bears in total. Despite the female polar bear with megaclitoris 12 bears with aberrant macroscopic divergation were reported of which 8 could be congenital maldeformation and/or due to other aetiology like endocrine disruption. The changes were malformation of a new born, papillae mammae accessoria, 2 bears with six claws, one bear with missing claws on left and right hind paws and 3 bear with diverging degrees of focal macular melanoses (due to inflammation and/or formation of connective tissue). This is a 0.81% (9/1110) frequency of aberrant polar bears due to environmental estrogens and/or with other aetiology which is lower than expected compared to e.g. frequencies in populations in domestic and wild animals. The frequency of pseudohermaphroditism among east Greenland polar bears are 0.09% (1/1110) and lower than the frequency of for example female pseudohermaphrodites oberserved at Svalbard (2-3%) (Wiig et al. 1998, Derocher pers. comm.).

<u>Female pesudohermaphrodite polar bears in east Greenland and at Svalbard</u> The female pseudohermaphrodite from east Greenland were investigated by veterinarian-pathologists in March 2002 and macroscopically both the internal and external reproductive organs were normoanatomical and -functional except for the megaclitoris (Figure 6.2.1). Compared to samples obtained from other female polar bears the reproductive organs are normal in anatomy and functionality (see Table 6.2.1). The female polar bear pseudohermaphrodite was in estrus with an active ovarium without a dominating follicle (>10 follicles in each ovarium and a corpus luteum).



FIGURE 6.2.1. EXTERNAL AND INTERNAL GENITALIA FROM THE FEMALE PSEUDOHERMAPHRODITE POLAR (FORMALDEHYDE-ALCOHOL-PRESERVED) BEAR SHOT IN CENTRAL EAST GREENLAND (SCORESBY SOUND) 1999. A.THE EXTERNAL GENITALIA (NOTE THE MEGACLITORIS). B. CROSS-SECTION OF THE EXTERNAL GENITALIA (NOTE THE SPONGIOUS/CARTILAGE TISSUE FROM THE OS ISCHIATICUS INTO THE CLITORIS). C. THE INTERNAL ORGANS SHOWING NORMO-ANATOMICAL FUNCTIONAL OVARIES, SALPHINX, CORNI UTERI AND CORPUS UTERUS. BAR INDICATES CM.

Genetically the female polar bear were a female with no chormosomal abnormalities or presence of a y-chromosome (Andersen pers. comm.).

At Svalbard 4 polar bear female pseudohermaphrodites have been reported from 1990-97 (Wiig et al. 1998). Afterwards app. 13 suspected female polar bear pseudohermaphrodites has been clinically examined during helicopter survey and radiotelemetry investigations but these are not reported yet (Derocher pers. comm). The east Greenland bear has been examined post mortem after formaldehyde-alcohol fixation of reproductive organs and endocrine glands. Table 6.2.1 summarises the results from the clinically macroscopic examinations of the external genitalia of the bears.

Female pseudohermaphroditism is known to be induced by endocrine disruption foetally or post partum (Benirschke 1981, Polani 1981, Capen 1995, Feldman 1995, Mickelsen & Menon 1995, Wiig et al. 1998). Four hypotheses have been mentioned (Ibid.):

(1) *Freemartiinism* (when the male of two twins influence the female foetus by its androgens through the anasotmoses in the foetal vascular system).

(2) *Tumors* (the mother has produced more testosterone than normal due to a tumor in the brain or the ovaries which gives the female foetus male characteristics).

(3) *Mutations* (genetic mutations where pseudohermaphroditism becomes congenital).

(4) *POPs* (persistent organic pollutants where anthropogenic xenoandrogens and/or estrogens disrups the endocrine homeostasis in the mother and the foetus are malformed due to altered hormonal status).

Table 6.2.1. Comparison of changes in female external genitalia described in four polar bears from Svalbard by Wiig et al. (1998) and in one polar bear from Central East Greenland (Scoresby Sound).

		Svalbard two yearlings	Svalbard two 15-yrs	Central E	ast Greenland 1 specimen	
Year		1996	1990/97		1999	
Location		Svalbard	Svalbard	Svalbard Score		
Sex		F	F	F		
Age		Yearling	15-yr		App. 15-yr	
Vulvae (undevelop-	enlarged-swollen)	Undeveloped	Swollen		Swollen	
Status of reproduct	ion	Juvenile	Estrous		Estrous	
Gll. mammae		Undeveloped	No milk			
Female with cup(s)		No	No/weaned or le	ost cubs	No	
Female in company	r (adult male)	No	No/Yes		No	
Vaginal opening	. ,	Normal	Normal		Normal	
Penis/clitoris	Length	≥20 mm penis	≥20 mm		≥27 mm	
	Width	≥22 mm				
	Height	≥21 mm				
Baculum		Yes	No		;	
Location of penis/ of	clitoris	Caudal to normal	Normal		Normal	
Concealing		The vaginal opening	Normal		Normal	
		by a single pair of labia				
Urethral opening		5 mm laterally to the	Normal		Not investigated	
		distal end of the penis				
Y-chromosomes		No	Not investigated	No		

The female pseudohermaphrodite polar bears from Svalbard could hence reflect a congenital pseudohermaphrodite complex, an androgenproducing tumor or POP pollution but pobably not due to freemartiinism (Benirschke 1981). The east Greenland female pseudohermaphrodite polar bear - as it is the single one observed in this study and by local hunters – is likely to be caused by an androgenproducing tumor, androgensubstances (OCs) or be a polar bear from Svalbard.

## Fluctuating asymmetry and osteopenia and macroscopic skull pathology in east Greenland polar bears

A total of 283 polar bear skulls were investigated to detect fluctuating asymmetry and macroscopic pathology (parodontitis) over time. Fluctuating asymmetry has been used as a stress indicator, in numerous animal and plant organisms in wildlife and laboratory mammals, to reflect developmental instability (e.g. Palmer & Strobeck 1986, Nachman & Heller 1999). To detect the degree of fluctuating asymmetri 16 metric bilaterally traits and 17 meristric as foraminas (canal openings in the skull for nerves and blood vessels) were examined in the skulls covering the time period from 1892 to 2000. In a preliminary analyses, the skulls were divided into two groups; before and after 1960 and it was tested whether fluctuating asymmetry was occuring and whether there was differences between the two peiod. The analyses was preliminary because the skulls could not be divided according to the age of the bears. The analysis gave no indications of the skulls from after 1970 (the OC pollutants affected period) to have higher degree of fluctuating asymmetry than skulls before 1970.

The frequency of parodontitis within preliminary age groups was also investigated in skulls before and after 1970 (Figure 6.2.2). The frequency of parodontitis increased significantly at the 5% level with age and no differences was found between sampling periods (logistic regression analysis).



Figure 6.2.2. Frequency of parodontitis by perliminary age groups (juvenile, suvadult, adult and old) and sampling period (before and after 1970). Barnumbers indicate no. of skulls.

A X-ray bone densitometer was used to determine the mineralisation of the skulls (calcium-phospate content). The data were analysed using a software programme, which generates a picture of the bone segment and calculates the bone mineral content (BMD, g/cm<sup>2</sup>). Figure 6.2.3 shows the relationship between BMD and the preliminary age, indicating lower BMD in females than in males. This may be expected as female mobilises calcium-phosphate to the foetus and later on also to the weaning pub.



Figure 6.2.3. The bone mineral density (BMD,  $g/cm^2$ ) as a function of age by gender (female = blue; male = red)

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## 7 Conclusions and recommendations

#### 7.1 CONCLUSIONS

#### 7.1.1 Atmospheric environment

- The High Arctic is burdened with a considerable atmospheric pollution, consisting of a wide variety of acidic and toxic compounds, which originate in mid-latitude industrial areas. It has been demonstrated by the combined use of long-term field measurements and sophisticated large-scale meteorological and chemical transport models.
- For the northern part of Greenland mainly Russian sources contribute, while for the western and the southern parts it is North American and European sources.
- The combination of long term field data measurements and model calculations has also been highly useful in assessing trends in atmospheric concentrations. The emissions of Pb, Zn, Ni, As, Cu and S from the source areas in the Northern Hemisphere, which contributes to the concentrations in the High Arctic, have decreased with 50 % between 1990 and 2000.
- The levels of Hg have increased considerably due to the human activities. Furthermore new results have shown, that the Arctic acts as global sink for Hg due to the depletion process for Hg during the Polar Sunrise. Measurements and atmospheric modelling have shown that the deposition of Hg in the northern part of Greenland increases with up to a factor of 3 due to this phenomenon dependent on the ratio between re-emission of Hg from the snow pack during melting period.

#### 7.1.2 Terrestrial environment

- Cadmium concentrations in terrestrial biota are low compared to marine biota. The Cd levels in Greenland terrestrial birds and mammals are in the range found in other Arctic regions. No temporal trend could be detected in Cd levels from 1994 to 1999.
- Mercury and selenium concentrations in terrestrial biota are low compared to marine biota but relatively high compared to the levels found in other Arctic regions. There were indications of lower Hg and Se levels in terrestrial biota in 1999 than in 1994/95.
- Peat studies in the AMAP area show a general elevation of deposition of Pb and Hg since the beginning of industrial times yet falling in the last 10-20 years in case of Pb and possibly also for Hg.
- Organochlorine levels in Greenland terrestrial biota were low and much lower than in the marine biota. Even in fat of musk ox and lamb were OC levels low. The dominant OC was PCB.

• Caribou and lamb hold the highest <sup>137</sup>Cs concentrations in the terrestrial environment, and long ecological half-lives are seen because of the environmental conditions.

#### 7.1.3 Fresh water environment

- Mercury concentrations in landlocked Arctic char in Greenland are relatively high especially in southwest Greenland. No significant difference was found in Hg concentrations in Arctic char from southwest Greenland between 1994/95 and 1999.
- Organochlorine levels in landlocked Arctic char were in the same range as found in marine fish species. No consistent geographical pattern of OC concentrations was observed. Concentrations of ∑DDT, ∑HCH and ∑CHL were lower in a southwest Greenland Arctic char population in 1999 than in 1994. No significant changes were found of ∑PCB-10 and HCB concentrations between 1999 and 1994.
- <sup>137</sup>Cs / <sup>90</sup>Sr activity ratios in fresh waters have decreased from the fallout level around 1.5 to the present levels varying between 0.03 and 0.46. This indicates a large variability in drainage area and lake characteristics.
- Due to special environmental conditions, <sup>137</sup>Cs from global fallout is still transferred to landlocked Arctic char with extremely high efficiency in south Greenland.

#### 7.1.4 Marine environment

- Greenland marine sediments are not enriched by arsenic as reported for large areas of the Barents Sea.
- Recently observed Cd, Hg and Se levels in marine biota were generally within the range observed previously. The recent Cd data confirms the previously observed relative high level in the marine biota from Qeqertarsuaq (central west Greenland) compared to other Arctic regions. Beside that, no pronounced difference in Cd levels between marine biota from west and east Greenland was observed. Hg levels tended to be higher in east Greenland than in west Greenland for shorthorn sculpin, black guillemot (egg) and ringed seals, whereas polar bears appear to show the opposite trend.
- Only few time series of Cd and Hg data covering the recent 20 years are available so no firm conclusions can be made concerning trends. Cd in ringed seals from Avanersuaq and Ittoqqortoormiit tended to have lower levels in 1994 and 1999/2000 than in the mid 80'ies. In Qeqertarsuaq Cd levels tended to be higher in 1994 than in 1999/2000 in ringed seals, and Hg concentrations in blue mussels and ringed seals tended to have higher levels in 1994 than in 1999. In Avanersuaq, Hg levels in ringed seals showed an increasing trend from the mid 80'ies to mid 90'ies and again to 1999/2000. In Ittoqqortoormiit, no appearent trend in Hg levels was observed in ringed seals and polar bears.
- Seabirds hunted with lead shot have significantly elevated lead levels in their muscles. This probably constitudes the most important single lead source in Greenland human diet.

- A considerable amount of new OC data in marine biota has become available since AMAP phase 1. In marine fish the highest OC levels were found in bottom fish-eating species such as Greenland halibut. In seabirds, the highest OC levels were found in opportunistic feeders such as glaucous gull and in species wintering off North America and Europe such as kittiwake. The highest OC levels in marine mammals were found in narwhals, beluga and polar bear. Considerable evidence now exists of higher OC levels in marine biota from east Greenland than from west Greenland.
- In general, OC levels in biota from west Greenland were comparable with OC levels found in similar species from east Arctic Canada, whereas biota from east Greenland were intermediate the levels in west Greenland and Svalbard or at the same level as found in Svalbard. Circumpolar patterns of ∑PCB, ∑DDT, ∑CHL in ringed seal, minke whales and polar bears generally increase eastward from east Arctic Canada, west Greenland to east Greenland and Svalbard, whereas the opposite trend was found for ∑HCH.
- OC concentrations in biota from Qeqertarsuaq showed no consistent changes from 1994 to 1999/2000. In shorthorn sculpin from Ittoqqortoormiit ∑PCB and ∑HCH were significantly lower in 1999/2000 than in 1994. This was also the case ∑HCH in male ringed seals. In polar bears from Ittoqqortoormiit in 1999/2000, ∑PCB and ∑CHL levels were considerably lower than in 1990.
- Concentrations of <sup>99</sup>Tc, <sup>137</sup>Cs and <sup>90</sup>Sr in seawater are decreasing in the order North East Greenland and the coastal East Greenland Current > south west Greenland > central west Greenland and north west Greenland > Irminger Sea ~ Faroe Islands. This is caused by the general large-scale oceanic circulation combined with European coastal discharges and previous contamination of the Arctic Ocean. The same tendency is seen in marine biota. The peak <sup>99</sup>Tc discharge from Sellafield 1994-1995 has only been slightly visible in year 2000. The concentrations are expected to increase in the future, especially in east Greenland.
- In the plutonium contaminated Bylot Sound, biological activity has mixed plutonium efficiently into the 5-12 cm new sediment resulting in continued high surface sediment concentrations 3 decades after the accident in 1968. Transfer of plutonium to benthic biota is low and lower than observed in the Irish Sea. This is supposed to be caused by the physico-chemical form of the accident plutonium. A recent study indicates that "hot particles" hold considerably more plutonium than previously anticipated and that the Bylot Sound sediments may account for the major part of the un-recovered amount, i.e. around 3 kg.

#### 7.1.5 Other contaminants

• Tributyltin (TBT)

TBT and degradation products were detected in the marine environment in mussels sampled outside Nuuk and in harbour sediments. The TBT levels in mussels were low compared to Danish coastal waters.

 Dioxins, furans and coplanar PCBs Dioxins, furans and coplanar PCBs were detected in polar bears. Compared to marine mammals in other Arctic regions the concentrations were relatively low. • Toxaphene

Toxaphene concentrations in the Greenland marine biota were within the range observed in other Arctic regions. Toxaphene levels in Greenland terrestrial biota were lower than in marine biota. The highest toxaphene levels were found in marine mammals especially narwhals.

• Chlorobenzene

The highest chlorobenzene concentrations were found in blubber of narwhal and beluga. The by far dominating chlorobezene in Greenland biota is hexachlorobenzene (HCB).

• New chlorinated pesticides

The highest levels of aldrin, dieldrin, endrin, heptaclor, endosulfan, methoxychlor and mirex were comparable to levels detected elsewhere in the Arctic. Data on levels of endosulfan and methoxychlor, two chlorinated pesticides still in use, in Arctic biota are sparse. The concentrations found were lower than observed in more industrialized parts of the world.

• Polybrominated diphenyl ethers (PBDE)

PBDEs are found in all organisms analysed, as a result of not only long-range transport but also local sources. The concentrations measured are lower than found in industrialized parts of the world and below levels that can acutely affect organisms detrimentally.

- Polycyclic aromatic hydrocarbons (PAH)
  PAH levels in south Greenland are of the same magnitude as levels measured in more urbanized parts of the world, even exceeding the EAC values (OSPAR) for e.g. anthracene. The highest levels were found in fish, e.g. shorthorn sculpin indicating a higher potential for bioaccumulation than seen in the Temperate Zone.
- Contaminants of future concern

The compound groups PFOS, synthetic musks, polychlorinated naphthalenes, other brominated flame retardants (HBCD, TBBPA and PBB), polybrominated dibenzodioxins and dibenzofurans, aromatic amines and the biocide triclosan are examples of high volume chemicals of high international concern found in the environment at lower latitudes. Studies have indicated the presence of some of these compounds in the Arctic.

#### 7.1.6 Effects

- Although histopathological changes were observed in 10% of the ringed seal kidneys these were not specific enough to be concluded as cadmium induced. No demineralisation in the skeletal system could be linked to cadmium levels and/or nephropathological changes in selected ringed seals from northwest Greenland with high cadmium levels in the kidney. Furthermore the degree of mineralisaton of the skeleton was not correlated with gender but was highly significant correlated to age.
- Based on interviews of aboriginal polar bear hunters in East Greenland 13 macroscopic pathological changes in 1110 bears were reported. However, it is yet unknown whether these abnormalities are related to contaminant levels.
- So far a single pseudohermaphrodite (female) out of 94 (35 identified females) examined polar bears have been observed.

- Preliminary results shows that female polar bears are lower in bone mineral density than males, but it is so far uncertain to say whether post menopansa bears and recently sampled bears suffer from contaminant induced osteopenia.
- Frequencies of parodontitis increase significantly with age of polar bears but no temporal trends have so far been detected.

#### 7.2 Recommendations

#### 7.2.1 Atmospheric environment

- Maintain Station Nord as a High Arctic monitoring and research station as basis for field campaigns, and continuing measurements at Station Nord in order to maintain the long time series of measurements and to have a place for process studies.
- Perform long term monitoring in the high Arctic of atmospheric Hg and other relevant species and components.
- Identify the composition of reactive gaseous Hg as at present, it is unknown if the model results and measurements describe the same thing.
- Identify and describe the processes responsible for the removal of Hg from the atmosphere leading e.g. to accumulation in the snow pack.
- Develop tools (function/model) that would describe the above process and introduce these tools to the existing DEHM model, so that reliable model calculations can be made of the burden of atmospheric Hg to Arctic environment.
- Establish monitoring and model programs for POP's based on the experience gained from the study of heavy metals including Hg.

#### 7.2.2 Terrestrial environment

- The monitoring of Cd and Hg levels in lichens, ptarmigan and caribou should continue at five year intervals in order to detect temporal trends.
- Studies of post depositional processes in peat should be continued supplementary to work in other environmental archives (sediments, snow/ice).
- Survey of <sup>137</sup>Cs levels in caribou and lamb should be continued from earlier sampling areas and preferably extended in south Greenland.
- A follow-up survey of plutonium levels in the terrestrial environment based on organic surface soil samples from areas where plutonium was detected after the Thule accident is suggested.

#### 7.2.3 Fresh water environment

- The annual monitoring of Hg and OC levels in Arctic char from east Greenland, and the monitoring of Hg and OC levels in Arctic char from southwest Greenland at five year intervals should be continued in order to detect year to year variations and temporal trends.
- Radionuclide concentrations should be examined in landlocked Arctic char from a number of lakes in south Greenland preferentially oligotrophic, low-ionic lakes from areas with a high precipitation rate. In addition to <sup>137</sup>Cs, the naturally occurring radionuclides <sup>210</sup>Po and <sup>226</sup>Ra should be assessed in selected samples.

#### 7.2.4 Marine environment

- The annual monitoring of Hg and Cd levels in sculpin, black guillemot and ringed seal from west Greenland and OC levels in sculpin, black guillemot and ringed seal from west Greenland should be continued in order to detect year to year variations.
- The monitoring of Hg, Cd and OC levels in sculpin, black guillemot and ringed seal from west and east Greenland at five year intervals should be continued in order to detect temporal trends.
- Supplement the existing time series of Hg levels in hair from polar bears back in time based on museum specimens is recommended.
- Few time series of OC levels in marine biota covering the last 25 years exist. Supplementing existing time series with samples from previously collected marine species would add considerably to the knowledge of recent temporal trends.
- Levels of especially <sup>99</sup>Tc and <sup>137</sup>Cs should be routinely monitored in seawater and biota especially from east and south Greenland and from the fishing banks.
- A survey of the naturally occurring radionuclide <sup>210</sup>Po in Greenlandic traditional diet, especially in seal, is recommended.
- A survey of the plutonium contamination in the Bylot Sound should be carried out in 2003 with special attention to be paid to the effect of hot particles and to possible changes in physico-chemical form that may increase bioavailability and mobility. The plutonium contamination in Bylot Sound should be monitored regularly, e.g. every 5 years.

#### 7.2.5 Other contaminants

- Tributyltin (TBT)Screening of TBT baseline levels away from point sources in southwestGreenland is recommended, eventually in combination with effect studies.Furthermore, analyses of TBT in marine mammals are recommended because of the potential for bioaccumulation.
- Dioxins, furans and coplanar PCBs
  Further investigations regarding sources of these compounds and concentrations at lower trophic levels are recommended, taking the high potential for long-term detrimental effects into account.

• Toxaphene

Time trend studies of toxaphene in key species are recommended in order to reveal if the ban of toxaphene at lower latitudes leads to a decrease in the marine Greenland environment.

- Chlorobenzene Time trend studies of HCB in key marine species are recommended.
- New chlorinated pesticides Time trend studies of these compounds in key marine species are recommended.
- Polybrominated diphenyl ethers (PBDE) An exponential increase in PBDE levels has been reported elsewhere, therefore it is recommended to incorporate this group of compounds in time trend studies for marine key species.
- Polycyclic aromatic hydrocarbons (PAH) The high PAH levels measured in fish call for further attention. Further studies including metabolism and effect studies are recommended. Furthermore additional baseline studies of PAHs are important, especially in connection with eventual oil exploration in Greenland.
- Contaminants of future concern A screening of the Greenland environment for the compounds PFOS, synthetic musks, polychlorinated naphthalenes, other brominated flame retardants (HBCD, TBBPA and PBB), polybrominated dibenzodioxins and dibenzofurans, aromatic amines and the biocide triclosan is recomended. If the screening reveals abundance for these compounds in the Greenland environment further studies regarding baseline levels and bioaccumulation are recommended.

#### 7.2.6 Effects

- Clinical parameters (reproduction parameters a.o.) are difficult to study in Arctic wildlife like polar bears, as they range over vast and inaccessible areas, which may be very costly to approach. On the other hand laboratory studies on test set-ups and organisms like e.g. mink may not reflect the Arctic species and ongoing contaminant exposure. It is therefore important to conduct controlled studies on Arctic species, which have an intake of the actual high trophic marine Arctic diet.
- Cadmium kidney levels in seabirds from northwest Greenland and other Arctic areas are high enough to pose a threat for kidney damage. An effect study of renal changes in seabirds from the highest exposed areas and species in Greenland is therefore recommended.

# Appendix A. Cd, Hg, Se and As concentrations (mg/kg ww) in Greenland biota obtained in AMAP phase II. Mean • standard deviation.

Species Terrestrial	Location	Year	Tissue	n	Sex	Size/age	Unit	Cadmium	Mercury	Selenium	Arsen
Lichens	Nuuk	1999	whole	4	-	-	mg/kg dw	0.170±0.238	0.036±0.001	0.040±0.006	
( <i>Cetraria nivalis</i> )	Qaqortoq	1999	whole	6	-	-	mg/kg dw	0.086±0.026	0.048±0.011	0.096±0.024	
Crowberry	Southwest Greenland	1999	Berries	5	-	-	mg/kg ww	0.004±0.006	<0.002	<0.05	
(Empetrum hermaph	proditum)										
Arctic blueberry	Southwest Greenland	1999	Berries	4	-	-	mg/kg ww	0.028±0.007	<0.001	<0.03	
(Vaccinium uliginosu	<i>ım</i> )										
Ptarmigan	Nuuk	1999	Muscle	5	F	-	mg/kg ww	0.116±0.150	<0.002	0.169±0.068	
(Lagupus mutus)			Liver	9	F+M	-	mg/kg ww	2.87±3.83	0.022±0.007	0.181±0.089	
			Kidney	12	F+M	-	mg/kg ww	21.6±24.3	0.037±0.008	0.525±0.156	
	Qeqertarsuaq	1999	Liver	19	F+M	-	mg/kg ww	1.91±1.26	0.036±0.018	0.174±0.052	
			Kidney	20	F+M	-	mg/kg ww	15.7±12.9	0.046±0.019	0.524±0.201	

Species	Location	Year	Tissue	n	Sex	Size/age	Unit	Cadmium	Mercury	Selenium	Arsen
Domestic sheep	South Greenland	1999	Muscle	10	-	lamb	mg/kg ww	<0.002	<0.002	<0.05	
(Ovis sp.)			Liver	5	-	lamb	mg/kg ww	0.108±0.059	0.005±0.001	0.098±0.054	
			Kidney	5	-	lamb	mg/kg ww	0.200±0.081	0.012±0.010	0.707±0.165	
			Fat	5	-	lamb	mg/kg ww	<0.005	<0.005	<0.2	
Arctic hare	Qeqertarssuaq	1999	Muscle	5	F+M	Adult	mg/kg ww	0.005±0.003	<0.002	<0.05	
(Lepus arcticus)			Liver	5	F+M	Adult	mg/kg ww	0.186±0.021	0.029±0.010	0.102±0.046	
			Kidney	5	F+M	Adult	mg/kg ww	3.81±1.71	0.052±0.006	0.841±0.174	
Caribou	Kangerlussuaq	1996	Muscle	22	F+M	-	mg/kg ww	0.002±0.005	0.005±0.001	0.031±0.008	
(Rangifer tarandus)	0		Liver	23	F+M	-	mg/kg ww	0.154±0.101	0.041±0.012	0.086±0.017	
		1997	Muscle	24	F+M	-	mg/kg ww	0.004±0.004	0.010±0.002	0.046±0.009	
			Liver	24	F+M	-	mg/kg ww	0.211±0.106	0.064±0.019	0.095±0.019	
	Akia	1996	Muscle	22	F+M	-	mg/kg ww	0.005±0.004	0.011±0.003	0.128±0.018	
			Liver	24	F+M	-	mg/kg ww	0.631±0.285	0.128±0.056	0.414±0.101	
		1997	Muscle	25	F+M	-	mg/kg ww	0.003±0.002	0.030±0.007	0.175±0.030	
			Liver	25	F+M	-	mg/kg ww	0.829±0.536	0.282±0.103	0.305±0.099	
	ltinnera	1996	Muscle	7	F+M	-	mg/kg ww	0.001±0.001	0.003±0.001	0.078±0.012	
			Liver	7	F+M	-	mg/kg ww	0.350±0.251	0.071±0.023	0.171±0.048	
		1997	Muscle	10	F+M	-	mg/kg ww	0.002±0.002	0.006±0.002	0.100±0.017	
			Liver	10	F+M	-	mg/kg ww	0.280±0.195	0.063±0.033	0.171±0.042	
		1999	Liver	18	F+M	-	mg/kg ww	0.265±0.123	0.032±0.022	0.163±0.108	
			Kidney	18	F+M	-	mg/kg ww	1.424±0.822	0.093±0.046	0.639±0.160	
	lsortoq	1999	Liver	20	F+M	-	mg/kg ww	0.496±0.398	0.142±0.112	0.261±0.081	
			Kidney	20	F+M	-	mg/kg ww	1.73±1.08	0.115±0.030	0.820±0.094	
		2000	Kidney	5	F	-	mg/kg ww	0.276±0.117	0.038±0.008	0.563±0.065	
			Fat	5	F	-	mg/kg ww	0.003±0.002	<0.003	<0.2	

Species	Location	Year	Tissue	n	Sex	Size/age	Unit	Cadmium	Mercury	Selenium	Arsen
Musk ox	Kangerlussuaq	1999	Muscle	9	-	-	mg/kg ww	0.002±0.004	0.002±0.001	<0.05	
(Ovibos moschatus)			Liver	4	-	-	mg/kg ww	0.051±0.007	0.023±0.004	0.062±0.044	
			Kidney	4	-	-	mg/kg ww	0.284±0.202	0.072±0.025	0.757±0.246	
			Fat	4	-	-	mg/kg ww	<0.005	<0.005	<0.2	
Fresh water											
Arctic char (landlocked)	lsortoq	1999	Muscle	20	F+M	-	mg/kg ww	0.001±0.001	0.907±0.419	0.997±0.127	
(Salvelinus alpinus)	Zackenberg	1999	Muscle	20	F+M	-	mg/kg ww	0.002±0.001	0.159±0.111	1.182±0.430	
	Ittoqqortoormiit	2000	Muscle	20	F+M	-	mg/kg ww	-	0.062±0.043	0.809±0.862	
Marine											
Sediment	Around Greenland	1985-94	Surface	41	-	-	mg/kg dw	-	0.062±0.070	-	7.87±5.68
Blue mussels	Qeqertarsuaq	1999	soft tissue	2	-	3-4 cm	mg/kg ww	1.205±1.019	0.0122±0.0036	0.485±0.100	
( <i>Mytilus edulis</i> )			soft tissue	3		4-5 cm	mg/kg ww	0.552±0.152	0.0106±0.0046	0.517±0.018	
			soft tissue	3	-	5-6 cm	mg/kg ww	0.892±0.198	0.0133±0.0013	0.467±0.042	
			soft tissue	3	-	6-7 cm	mg/kg ww	1.173±0.185	0.0156±0.0046	0.417±0.032	
			soft tissue	3	-	7-8 cm	mg/kg ww	1.204±0.234	0.0119±0.0012	0.474±0.160	
			soft tissue	1	-	8-9 cm	mg/kg ww	2.269	0.0196	0.365	
Iceland scallop	Qeqertarssuaq	2000	Muscle	8 pools	-	5.9-8.5 cm	mg/kg ww	2.04±0.65	0.022±0.002	0.129±0.010	
(Chlamys islandica)				poors							
Queen crab	Qeqertarssuaq	1999	Muscle	10	М	8,9-11,9 cm	mg/kg ww	0.035±0.032	0.096±0.066	0.599±0.157	

(Chionoecetes opilio)			Hepatopan creas	5	М	8,9-9,8 cm	mg/kg ww	5.06±1.71	0.074±0.023	3.27±1.15	
Species	Location	Year	Tissue	n	Sex	Size/age	Unit	Cadmium	Mercury	Selenium	Arsen
Deep sea shrimp ( <i>Pandalus borealis</i> )	Uummannaq	1999	Muscle	11 pools	F	24-30 mm	mg/kg ww	-	0.050±0.016	0.142±0.014	
Shorthorn sculpin	Qeqertarsuaq	1999	Liver	15	F	27.3 cm	mg/kg ww	0.662±0.360	0.014±0.006	0.88±0.15	
(Myoxocephalus qua	dricornis)		Liver	4	Μ	23.3 cm	mg/kg ww	1.26±0.59	0.008±0.001	0.88±0.05	
		2000	Liver	14	F	29.3 cm	mg/kg ww	1.22±1.02	0.014±0.005	1.13±0.23	
				6	Μ	22.8 cm	mg/kg ww	1.40±0.41	0.011±0.005	1.17±0.12	
	Ittoqqortoormiit	1999	Liver	20	F+M	-	mg/kg ww	1.03±0.70	0.049±0.026	1.05±0.23	
		2000	Liver	13	F	24.8 cm	mg/kg ww	0.75±0.23	0.061±0.048	0.89±0.20	
				5	М	21.6 cm	mg/kg ww	1.10±0.57	0.045±0.006	1.16±0.23	
Atlantic cod	Nuuk	1999	Muscle	9	M+F	35-43 cm	mg/kg ww	<0.001	0.014±0.001	0.293±0.018	
(Gadus morhua)			Liver	5	M+F	38-42 cm	mg/kg ww	0.050±0.024	0.007±0.002	0.779±0.146	
Greenland cod ( <i>Gadus ogac</i> )	Nuuk	1999	Muscle	5	M+F	29-45 cm	mg/kg ww	-	0.020±0.010	0.209±0.023	
Atlantic salmon	Nuuk	1999	Muscle	20	M+F	61-73 cm	mg/kg ww	0.003±0.001	0.040±0.010	0.269±0.030	
(Salmo salar)			Liver	10	M+F	61-73 cm	mg/kg ww	0.190±0.040	0.043±0.006	7.93±1.27	
Greenland halibut	Nuuk	1999	Muscle	10	M+F	54-105 cm	mg/kg ww	<0.002	0.154±0.134	0.313±0.116	
(Reinhardtius hippog	glossoides)		Liver	5	M+F	56-105 cm	mg/kg ww	-	0.151±0.151	1.49±0.76	
Capelin	Nuuk	1999	Muscle	20	М	158-199 mm	mg/kg ww	0.003±0.001	0.009±0.002	0.163±0.021	
(Mallotus vfillosus)			Whole fish	10	М	143-187 mm	mg/kg ww	-	0.007±0.002	0.131±0.014	

Species	Location	Year	Tissue	n	Sex	Size/age	Unit	Cadmium	Mercury	Selenium	Arsen
Thick-billed murre	Nuuk	1999	Muscle	20	M+F	-	mg/kg ww	0.089±0.119	0.076±0.021	0.538±0.230	
( <i>Uria lomvia</i> )			Liver	10	M+F	-	mg/kg ww	4.99±3.96	0.277±0.085	1.069±0.108	
Black guillemot	Qeqertarsuaq	1999	Liver	3	Juvenile	-	mg/kg ww	3.07±1.33	1.02±0.14	3.7±0.7	
(Cepphus grylle)			Liver	15	Adult	-	mg/kg ww	1.85±1.19	0.61±0.19	2.8±0.6	
			Kidney	3	Juvenile	-	mg/kg ww	22.0±6.1	0.54±0.29	3.74±0.68	
			Kidney	15	Adult	-	mg/kg ww	15.0±10.4	0.51±0.16	4.13±0.68	
		2000	Liver	20	Adult	-	mg/kg ww	3.72±2.27	0.66±0.26	3.21±0.56	
			Egg	7	-	-	mg/kg ww	-	0.26±0.06	0.50±0.02	
	lttoqqortoormiit	1999	Egg	10	-	-	mg/kg ww	0.0013±0.000	5 0.34±0.06	0.45±0.05	
Ringed seal	Avanersuaq	1998	Liver	21	-	9.2 yrs	mg/kg ww	8.48±7.98	6.22±5.54	3.97±2.90	
(Phoca hispida)	Qeqertarsuaq	1999	Liver	20	-	2.4 yrs	mg/kg ww	16.8±17.1	1.78±3.42	1.79±1.77	
		2000	Liver	20	-	1.2 yrs	mg/kg ww	9.28±5.32	1.03±0.93	1.45±0.51	
		2000	Blubber	10	F+M	-	mg/kg ww	0.011±0.007	<0.005	<0.2	
	lttoqqortoormiit	1999	Liver	20	-	4.9 yrs	mg/kg ww	8.92±8.66	4.36±4.42	3.73±2.96	
		2000	Liver	20	-	4.3 yrs	mg/kg ww	9.28±5.32	1.03±0.93	1.45±0.51	
Minke whale	West Greenland	1998	Muscle	38-42	-	-	mg/kg dw	0.21±0.37	0.288±0.185	0.65±0.19	
(Balaenoptera acuto)	<i>rostrata</i> )		Liver	36	-	-	mg/kg dw	3.89±3.12	1.00±1.12	4.88±2.23	
			Kidney	39-41	-	-	mg/kg dw	16.9±11.3	0.856±0.840	5.59±1.55	
			Baleen	32-34	-	-	mg/kg dw	<0.018	0.068±0.060		
			Epidermis (Muktuk)	4	F+M	-	mg/kg ww	0.007±0.003	0.031±0.021	6.28±3.73	
			Blubber ´	6	F+M	-	mg/kg ww	0.006±0.004	0.011±0.017	0.143±0.064	
	East Greenland	1998	Muscle	4	-	-	mg/kg dw	0.19±0.19	.403±0.135	0.69±0.35	
			Liver	2	-	-	mg/kg dw	5.26±2.90	1.92±0.39	3.77±0.20	

Species	Location	Year	Tissue	n	Sex	Size/age	Unit	Cadmium	Mercury	Selenium	Arsen
			Kidney	2	-	-	mg/kg dw	35.5±26.2	2.70±1.67	6.06±1.21	
			Baleen	2	-	-	mg/kg dw	0.030±0.029	0.28±0.15		
	Jan Mayen, Norway	1998	Muscle	20-21	-	-	mg/kg dw	0.101±0.073	0.791±0.326	0.98±0.31	
			Liver	24	-	-	mg/kg dw	3.96±1.64	2.04±0.73	4.68±0.86	
			Kidney	23	-	-	mg/kg dw	20.4±10.6	2.38±1.63	7.06±2.34	
			Baleen	22-23	-	-	mg/kg dw	<0.016	0.255±0.166		
	Svalbard, Norway	1998	Muscle	14	-	-	mg/kg dw	0.161±0.102	0.315±0.166	0.85±0.28	
			Liver	16	-	-	mg/kg dw	3.76±1.49	0.728±0.352	5.53±1.02	
			Kidney	16	-	-	mg/kg dw	15.4±8.7	0.694±0.337	6.81±1.11	
			Baleen	1-2	-	-	mg/kg dw	<0.018	0.230		
	Barents Sea, Norway	1998	Muscle	33	-	-	mg/kg dw	0.127±0.076	0.505±0.204	0.95±0.35	
			Liver	31	-	-	mg/kg dw	3.50±1.45	1.12±0.65	6.30±1.51	
			Kidney	32	-	-	mg/kg dw	18.2±7.6	1.17±0.59	7.22±1.57	
			Baleen	31	-	-	mg/kg dw	<0.018	0.159±0.093		
	Norway coast	1998	Muscle	10	-	-	mg/kg dw	0.062±0.058	0.593±0.604	0.82±0.27	
			Liver	14	-	-	mg/kg dw	2.39±1.86	1.74±2.19	5.31±2.15	
			Kidney	11	-	-	mg/kg dw	10.5±5.8	1.18±1.06	6.87±1.04	
	North Sea	1998	Muscle	23	-	-	mg/kg dw	0.070±0.041	0.902±0.400	1.01±0.26	
			Liver	22	-	-	mg/kg dw	1.85±0.74	2.04±1.26	7.07±2.14	
			Kidney	21	-	-	mg/kg dw	13.6±8.3	2.45±1.48	9.23±2.29	
			Baleen	21-22	-	-	mg/kg dw	<0.018	0.163±0.070		
Beluga	Saqqaq	2000	Blubber	5	F	245-398 cm	mg/kg ww	<0.005	0.020±0.016	0.100±0.040	
(Delphinapterus leuca	<i>яs</i> )		Epidermis (muktuk)	5	F	245-398 cm	mg/kg ww	0.009±0.009	0.291±0.159	5.67±2.27	
Narwhale	Avanersuaq	1993	Muscle	4	-	-	mg/kg ww	0.374±0.156	1.16±0.15	0.39±0.07	
(Monodon monocero	<i>s</i> )		Liver	1	-	-	mg/kg ww	11.6	7.88	4.49	
			Kidney	1	-	- m	ng/kg ww	75.7	1.20	2.89	

Species	Location	Year	Tissue	n	Sex	Size/age	Unit	Cadmium	Mercury	Selenium	Arsen
	Uummannaq	1993	Muscle	53	-	-	mg/kg ww	0.163±0.160	0.90±0.36	0.34±0.04	
			Liver	53	-	-	mg/kg ww	20.9±17.2	6.49±4.98	3.94±2.03	
			Kidney	52	-	-	mg/kg ww	49.4±24.5	1.40±1.33	2.54±0.82	
		2000	Blubber	5	F	-	mg/kg ww	0.010±0.005	0.017±0.007	0.059±0.007	
			Epidermis (muktuk)	5	F	-	mg/kg ww	0.019±0.015	0.431±0.146	5.26±0.93	
	Kitsissuarsuit	1990	Muscle	3	-	-	mg/kg ww	0.178±0.093	0.64±0.16	0.26±0.03	
			Liver	2	-	-	mg/kg ww	21.6±12.9	3.20±2.08	1.47±0.56	
			Kidney	2	-	-	mg/kg ww	46.2±6.1	1.69±0.35	2.65±0.11	
	Kitsissuarsuit	1994	Muscle	2	-	-	mg/kg ww	0.041±0.040	0.35±0.30	0.30±0.00	
			Liver	2	-	-	mg/kg ww	3.81±4.24	1.41±1.46	1.78±1.34	
Polar bear	lttoqqortoormiit	1999	Muscle	6	-	adult	mg/kg ww	0.022±0.024	0.12±0.06	0.51±0.10	
(Ursus maritimus)			Liver	6	-	adult	mg/kg ww	0.733±0.408	8.20±2.00	4.29±1.09	
			Kidney	6	-	adult	mg/kg ww	20.1±12.1	22.6±14.3	10.5±5.7	
			Hair	6	-	adult	mg/kg dw		4.55±0.69		
	Ittoqqortoormiit	2000	Muscle	6	-	adult	mg/kg ww	0.027±0.014	0.14±0.05	0.50±0.12	
			Liver	6	-	adult	mg/kg ww	1.82±1.03	16.4±5.30	7.51±1.80	
			Kidney	6	-	adult	mg/kg ww	36.7±21.3	29.8±16.6	12.3±5.5	
			Hair	6	-	adult	mg/kg dw	-	5.17±1.22	-	
	Ittoqqortoormiit	2000	Muscle	3-4	-	subadult	mg/kg ww	0.016±0.010	0.089±0.027	0.50±0.03	
			Liver	3-4	-	subadult	mg/kg ww	1.73±0.97	4.02±1.63	2.71±0.85	
			Kidney	3-4	-	subadult	mg/kg ww	23.1±13.6	8.90±3.70	5.29±1.18	
			Hair	3-4	-	subadult	mg/kg dw	-	2.67±0.73	-	
## Appendix B. Organoclorine concentrations (ng/g ww) in Greenland biota obtained in AMAP phase II. Mean • standard deviation.

Species	Location	Year	Tissue	n	Sex	Age. years	Length. cm	% lipid	ΣCBz	НСВ	ΣΗCΗ	ΣCHL	ΣDDT	ΣΡСΒ	ΣΡСΒ10	Labora- torie
Terrestrial																
Ptarmigan	Nuuk	1999	Muscle	5	both	-	-	3.8±0.7	0.22±0.08	-	0.22±0.12	1.66±0.06	0.04±0.02	9.03±4.16	1.76±0.62	NWOC
			Liver	5	both	-	-	6.8±0.5	0.79±0.7	-	0.16±0.03	0.68±0.43	0.69±0.46	18.3±13.7	1.55±1.12	NWOC
Hare	Qeqertarssuaq	1999	Muscle	5	both	-	-	5.4±6.4	0.36±0.2	-	0.05±0.03	0.16±0.09	0.02±0.02	1.55±1.08	0.11±0.08	NWOC
			Liver	5	both	-	-	4.1±0.5	0.22±0.05	-	0.05±0.02	3.14±2.19	0.05±0.06	0.44±0.14	0.1±0.04	NWOC
			Kidney	5	both	-	-	32.5±18.8	2.46±1.65	-	0.46±0.27	0.92±0.67	0.18±0.18	6.09±3.78	0.8±0.76	NWOC
Lamb	Narsaq	1999	Muscle	5	both	-	-	12.3±9.8	0.59±0.32	-	0.08±0.04	0.11±0.05	0.33±0.12	1.19±0.81	0.71±0.39	NWOC
			Liver	5	both	-	-	9.6±2	0.51±0.13	-	0.15±0.16	0.08±0.04	0.4±0.26	5-33±7-45	2.04±1.93	NWOC
			Kidney	5	both	-	-	4.2±0.4	0.21±0.06	-	0.17±0.18	0.03±0.02	0.12±0.06	2.31±1.82	0.51±0.33	NWOC
			Fat	5	both	-	-	90.2±3.1	1.21±0.29	-	0.19±0.20	0.28±0.07	1.2±0.65	7.13±10.9	1.85±0.75	NWOC
Musk ox	Kangerlussuaq	1999	Muscle	5	both	-	-	1.88±0.43	1.97±2.94	-	0.21±0.22	0.33±0.33	0.15±0.19	2.38±2.92	1.06±1.43	NWOC
			Liver	5	both	-	-	10.3±1.8	1.24±0.2	-	0.23±0.24	0.68±0.3	0.11±0.02	2.22±0.44	0.84±0.21	NWOC
			Kidney	5	both	-	-	3.2±0.6	0.43±0.1	-	0.25±0.26	0.1±0.02	0.06±0.04	1.08±0.96	0.4±0.41	NWOC
			Fat	5	both	-	-	85.5±10.7	4.26±0.04	-	0.27±0.28	0.45±0.1	0.38±0.39	3.57±0.59	1.88±0.31	NWOC
Fresh water																
Arctic char	lsortoq	1999	Muscle	9	m	-	44.1±2.8	1.1±1.1	0.33±0.31	0.31±0.28	0.13±0.13	1.5±0.8	1.6±0.8	14±6	1.6±0.5	NWOC
			Muscle	9	f	-	39.9±2.8	1.4±0.8	0.45±0.2	0.42±0.18	0.14±0.08	2.1±0.9	2.1±1.2	16±7	2.7±2.5	NWOC
	Zackenberg	1999	Muscle	2	m	-	45.3±6.0	2.5±0.7	1.29±0.06	1.22±0.04	0.2±0.05	2.3±0.4	1.7±0.4	11±2	4.5±0.9	NWOC
			Muscle	11	f	-	41.7±5.9	2.2±1.4	1.13±0.62	1.06±0.58	0.2±0.12	2.0±1.8	1.5±1.1	6±4	2.5±1.3	NWOC

Species	Location	Year	Tissue	n	Sex	Age. years	Length. cm	% lipid	ΣCBz	НСВ	ΣΗCΗ	ΣCHL	ΣDDT	ΣΡϹΒ	ΣΡϹΒιο	Labora- torie
											_		_			
			Muscle	8	both	-	40.5±2.2	1.0±0.4	0.51±0.18	0.49±0.17	0.06±0.05	2.1±1.0	2.6±1.7	14±9	4.7±3.2	NWOC
	Ittoqqortoormii	t 2000	Muscle	6	m	-	35.0±6.8	2.9±1.4	0.74±0.25	0.65±0.2	0.65±0.5	4.9±4.10	5.3±2.6	23±12	7.7±3.9	NWOC
			Muscle	14	f	-	34.1±8.1	2.4±1.1	0.69±0.26	0.62±0.23	0.43±0.39	4.11±4.12	3.8±2.4	16±8	5.4±2.8	NWOC
Marine																
Blue mussel	Usuk	2000	Soft tissue	1 pool	-	-	-	2.0	-	0.08	0.28	1.1	0.44	0.78	0.64	NERI
Deep sea shrimp	Nuuk	2000	Muscle	11	f			0.9±0.1	0.69±0.70	-	0.06±0.04	0.51±0.11	0.15±0.07	1.7±2.93	0.69±0.87	NWOC
Snow crab	Nuuk	2000	Muscle	5	m			0.7±0.2	0.71±0.72	-	0.48±0.18	0.36±0.16	3.52±0.87	2.15±0.82	1.97±1.34	NWOC
			Liver	5	m			6.0±5.6	0.73±0.74	-	2.36±1.64	5.25±4.46	37.9±46.2	69.5±75.9	41.2±44.8	NWOC
Atlantic cod	Nuuk	2000	Muscle	9	both			0.7±0.1	0.75±0.76	-	0.13±0.07	0.43±0.09	0.6±0.3	3.96±3.27	1.44±1.86	NWOC
			Liver	3	both			57.6±3.8	0.77±0.78	-	15.1±1	65.2±19.9	82.8±18.6	162±24.4	53±8.61	NWOC
	Usuk	2000	Liver	1 pool	m	-	-	34.9	-	18.2	8.3	244	156	178	161	NERI
			Liver	1 pool	f	-	-	43.9	-	20.9	11.1	138	102	120	105	NERI
Redfish	Nuuk	2000	Muscle	5	both	-	-	2.5±1.6	0.92±0.69	-	0.66±0.57	3.45±2.77	4.75±3.96	9.31±6.06	3.17±2.05	NWOC
Atlantic salmon	Nuuk	2000	Muscle	7	both	-	-	11.2±5.6	1.84±0.72	-	3.77±1.9	5.1±2.04	12±3.97	17.9±5.26	5.96±1.71	NWOC
Capelin	Nuuk	2000	Muscle	10	m	-	-	1.8±0.7	0.92±0.25	-	0.45±0.2	3.38±0.68	5.62±1.01	6.12±1.45	1.84±0.41	NWOC
Greenland halibut	Nuuk	2000	Muscle	6	both	-	-	11.2±5.6	1.84±0.72	-	3.77±1.9	5.1±2.04	12±3.97	26.7±17.1	11.5±7.04	NWOC
			Liver	5	both	-	-	33.9±10.2	3.34±3.97	-	44.7±49.9	4.58±1.27	205±286	1147±2165	492±921	NWOC
Starry ray	Usuk	2000	Liver	1 pool	m	-	-	42.0	-	17.2	12.6	101	78	88	80	NERI
Spottet wolffish	Usuk	2000	Liver	1 pool	m	-	-	15.5	-	4.0	4.4	44.4	30	29	26	NERI
Shorthorn sculpin	Usuk	2000	Liver	1 pool	m	-	-	19.1	-	6.1	4.2	84.8	34.3	42.7	39.1	NERI
	Usuk.Igaliko.	2000	Liver	3 pools	f	-	-	17.7	-	9.8±5.7	4.6±1.2	48.9±4.2	41.8±9.5	140.3±159.9	128.5±146.3	NERI
	Qaqortoq			- 1						2 2 .						
	Qeqertarsuaq	1999	Liver	5	m	-	26.4±7.2	19.6±7.0	2.9±1.1	2.5±0.9	5.7±2.0	6.7±2.8	6.1±3.7	10.7±5.4	6.2±3	NWOC
			Liver	15	f	-	31.1±4.9	14.6±4.5	2.8±2.0	2.4±1.7	4.6±2.6	7.9±6.4	6.0±4.4	14.9±11.3	7.4±5.3	NWOC
		2000	Liver	4	m	-	21.6±2.8	9.4±1.3	1.9±0.6	1.7±0.5	2.8±0.3	6.3±5.6	7.1±4.2	52.7±40.5	14.7±8.9	NWOC
			Liver	11	f	-	29.6±4.7	11.1±3.0	3.8±1.2	1.7±0.6	2.9±0.9	3.8±1.2	4.4±1.9	29.0±13.4	8.4±2.9	NWOC

Species	Location	Year	Tissue	n	Sex	Age. years	Length. cm	% lipid	ΣCBz	НСВ	ΣΗϹΗ	ΣCHL	ΣDDT	ΣΡϹΒ	ΣΡСΒ10	Labora- torie
	Ittoqqortoormii	t 1999	Liver	20		-	-	19.3±7.5	12.9±5.5	11.2±4.9	14.2±5.2	49.7±25.9	44.3±23.0	101±41	47±19	NWOC
		2000	Liver	6	m	-	20.9±1.9	23.3±10.5	13.0±5.9	11.0±5.0	14.4±4.8	40.3±17.3	37.9±18.8	137±37	59±15	NWOC
			Liver	13	f	-	24.8±2.5	22.0±6.7	13.1±3.2	10.9±2.8	13.6±3.8	38.1±10.6	40.6±14.2	111±27	46±16	NWOC
Black guillemot	Qeqertarsuaq	2001	Egg	7		-	-	10.3±0.6	-	22.9±4.7	5.6±0.9	37.2±6.4	44.5±9.8	109±23	82.2±17.7	NERI
		1999	Liver	2	m	juvenile	-	4.3±0.1	10.6±5.9 <sup>1</sup>	9.6±5.4	2.2±1.5	15.8±9.3	22.3±2.7	53.6±11.5	22.7±2.6	NERI
			Liver	1	f	juvenile	-	3.9	13.6 <sup>1</sup>	12.2	2.3	17.4	26.1	16.3	44.7	NERI
			Liver	6	m	adult	-	4.9±1.2	17.1±6.4 <sup>1</sup>	15.7±6.0	3.3±1.4	25.9±7.6	37.3±14.3	103±34	50.8±18.4	NERI
			Liver	9	f	adult	-	5.5±0.9	19.7±3.0 <sup>1</sup>	17.6±2.8	3.5±0.6	26.8±3.9	39.9±10.5	135±62	69.5±36.3	NERI
		2000	Liver	9	m	adult	-	6.6±1.8	-	20.6±7.0	3.7±1.3	22.5±6.9	28.3±7.2	45.2±16.4	34.6±12.8	NERI
			Liver	10	f	adult	-	6.0±1.5	-	14.6±6.3	2.8±1.2	16.8±7.2	24.4±9.9	34.3±16.6	27.1±14.3	NERI
Black guillemot	Ittoqqortoormii	t 1999	Egg	10		-	-	9.3±0.6	34.1±5.3 <sup>1</sup>	30.1±4.8	17.3±2.4	60.0±8.9	110±17.0	293±55	153±31	NERI
		2000	Liver	1	m	juvenile	-	5.0	-	9.4	4.1	9.7	12.4	20.9	14.6	NERI
			Liver	2	f	juvenile	-	5.4±3.1	-	10.4±1.9	4.7±1.0	12.7	14.5±0.9	27.1±5.0	17.7±2.0	NERI
			Liver	8	m	adult	-	3.6±1.8	-	20.1±13.1	4.0±3.7	26.9±9.7	47.8±33.3	102±63	64.4±48.0	NERI
			Liver	4	f	adult	-	8.±4.1	-	31.7±19.9	6.9±5.1	71.9±40.3	79.9±47.9	164±106	113±74	NERI
Thick-billed murre	Nuuk	1999	Muscle	19	both	-	-	3.5±0.4	3.95±2.37	-	0.73±0.24	4.97±5.17	6.97±5.22	19.7±11.1	8.42±5.03	NWOC
			Liver	5	both	-	-	5.4±0.7	6.47±2.14	-	0.63±0.17	4.57±1.31	8.11±3.41	20.2±6.1	8.81±2.95	NWOC
Common eider	Nuuk	1999	Muscle	10	both	-	-	3.9±0.8	2.51±0.82	-	0.58±0.21	4.57±0.692	3.84±1.4	23±31.2	12.9±20	NWOC
			Liver	5	both	-	-	5.1±0.3	3.63±0.96	-	0.81±0.23	12.8±5.55	5.78±4.14	25.5±17.7	13.2±11	NWOC
King eider	Nuuk	1999	Muscle	10	both	-	-	3.9±1.2	3.14±1.4	-	1.03±0.38	4.98±1.78	3.89±2.15	14.5±5.55	6.46±2.33	NWOC
			Liver	5	both	-	-	5.2±0.3	4.13±1.79	-	1.28±0.72	16±9.7	5.7±2.66	27.3±10.7	8.71±2.77	NWOC
Kitttiwake	Nuuk	1999	Muscle	9	both	-	-	14.3±5.4	18.8±3.37	-	4.08±0.73	23.9±6.46	30.9±12.1	191±140	98.1±77	NWOC
			Liver	5	both	-	-	6.9±2.3	9.1±4.62	-	1.09±0.67	4.68±4.65	8.31±5.65	125±125	73.8±73.7	NWOC
Ringed seal	Qeqertarsuaq	1999	Blubber	6	m	1.6±1.9	91.7±12.7	92.1±6.1	18.4±7.4	6.9±0.8	83.7±28.4	285±102	528±213	645±254	43±11	NWOCI
			Blubber	4	f	3.5±2.9	96.0±14.3	92.3±3.0	17.8±3.4	8.3±3.4	59.8±19.3	148±49	305±100	403±73	31±5	NWOCI
			Muscle	10	m	1.3±1.4	88.4±10.5	5.3±5.3	1±1.4	0.4±0.5	3.8±6.3	9.3±12.8	17.6±23.9	31±30	2.0±2.1	NWOC

Species	Location	Year	Tissue	n	Sex	Age. years	Length. cm	% lipid	ΣCBz	НСВ	ΣΗϹΗ	ΣCHL	ΣDDT	ΣΡϹΒ	ΣΡϹΒιο	Labora- torie
			Muscle	٩	f	3.4+3.1	95.3+11.2	5.5+8.1	0.6+0.5	0.4+0.6	2.5+3.0	5.0+0.1	9.8+17.1	23+20	1.7+2.2	NWOC
			Liver	2	m	1	81.5+3.5	5.6+0.9	0.5+0.1	0.3+0.1	2.0+0.8	10.7+1.4	10.4+2.9	24+0.4	1.8+0.2	NWOC
			Liver	3	f	1.3+2.0	100.3+13.0	5.4+0.6	0.4+0.2	0.4+0.4	2.3+1.0	8.4+3.0	6.8+2.5	69+61	2.1+0.9	NWOC
			Kidney	2	m	1	81.5±3.5	3.6±0.5	1.1±0.3	0.2±0.1	0.8±0.2	2.0±1.1	2.1±0.3	8±2	0.7±0.2	NWOC
			Kidney	3	f	4.3±2.9	100.3±13.9	3.9±0.5	0.5±0.1	0.3±0.1	0.8±0.2	1.5±0.5	2.2±0.7	12±2	0.6±0	NWOC
		2000	Blubber	14	m	1.3±1.2	94.4±6.5	91.2±2.8	-	8.0±2.1	69.5±21.3	268±101	298±148	237±89	203±79	NERI
			Blubber	6	f	1.0±0	89.7±11.4	92.5±3.0	-	6.3±2.1	59.9±19.0	264±107	301±102	235±79	198±63	NERI
	Avanersuaq	1998	Blubber	13	m	14.9±11. 5	64.0±15.3	87.7±16.2	38.4±20.8	14.4±9.2	136±107	546±539	944±793	1478±1207	894±738	CWSC
			Blubber	14	f	) 15.3±13.2	57.9±12.4	85.8±13.0	24.9±10.9	11.0±3.5	68.1±21.3	187±98	390±225	⊿76±282	269±165	CWSC
	Ittoggortoorm	iit 1999	Blubber	11	m	4.7±2.9	102.6±15.8	101.6±14.0	18.2±13.3	9.1±5.4	108.1±64.1	395±368	671±381	969±828	312±227	NWOCI
	11		Blubber	8	f	4.7±2.6	99.1±20.9	, 100.6±16.3	20.5±10.7	12.4±2.3	97.8±63.3	287±140	598±244	921±470	339±470	NWOCI
			Liver	2	m	6.5±4.9	115.5±2.1	6.6±1.6	1.75±1.12	0.94±0.49	5.1±4.2	34±24.2	47±38.1	111±86	8.4±6.0	NWOC
			Liver	3	f	4	86.0±15.6	5.3±0.8	1.05±0.31	0.61±0.1	2.8±1.1	10.7±1.6	12.6±2.7	35.9±18.3	2.67±1.84	NWOC
			Muscle	11	m	4.7±2.9	102.6±15.8	11.9±10.3	2.87±4.16	1.44±1.57	11.6±19.2	30.9±42.7	42.8±25.7	111±160	8.7±12.7	NWOC
			Muscle	9	f	4.7±2.6	96.7±20.9	12.2±6.9	3.36±2.66	1.99±1.74	11.3±9.0	30.0±22.6	95.0±95.8	181±182	19.2±23.1	NWOC
		2000	Blubber	8	m	4.5±2.3	130.0±13.9	88.1±5.9	-	15.1±7.7	83.6±30.3	558±487	1049±1217	1447±1750	1191±1520	NERI
			Blubber	11	f	4.4±2.4	114.9±16.4	90.0±3.4	-	14.9±6.1	93.1±59.1	461±301	892±304	924±171	719±158	NERI
Walrus	Avanersuaq	1978	Blubber		m	15±3		79.6±14.8	16.6±12.3	0.97±0.68	74.9±52.8	89.1±62.2	60.7±43.2	246±138		NWOC
			Blubber		f	15±4		85.8±5.2	13.3±10	0.74±0.48	60.1±51.2	71.0±60.6	48.2±50.4	189±131		NWOC
		1988	Blubber		m	10±0		86.9±4.7	19.3±5.9	0.92±0.35	109±29	116±45	79.3±48.2	301±99		NWOC
			Blubber		f	10±1		86.3±3.4	20.7±4.4	1.04±0.54	107±20	98.6±38.9	70.4±39.0	244±67		NWOC
	lttoqqortoorm	iit 1989	Blubber		m	18±6		83.7±2.2	56.7±16.7	1.52±0.37	66.7±34.1	744±226	3406±1350	2856±1009		NWOC
Narwhals	Avanersuaq	1984	Blubber	4	f	5.4±4.0	350	97.7±10.9	-	350±316	119±53	559±383	1904±1230	-	766±476	NERI <sup>2</sup>
		1985	Blubber	15	m	5.1±3.3	351±103	89.1±9.2	-	618±293	203±72	919±312	3625±1353	-	1619±578	NERI <sup>2</sup>
			Blubber	7	f	5.2±2.8	350±85	90.6±5.1	-	404±489	139±95	611±564	2169±2173	-	972±893	NERI <sup>2</sup>
		1993	Blubber	1	m	13.0	454	96.6	-	1300	227	2000	3650	-	2114	NERI <sup>2</sup>
			Blubber	3	f	8.7±1.5	390±22	96.0±2.8	-	80±20	68±16	233±101	436±147	-	246±71	NERI <sup>2</sup>
	Balgoni island	1993	Blubber	4	m	3.4±3.9	298±97	95.7±2.5	-	1448±1274	156±36	3250±2778	9720±11742	-	4541±5191	NERI <sup>2</sup>
			Blubber	2	f	4.6±4.9	345±121	96.6±0.6	-	865±1039	150±133	2360±2319	6920±6619	-	2981±2978	NERI <sup>2</sup>

Species	Kitsissuarsuit <b>Location</b>	1990 <b>Year</b>	Blubber <b>Tissue</b>	2 n	m <b>Sex</b>	16.0 <b>Age.</b> years	441±23 Length. cm	96.8±0.5 <b>% lipid</b>	- ΣCBz	830±170 <b>HCB</b>	204±11 ΣΗCΗ	1950±354 <b>ΣCHL</b>	6605±2496 <b>ΣDDT</b>	- ΣΡCΒ	3210±589 <b>ΣΡСΒ10</b>	NERI <sup>2</sup> Labora- torie
								<i>c c</i>		0 (	0.00		0		0 0	
			Blubber	2	m	2.9±0.7	299±19	96.2±4.6	-	835±106	178±88	1010±127	1715±587	-	1187±383	INERI
	Uummannaq	1993	Blubber	33	m	9.7±7.6	385±94	93.1±5.7	-	662±293	179±64	1218±292	3456±1350	-	1536±468	NERI
			Blubber	17	f	6.1±4.5	349±72	93.8±4.0	-	522±537	158±107	1014±942	2264±2443	-	1143±1202	NERI <sup>2</sup>
	Saqqaq	2000	Blubber	3		-	-	78.6±16	462±253	-	128±86	1190±736	1912±1327	3284±1866	991±557	NWOC
Beluga	Saqqaq	2000	Muscle	20	both	-	-	2.3±1	8.2±5.55	-	2.64±1.6	23.6±20.1	29.2±25.2	59.5±46	21.7±17.9	NWOC
Ū.			Liver	5	both	-	-	6.8±3	13.3±7.96	-	2.6±1.22	17.4±8.59	24.1±12.1	55.3±25.2	20.4±8.93	NWOC
			Kidnev	5	both	-	-	4.4±2.2	10.9±9.28	-	2.48±1.99	21.2±19	35.2±36.5	76.7±72.9	26.1±24.3	NWOC
			Blubber	10	both	-	-	87.9+2.4	260+158	-	136+72.2	1203+624	1558+765	2110+1131	1018+483	NWOC
			Skin	5	both	-	-	3.6+0.8	6.76+4.97	-	3.1+1.45	11.7+21.1	57.1+26.5	78.5+42.6	35.4+18.8	NWOC
Minke whale	Davis Strait	1998	Blubber	34	f	juvenile s. adults	683±124	72±10.4	-	81.8±73.9	67.9±58.7	311±261	650±561	2290±2900	-	NWOC
			Blubber	8	m	juvenile s. adults	663±117	73.3±14.8	-	83.3±61.8	73.3±25.6	356±213	732±383	2560±2130	-	NWOC
	West Greenland	1998	Blubber	4	f	juvenile s. adults	795±125	73.4±12.4	-	41.8±32.5	70.0±45.9	408±396	242±173	855±320	-	NWOC
Polar bears	Ittoqqortoormiit	1999/2000	Blubber	9	f	9.4±7.0	-	79.0±11.7	-	32.0±32.7	122±57	667±275	270±61	5708±2315	3552±1383	NWOC
		1999/2000	Blubber	10	m	8.3±6.0	-	80.6±8.6	-	16.8±12.1	219±165	493±213	380±220	5892±2703	3530±1127	NWOC

ΣCBz = NWOC: sum of 1,2 DCB, 1.3 DCB, 1.4 DCB, 1,3,5 TCB, 1,2,4 TCB, 1,2,3 TCB, 1,2,3,4 TTCB, PECB

ΣHCH= all laboratories: sum of α, β, γ - HCH

ΣDDT= NWOC and GWOC: sum of o,p- and p,p- DDE,-DDD,-DDT
NERI: sum of o,p-DDT and p,p-DDE,-DDD,-DDT

ΣCHL= NWOC sum of cis- and trans-chlordane, oxychlordane, cis- and trans-nonachlor, heptachlor, heptachlor epoxide and methoxychlor
GWOC: sum of cis- and trans-chlordane, oxychlordane, cis- and trans-nonachlor, heptachlor, heptachlor, MC1, MC3,MC4, MC5, MC6 and photoheptachlor
NERI: sum of cis- and trans-chlordane, oxychlordane, cis- and trans-chlordane, cis- and trans-chlordane, oxychlordane, cis- and trans-chlordane, cis- and trans-ch

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## Appendix C. Toxaphene concentrations (ng/g ww) in biota from Greenland. Mean $\pm$ standard deviation

	Location	Tissue	Sex	Year	Age,	Length	Laboratory	n	% lipid	Toxaphene	CHB-26	CHB-40	CHB-41	CHB-44	CHB-50	CHB-62
					years	cm										
Terrestria																
Ptarmigan	Nuuk	Muscle	both	1999	-	-	NWOC	5	3.8±0.7	0.69±0.49	<0.02				<0.02	<0.02
		Liver	both	1999	-	-	NWOC	5	6.8±0.5	0.73±0.45	<0.02				<0.02	<0.02
Hare	Qeqertarssuaq	Muscle	both	1999	-	-	NWOC	5	5.4±6.4	0.04±0.04	<0.02				<0.02	<0.02
		Liver	both	1999	-	-	NWOC	5	4.1±0.5	0.48±0.30	<0.02				<0.02	<0.02
		Kidney	both	1999	-	-	NWOC	5	32.5±18.8	2.63±0.08	<0.02				0.01±0.01	<0.02
Lamb	Narsaq	Muscle	both	1999	-	-	NWOC	5	12.3±9.8	<0,1	<0.02				<0.02	<0.02
		Liver	both	1999	-	-	NWOC	5	9.6±2.0	<0,1						
		Kidney	both	1999	-	-	NWOC	5	4.2±0.4	<0,1	<0.02				<0.02	<0.02
		Fat	both	1999	-	-	NWOC	5	90.2±3.1	<0,1	<0.02				<0.02	<0.02
Musk ox	Kangerlussuaq	Muscle	both	1999	-	-	NWOC	5	1.88±0.43	<0,1	<0.02				<0.02	<0.02
		Liver	both	1999	-	-	NWOC	5	10.3±1.8	<0,1	<0.02				<0.02	<0.02
		Kidney	both	1999	-	-	NWOC	5	3.2±0.6	<0,1	<0.02				<0.02	<0.02
		Fat	both	1999	-	-	NWOC	5	85.5±10.7	<0,1	<0.02				<0.02	<0.02
Marine																
Blue mussel	Usuk	Soft tissue	-	2000	-	-	NERI	1 pool	2.0		0.21	0.24	0.05	0.10	0.49	0.21

	Location	Tissue	Sex	Year	Age,	Length	Laboratory	n	% lipid	Toxaphene	CHB-26	CHB-40	CHB-41	CHB-44	CHB-50	CHB-62
					years	cm										
Atlantic cod	Usuk	Liver	m	2000	-	-	NERI	1 pool	34.9		41.4	3.32	4.23	7.57	62.9	23.6
		Liver	f	2000	-	-	NERI	1 pool	43.9		28.4	4.13	3.80	5.32	46.1	19.9
Starry ray	Usuk	Liver	m	2000	-	-	NERI	1 pool	42.0		19.3	4.57	2.45	3.06	29.9	14.0
Spottet wolffish	Usuk	Liver	m	2000	-	-	NERI	1 pool	15.5		8.52	1.32	1.04	1.68	14.5	8.30
Shorthorn sculpin	Usuk	Liver	m	2000	-	-	NERI	1 pool	19.1		8.39	2.15	1.02	1.52	14.2	9.03
·		Liver	f	2000	-	-	NERI	3 pools	17.7		9.58±0.43	1.81±0.62	1.19±0.16	1.57±0.03	15.4±0.3	8.20±1.63
Black guillemot	Qeqertarsuaq	Liver	f	1999	juveni le	-	NERI	1	3.9		3.93	3.87	1.43	2.16	4.05	0.18
		Liver	m	1999	adult	-	NERI	3	4.6±0.4		4.20±1.64	5.68±4.17	0.83±0.3	2.57±0.94	6.18±2.53	0.09±0.10
		Liver	f	1999	adult		NERI	5	5.4±0.7		3.78±1.03	6.07±1.5 9	, 0.93±0.2 4	3.16±1.53	7.33±1.70	0.17±0.14
		Egg		2001	-	-	NERI	7	10.3±0.6		10.3±3.2	, 10.1±2.5	' 2.15±0.42		23.9±5.9	11.4±3.2
		Liver	m	2000	adult	-	NERI	10	6.6±1.8		6.99±2.70	6.48±2.6 4	1.25±0.61	3.87±2.15	8.95±3.73	0.65±0.51
		Liver	f	2000	adult	-	NERI	10	6.0±1.5		4.87±2.56	5.57±2.98	0.96±0.5 8	2.74±2.06	6.86±3.25	0.56±0.71
	Ittoqqortoormi	it Liver	m	2000	juveni le	-	NERI	1	5.0		4.73	3.72	0.80		3.90	0.33
		Liver	f	2000	juveni le	-	NERI	2	5.4±3.1		4.17	3.85	0.73		4.12	0.25
		Liver	m	2000	adult	-	NERI	8	4.0±1.4		10.0±3.8	10.9±4.2	1.90±1.03		8.41±6.54	0.77±0.94
		Liver	f	2000	adult	-	NERI	4	8.7±4.1		15.8±10.6	16.8±7.9	3.15±2.24		25.6±23.8	2.72±3.86
		Egg		1999	-	-	NERI	20	10.9±0.9		19.2±4.2	18.2±2.7	3.32±0.63	6.05±1.23	41.0±7.6	22.0±4.2

	Location	Tissue	Sex	Year	Age, years	Length cm	Laboratory	n	% lipid	Toxaphene	CHB-26	СНВ-40	СНВ-41	СНВ-44	СНВ-50	CHB-62
	Location	Tissue	Sex	Year	Age, years	Length cm	Laboratory	n	% lipid	Toxaphene	CHB-26	CHB-40	CHB-41	CHB-44	CHB-50	CHB-62
Thick-billed murre	Nuuk	Muscle	both	1999	-	-	NWOC	19	3.5±0.4	28.3±13.9	0.02±0.03				0.07±0.06	<0.02
		Liver	both	1999	-	-	NWOC	5	5.4±0.7	53.0±15.1	0.11±0.04				0.16±0.14	<0.02
Common eider	Nuuk	Muscle	both	1999	-	-	NWOC	10	3.9±0.8	13.5±7.5	0.06±0.04				0.21±0.12	<0.02
		Liver	both	1999	-	-	NWOC	5	5.1±0.3	12.4±4.9	0.09±0.04				0.32±0.17	<0.02
King eider	Nuuk	Muscle	both	1999	-	-	NWOC	10	3.9±1.2	8.67±11.2	0.04±0.05				0.19±0.22	<0.02
		Liver	both	1999	-	-	NWOC	5	5.2±0.3	13.5±10.2	0.02±0.03				0.19±0.11	<0.02
Kitttiwake	Nuuk	Muscle	both	1999	-	-	NWOC	9	14.3±5.4	96.4±32.7	0.16±0.33				2.28±2.15	0.10±0.22
		Liver	both	1999	-	-	NWOC	5	6.9±2.3	47.9±23.8	<0.02				0.09±0.10	<0.02
Ringed seal	Qeqertarsuaq	Blubber	both	1999	-	-	NWOC	10		219±81	0.46±0.34				3.63±2.61	1.14±1.87
		Muscle	both	1999	-	-	NWOC	19		8.58±14.5	0.01±0.01				0.09±0.13	<0.02
		Liver	both	1999	-	-	NWOC	5		39.6±12.3	0.00±0.01				0.02±0.02	<0.02
		Kidney	both	1999	-	-	NWOC	5		0.81±0.08	<0.02				0.01±0.01	<0.02
		Blubber	m	2000	1.3	94.4	NERI	14	91.2±2.8		4.99±5.08	1.19±1.06	1.24±1.0 0		4.58±4.67	0.47±0.71
		Blubber	f	2000	1.0	89.7	NERI	6	92.5±3.0		20.8±34.8	1.96±1.34	3.80±2.8 0		19.4±32.6	2.85±3.96
Ringed seals	Ittoqqortoormiit	Blubber	m	2000	4.5	130.0	NERI	11	88.1±5.9		8.92±7.10	1.72±1.20	3.29±2.55		9.07±7.12	3.65±3.14
-		Blubber	f	2000	4.4	114.9	NERI	8	90.0±3.4	41.4±60.1	15.8±26.6	3.36±4.53	4.16±4.3 0		13.6±20.2	4.43±4.90
Walrus	Avanersuaq	Blubber	m	1978	15		NWOC		79.6±14.8	321±95						
	•	Blubber	f	1978	15		NWOC		85.8±5.2	212±89						
		Blubber	m	1988	10		NWOC		86.9±4.7	319±39						
		Blubber	f	1988	10		NWOC		86.3±3.4	314±41						
	Ittoggortoormiit	Blubber	m	1989	18		NWOC		83.7±2.2	1610±305						
Narwhals	Avanersuaq	Blubber	f	1984	5.4	350	NERI+RIVO	4	97.7±10.9	4450±2949						

		Blubber	m	1985	5.1	351	NERI+RIVO	15	89.1±9.2	4967±1725					
	Location	Tissue	Sex	Year	Age,	Length	Laboratory	n	% lipid	Toxaphene	CHB-26	CHB-40	CHB-41	СНВ-44 СНВ-50	CHB-62
					years	cm									
		Blubber	f	1985	5.2	350	NERI+RIVO	7	90.6±5.1	4757±4578					
		Blubber	m	1993	13.0	454	NERI+RIVO	1	96.6	6700					
		Blubber	f	1993	8.7	390	NERI+RIVO	3	96.0±2.8	2033±321					
	Balgoni island	Blubber	m	1993	3.4	298	NERI+RIVO	4	95.7±2.5	8825±3923					
		Blubber	f	1993	4.6	345	NERI+RIVO	2	96.6±0.6	7250±5303					
	Kitsissuarsuit	Blubber	m	1990	16.0	441	NERI+RIVO	2	96.8±0.5	7500±1273					
		Blubber	m	1990	2.9	299	NERI+RIVO	2	96.2±4.6	6800±1556					
	Uummannaq	Blubber	m	1993	9.7	385	NERI+RIVO	33	93.1±5.7	5194±1150					
		Blubber	f	1993	6.1	349	NERI+RIVO	17	93.8±4.0	4024±2332					
Minke whale	west Greenland	Blubber					NWOC			369±531	2.1±6.7			22.6±47.0	6.7±10.4

NWOC= National Water Research Institute, Canada

NERI= National Environmental Research Institute,

Denmark

RIVO=DLO-Netherlands Institute for Fisheries

Research

Walrus data from Muir, D.C.G., E.W. Born, K. Koczansky, G.A. Stern 2000. Temporal and spatial trends of persistent organochlorines in Greenland walrus (*Odobenus rosmarus rosmarus*) Sci. Total Environ.245,1-3: 73-86

## Appendix D. Chlorobenzene concentrations (ng/g ww) in biota from Greenland. Mean $\pm$ standard deviation

	Location	Tissue	Sex	Year	Age,	Length cm	n	% lipid	TeCB	PeCB	НСВ	$\Sigma CBz$
					years							
Terrestria												
Ptarmigan	Nuuk	Muscle	both	1999	-	-	5	3.8±0.7	0.04±0.04	0.01±0.01	0.17±0.09	0.22±0.08
		Liver	both	1999	-	-	5	6.8±0.5	0.42±0.65	0.14±0.04	0.24±0.09	0.80±0.70
Hare	Qeqertarssuaq	Muscle	both	1999	-	-	5	3.8±2.7	0.16±0.16	<0.01	0.39±0.26	0.55±0.23
		Liver	both	1999	-	-	5	4.1±0.5	0.03±0.02	0.01±0.01	7.63±3.13	7.66±3.13
		Kidney	both	1999	-	-	5	32.5±18.8	0.04±0.07	0.13±0.09	7.23±0.82	7.41±0.88
Lamb	Narsaq	Muscle	both	1999	-	-	5	12.3±9.8	0.01±0.00	0.02±0.01	0.14±0.03	0.17±0.04
		Liver	both	1999	-	-	5	9.6±2.0	0.01±0.01	0.01±0.00	0.81±0.71	0.83±0.71
		Kidney	both	1999	-	-	5	4.2±0.4	0.02±0.01	0.01±0.01	0.25±0.11	0.28±0.11
		Fat	both	1999	-	-	5	90.2±3.1	0.01±0.01	0.03±0.01	0.21±0.11	0.24±0.11
Musk ox	Kangerlussuaq	Muscle	both	1999	-	-	5	1.88±0.43	0.02±0.02	0.16±0.34	16.3±3.8	16.5±3.8
		Liver	both	1999	-	-	5	10.3±1.8	0.01±0.01	0.07±0.01	14.4±5.9	14.5±5.9
		Kidney	both	1999	-	-	5	3.2±0.6	0.02±0.01	0.03±0.02	7.3±5.5	7.4±5.5
		Fat	both	1999	-	-	5	85.5±10.7	0.02±0.01	0.22±0.13	0.58±0.79	0.82±0.85
Fresh water												
Arctic char	lsortoq	Muscle	both	1999	-	42.4±3.7	19	1.2±0.9	0.01±0.01	0.02±0.02	0.35±0.24	0.38±0.26

	Location	Tissue	Sex	Year	Age, years	Length cm	n	% lipid	ТеСВ	PeCB	НСВ	$\Sigma CBz$
	Ittoqqortoormiit	Muscle	both	2000	-	34.0±7.6	20	2.5±1.2	0.02±0.02	0.05±0.02	0.63±0.22	0.70±0.25
	Zackenberg	Muscle	both	1999	-	41.6±4.9	20	1.7±1.2	0.01±0.01	0.04±0.04	0.86±0.52	0.91±0.56
Marine	-										-	
Snow crab	Nuuk	Muscle	both	2000	-	-	5	0.7±0.2	0.08±0.04	0.08±0.03	0.32±0.12	0.48±0.18
		Liver	both	2000	-	-	5	6.0±5.6	0.18±0.13	0.36±0.31	2.50±2.40	3.04±2.83
Shrimp	Nuuk	Muscle	both	2000	-	-	11	0.9±0.1	0.53±0.17	0.02±0.01	0.14±0.03	0.69±0.19
Atlantic cod	Nuuk	Muscle	both	2000	-	-	9	0.7±0.1	0.01±0.01	0.03±0.03	0.22±0.06	0.27±0.10
		Liver	both	2000	-	-	3	57.6±3.8	0.46±0.03	1.21±0.08	15.8±2.3	17.5±2.3
Redfish	Nuuk	Muscle	both	2000	-	-	5	2.5±1.6	0.03±0.03	0.07±0.06	0.82±0.61	0.92±0.69
Atlantic salmon	Nuuk	Muscle	both	2000	-	-	7	11.2±5.6	0.10±0.05	0.24±0.09	1.50±0.61	1.84±0.72
Capelin	Nuuk	Muscle	both	2000	-	-	10	1.8±0.7	0.01±0.01	0.08±0.04	0.83±0.21	0.92±0.25
Greenland halibut	Nuuk	Muscle	both	2000	-	-	6	9.9±3.0	0.27±0.08	0.41±0.15	4.04±1.82	4.72±1.96
		Liver	both	2000	-	-	5	33.9±10.2	0.70±0.24	1.73±0.63	42.3±49.6	44.7±49.9
Shorthorn sculpin	Qeqertarsuaq	Liver	М	1999	-	26.4±7.2	5	19.6±7.0	0.12±0.06	0.32±0.13	2.46±0.90	2.90±1.06
		Liver	F	1999	-	31.1±4.9	15	14.6±4.5	0.10±0.07	0.30±0.20	2.43±1.71	2.83±1.97
		Liver	М	2000	-	21.6±2.8	4	9.4±1.3	0.07±0.06	0.21±0.06	1.66±0.50	1.94±0.58
		Liver	F	2000	-	29.6±4.7	11	11.1±3.0	0.08±0.04	0.22±0.08	1.69±0.64	1.99±0.72
	Ittoqqortoormiit	Liver	both	1999	-	-	20	19.3±7.5	0.56±0.27	1.08±0.49	11.2±4.9	12.9±5.5
		Liver	М	2000	-	20.9±1.9	6	23.3±10.5	0.61±0.47	1.33±0.54	11.0±5.0	13.0±5.9
		Liver	F	2000	-	24.8±2.5	13	22.0±6.7	0.86±0.31	1.31±0.33	10.9±2.8	13.1±3.2
Thick-billed murre	Nuuk	Muscle	both	1999	-	-	19	3.5±0.4	0.16±0.07	0.35±0.17	3.44±2.16	3.95±2.37
		Liver	both	1999	-	-	5	5.4±0.7	0.25±0.07	0.51±0.19	5.72±1.90	6.48±2.14
Common eider	Nuuk	Muscle	both	1999	-	-	10	3.9±0.8	0.14±0.06	0.27±0.09	2.10±0.70	2.51±0.82

	Location	Tissue	Sex	Year	Age,	Length cm	n	% lipid	TeCB	PeCB	НСВ	$\Sigma CBz$
					years							
		Liver	both	1999	-	-	5	5.1±0.3	0.17±0.08	0.32±0.06	3.15±0.91	3.64±0.96
King eider	Nuuk	Muscle	both	1999	-	-	10	3.9±1.2	0.16±0.05	0.29±0.12	2.71±1.25	3.15±1.40
		Liver	both	1999	-	-	5	5.2±0.3	0.21±0.08	0.38±0.17	3.54±1.56	4.13±1.79
Kitttiwake	Nuuk	Muscle	both	1999	-	-	9	14.3±5.4	061±0.18	1.65±0.31	1.35±1.59	3.60±1.52
		Liver	both	1999	-	-	5	6.9±2.3	0.24±0.08	0.66±0.34	0.21±0.11	1.11±0.36
Ringed seal	Qeqertarsuaq	Blubber	both	1999	-	-	10	92.2±4.9	1.43±0.53	6.00±5.32	7.43±2.17	14.9±5.6
		Muscle	both	1999	-	-	20	5.4±6.4	0.04±0.14	0.26±0.38	0.45±0.56	0.75±1.00
		Liver	both	1999	-	-	5	5.5±0.6	0.09±0.03	0.19±0.06	0.39±0.26	0.66±0.31
		Kidney	both	1999	-	-	5	3.8±0.5	0.09±0.04	0.09±0.03	0.21±0.11	0.39±0.17
	Ittoqqortoormiit	Muscle	Μ	1999	-	-	11	11.9±10.3	0.29±0.34	1.14±2.38	1.44±1.57	2.87±4.16
		Muscle	F	1999	-	-	9	12.2±6.9	0.49±0.44	0.89±0.68	1.99±1.74	3.37±2.66
		Liver	М	1999	-	-	2	6.6±1.6	0.36±0.30	0.46±0.34	0.94±0.49	1.76±1.12
		Liver	F	1999	-	-	3	5.3±0.8	0.15±0.09	0.29±0.17	0.61±0.10	1.05±0.31
		Blubber	М	1999	-	-	11	101±14	2.60±2.19	6.52±6.87	9.13±5.43	18.2±13.3
		Blubber	F	1999	-	-	8	101±16	2.55±1.89	5.56±2.61	12.4±7.3	20.5±10.7
Narwhale	Saqqaq	Blubber	both	2000	-	-	3	78.6±16.0	3.07±0.48	16.4±8.9	442±244	462±253
Beluga	Saqqaq	Skin	both	2000	-	-	5	3.6±0.8	0.04±0.02	0.25±0.13	6.46±4.86	6.76±4.97
		Muscle	both	2000	-	-	19	2.3±1.0	0.14±0.08	0.60±0.37	6.71±4.19	7.45±4.55
		Liver	both	2000	-	-	5	6.8±3.0	0.17±0.05	0.86±0.43	12.2±7.6	13.3±8.0
		Kidney	both	2000	-	-	5	4.4±2.2	0.21±0.22	1.01±1.16	9.73±7.94	10.9±9.3
		Blubber	both	2000	-	-	10	87.9±2.4	3.69±1.01	21.8±17.9	234±142	260±158

 ${\sf TeCB} = {\sf tetrachlorobenzene}, \ {\sf PeCB} = {\sf pentachlorobenzene}, \ {\sf \SigmaCBz} = {\sf sum of tetra- and pentachlorobenzene and HCB}$