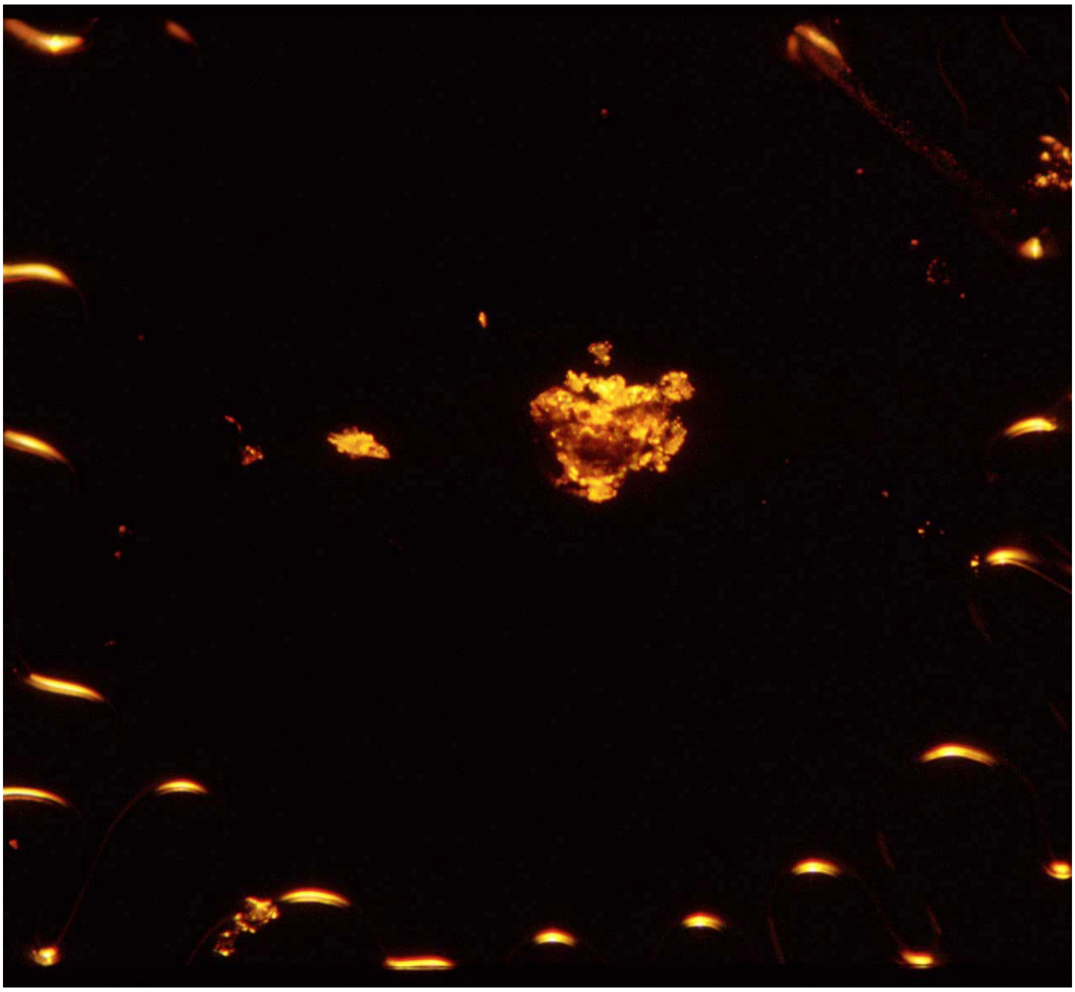
Risø-R-1321(EN)

On Weapons Plutonium in the Arctic Environment (Thule, Greenland)

Mats Eriksson



Risø National Laboratory, Roskilde, Denmark
April 2002

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Abstract

This thesis concerns a nuclear accident that occurred in the Thule (Pituffik) area, NW Greenland in 1968, called the Thule accident. Results are based on different analytical techniques, i.e. gamma spectrometry, alpha spectrometry, ICP-MS, SEM with EDX and different sediment models, i.e. (CRS, CIC). The scope of the thesis is the study of hot particles. Studies on these have shown several interesting features, e.g. that they carry most of the activity dispersed from the accident, moreover, they have been very useful in the determination of the source term for the Thule accident debris.

Paper I, is an overview of the results from the Thule-97 expedition. This paper concerns the marine environment, i.e. water, sediment and benthic animals in the Bylot Sound. The main conclusions are; that plutonium is not transported from the contaminated sediments into the surface water in this shelf sea, the debris has been efficiently buried in the sediment to great depth as a result of biological activity and transfer of plutonium to benthic biota is low.

Paper II, concludes that the resuspension of accident debris on land has been limited and indications were, that americium has a faster transport mechanism from the catchment area to lakes than plutonium and radio lead.

Paper III, is a method description of inventory calculation techniques in sediment with heterogeneous activity concentration, i.e. hot particles are present in the samples. It is concluded that earlier inventory estimates have been under estimated and that the new inventory is about 3.8 kg (10 TBq) of ^{239,240}Pu.

Paper IV, describes hot particle separation/identification techniques using real-time digital image systems. These techniques are much faster than conventionally used auto radiography and give the results in real time.

Paper V, is a study of single isolated hot particles. The most interesting result is that the fission material in the weapons involved in the accident mostly consisted of ^{235}U (about 4 times more in mass than ^{239}Pu). This paper concludes that there are at least two different source terms for the Thule accident debris. Another interesting feature is that it seems like uranium is leaching from the particles faster than plutonium and americium.

This thesis is submitted for the degree of Doctor of Philosophy, Department of Radiation Physics at Lund University, Sweden.

Cover image: Hot Particle from the Thule sediment
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Contents

Preface

This thesis reports the results of a Ph.D study on radionuclides originating from the Thule Accident. The work was carried out in the period from March 1998 to March 2002 as a joint venture between the Radiation Research Department, Risø National Laboratory, Denmark, and Department of Radiation Physics, Lund University, Sweden. The thesis includes and summarizes the five articles outlined below.

I. Dahlgaard H, Eriksson M., Ilus E., Ryan T., McMahon C.A. and Nielsen S.P.:
Plutonium in the marine environment at Thule, NW-Greenland after a nuclear weapons accident
In: "Plutonium in the environment", Ed. Kudo A., Elsevier, Oxford, UK, 15-30, 2001.

II. Eriksson M., Holm E., Roos P. and Dahlgaard H.:
Flux of $^{238,239,240}Pu$*,* ^{241}Am*,* ^{137}Cs *and* ^{210}Pb *to High Arctic Lakes in the Thule District (Greenland)*
Journal of Environmental Radioactivity, submitted (19 pp) 2001.

III. Eriksson M.:
Plutonium Inventory Calculations in Sediments when Hot Particles are Present
Manuscript, (25 pp), 2002.

IV. Eriksson M., Ljunggren K. and Hindorf C.:
Plutonium hot particle separation techniques using real-time digital image systems
Nuclear Instruments and Methods in Physics Research, A, in press (6 pp), 2002.

V. Eriksson M., Roos P., Dahlgaard H., Lindahl P. and Holm E.:
Isotopic ratios in Thule hot particles, source term of the Thule debris
Manuscript, (18 pp), 2002.

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”Tack, ni svenska vakttorn.
Med Plutonium tvingar vi dansken på knä.
Här – Danmark ...
Utskitet av kalk och vatten
Där – Sverige ...
Hugget i Granit ...”

Dr. Stig Helmer (Ernst Hugo Järegård)
i Lars von Triers film *Riget*

To my lovely Pia and Julliana!

1 Introduction

The Thule accident has been studied for over 34 years to date. So, is there more to say, one might ask? The present report gives a somewhat different view than previous conclusions. The differences are partly explained by the use of more sensitive analytical techniques and other methods, giving new knowledge of the radiological conditions in the Thule environment.

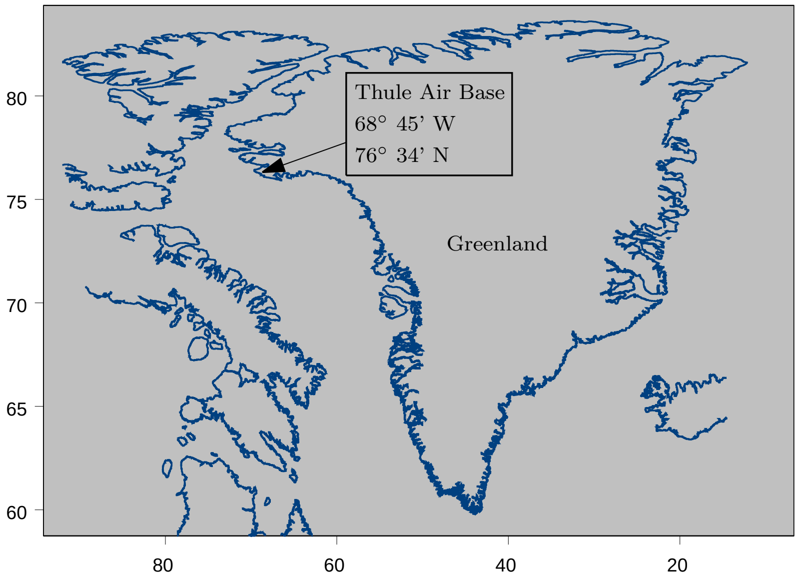


Figure 1. The position of Thule Air Base on Greenland.

Plutonium isotopes have been present in the universe ever since the first supernova occurred, i.e. about 100 000 years after the Big Bang, and have constantly been produced in supernovas since then [1]. When the formation of our planet took place, plutonium was therefore a natural component in the earth material. Today, about 100 amol kg^{-1} ($\sim$ 50 μBq kg^{-1}) of natural ^{239}Pu is left [2] in the earths crust.

Plutonium is also known as a man-made (anthropogenic) element. The first anthropogenic Pu was synthesized by Seaborg, McMillan, Kennedy and Wahl in the end of 1940 by bombardment of uranium with deuterium in a cyclotron [3]. Large amounts of plutonium isotopes are products in the nuclear fuel cycle by neutron capture (Figure 2). As ^{239}Pu has one of the largest neutron cross sections (for fission) of all known nuclides, and as there is an interest in raising the efficiency of nuclear reactors and increasing the power of nuclear weapons, enrichment of this isotope has been of pronounced interest. Different sources of plutonium, e.g. weapons plutonium, nuclear fuel, global fallout, effluents from plutonium reprocessing plants, plutonium powered satellites, have different isotopic ratios which can often be used to identify a specific source of plutonium in the environment. In Table 1 some typical plutonium isotopic ratios from different sources can bee seen.

Table 1. Typical plutonium atomic ratios in different sources. Extracted data from Cooper et al.[4].

Source	^{238}Pu/^{239}Pu	^{240}Pu/^{239}Pu	^{241}Pu/^{239}Pu^a
Weapons grade (Kyshtym accident)	$(3.34 \pm 0.89) \cdot 10^{-5}$	0.0282±0.0001	$(2.31 \pm 0.06) \cdot 10^{-4}$
Fallout from weapons test (Northern Hemisphere)	$(1.77 \pm 0.32) \cdot 10^{-4}$	0.1808±0.0057	$(2.64 \pm 0.20) \cdot 10^{-3}$
Waste from Sellafield	$1.18 \cdot 10^{-3}$	0.1838	0.0116
Bravo Test, Bikini Atoll	$(7.91 \pm 0.92) \cdot 10^{-6}$	0.32±0.03	$(3.8 \pm 0.2) \cdot 10^{-3}$
Chernobyl accident	$3.34 \cdot 10^{-3}$	0.563	0.140
Thule accident^b		0.027–0.057	

^{a}Decay corrected to: 01/01/95

^{b}Data from **Paper I**

The use of anthropogenic plutonium has caused the content in the biosphere to increase about five orders of magnitude compared to the natural level of ^{239}Pu [2]. Dispersion has mainly been from nuclear test programs, nuclear facilities and accidents. The present report concerns one such accident that occurred in NW Greenland in January 1968, called the Thule accident.

The following two sections are a summary of the joint report between American and Danish authorities and scientists, Project Crested Ice [5] (also published as a Risø Report, Risø–R–213).

1.1 The Thule accident

In the cold war period the super powers, USA and the former USSR, were patrolling the air space with aircrafts armed with nuclear weapons. One such aircraft was the U.S. B52 bomber, HOBO 28. On the morning of the 21st of January 1968, HOBO 28 took off on a 24 hour airborne alert mission with 7 crew members. After refueling and crew shift, about 5 hours into the mission, a series of problems started which later resulted in the aircraft crashing.

The temperature in the cabin was too low for the crews comfort, so to raise the temperature, maximum heat on the rheostat was ordered. Soon after, the air temperature was too hot and a decreased temperature of the rheostat was set. At this moment reports of fumes from burning rubber were reported. Soon, a fire was detected and an emergency landing on the Thule Air Base was started, as all attempts to extinguish the fire were unsuccessful. Shortly after the descent began, electrical power was lost and the aircraft became uncontrollable. Orders were given for the crew to bailout, six of them survived.

At 4:39 p.m. (Atlantic standard time) on Sunday the 21st of January, 1968, the aircraft, with 4 thermonuclear weapons on board crashed onto the sea ice of Bylot Sound (also called North Star Bay), about 11 km west of the shore of the Thule Air Base (Pituffik), see Figure 3. The aircraft crashed at a speed higher than 500 knots and at shallow angle. At impact the recently refueled aircraft and the weapons disintegrated in a powerful explosion. The accident was observed as flames on the ice in the polar mid winter darkness at the Thule air base (more than 11 km from the point of impact). The explosion and disintegration of the weapons

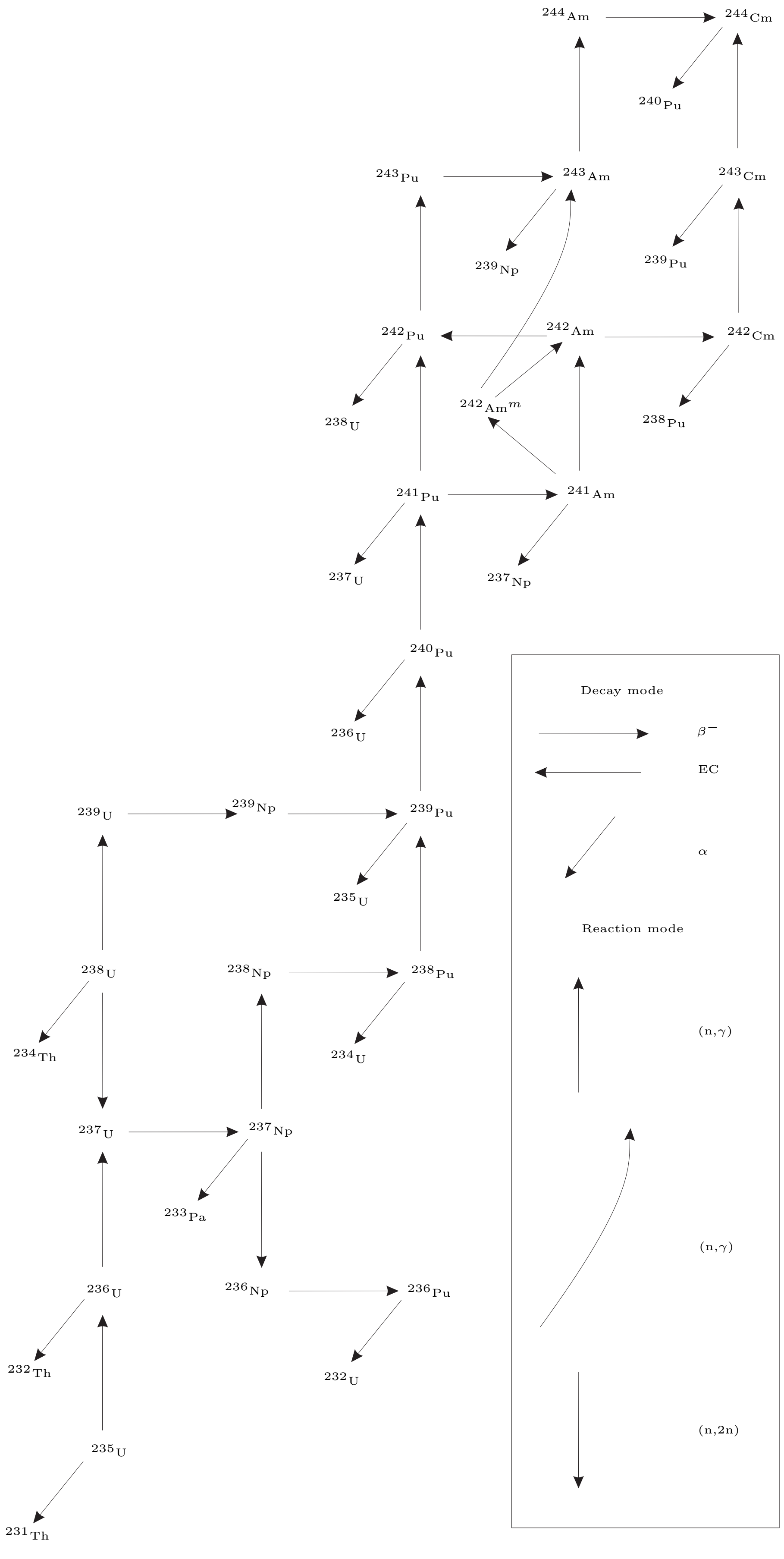


Figure 2. The nuclear fuel cycle of the transuranic element,[6].

did not produce any fission yield. The surroundings of the point of impact were, however, contaminated with fissile material and tritium from the weapons and wreckage of the aircraft. The seabed under the crash site was also contaminated, since the impact broke up about 2500 m^2 of the 60 cm thick ice, were an unknown amount of debris fell to the bottom of the bay. The plutonium contamination was in the form of oxide particles with a log-normal size distribution, with the mean diameter of 2 μm. The official amount of plutonium involved in the accident is 6 kg [7]. A more detailed description of the accident scenario and some information about the early investigations can be found in the report Project Crested Ice [5].

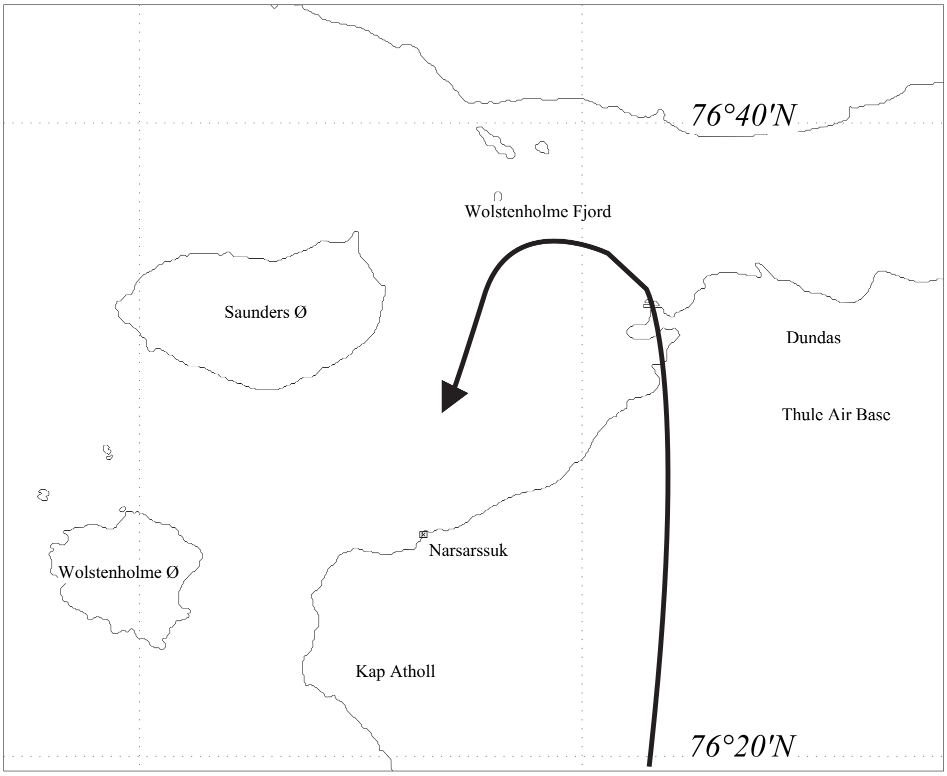
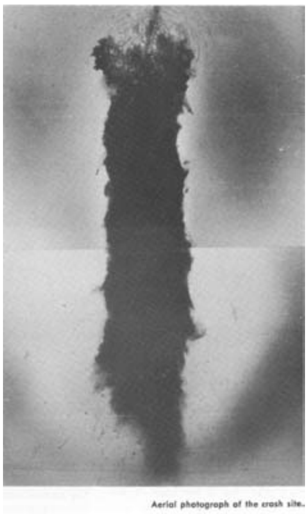


Figure 3. The last flight path of HOBO 28 on the 21th of January, 1968

Considering the political climate at that time, and the fact that a military aircraft with nuclear weapons from a foreign country crashed on Danish territory, it is not surprising if the official information released to the public was biased. Even today, some information on the incident is classified, and in Denmark the subject is infected. In the present report the author will not give any opinions about the political argumentation around the so called "Thule affair". Instead the report tries to give an objective view of the scientific conclusions, mostly derived from the results of the Thule expedition in 1997.

1.2 Project Crested Ice

The Danish and U.S. authorities decided to investigate if there was any radiation hazard to the environment around the Bylot Sound. It was soon clear that the accident occurred without any fission yield of the weapons material. Initial helicopter reconnaissance reported a blackend area approximately 150 × 850 m^2 stretching in a southern direction from the point of impact. The black area was a soot contaminated snow sheet on the ice. It consisted mostly of unburned fuel and,



Aerial photograph of the contaminated ice area. From [5] according to the report Project Crested Ice [5], most of the weapons material was to be found in this area. The first visit to the accident area was performed with dog sledges, as the ice conditions were unknown. Later it was concluded that the ice was strong enough to carry large vehicles, which were used in the clean up operation. The first investigations were performed with gamma and X-ray sensitive detectors; FIDLER (Field Instrument for Detection of Low Energy Radiation), PAC-1S instruments and Geiger-Müller instruments. The FIDLER used a 1/16 inch thick NaI(Tl) crystal with a diameter of 5 inches and the PAC-1S used a zinc sulphide scintillation detector. The investigations were troublesome because of the severe weather in the area. The coldness, -40 – -29°C, made the wires stiff and caused the batteries in the instruments to run out of power quickly and storms prevented occasionally outdoor work. From these investigations a contamination pattern around the point of impact was obtained and it was estimated that about 3.2 kg of Pu was within the blackend area. Ice cores were collected in the area, which were analyzed for alpha activity and results confirmed the first investigation that most of the activity was to be found in the blackend area on the ice.

After the analysis of the first investigations were finished, it was mutually agreed on a joint meeting between American and Danish scientists (15-16 February, 1968) that the radiation hazard was minimal and that, if all of the radioactive material in all of the weapons was allowed to sink into the water, the activity concentration would be well below the maximum concentration allowed for drinking water. It was agreed that, while no serious radiation hazard existed, good "housekeeping" demanded that the area should be cleaned up.

After this meeting the clean up operation started, which was entitled Project Crested Ice. The aim was that all the contaminated black snow sheet and the aircraft wreckage should be removed from the ice and be transported to the USA for disposal. Roads were built so that large vehicles could be used on the ice. Road grader, belt loaders and trucks were used to pile up, load and transport the contaminated debris. On land the debris was unloaded into large, 95 m^3 (25 000 gallon) tanks in an area called the Tank Farm. Project Crested Ice was finalized on Friday the 13th of September 1968, when the last tank was loaded onto a ship for transport to the USA.

Picture taken at the end of Project Crested Ice. From [5]

Several different investigations were performed before, during and after the clean up operation. These are presented in the report Project Crested Ice [5], however, not in detail. The content of the Project Crested Ice report is informational and not construed as directive. For that reason no presentation of the investigations will be given here.

1.3 Radioecological surveys

Soon after the accident it was decided to study the radioecological consequences of the debris from the accident, and to follow the environmental impact over several years [5]. The investigations should include both the terrestrial and marine environments. The marine environment was considered as the most important environment to study, as the inhabitants in the Thule region, the Inuits, mostly live off food collected from the sea, i.e. seal, walrus, white whale, sea bird, fish and bivalve.

The wind vector at the time of the accident was southerly, which would probably give contamination on land close to the Inuit settlement of Narsarssuk. Three days after the accident a easterly storm took place for 24 h with wind gusts up to 45 knots (23 m/s), which probably resuspended some of the contaminated snow to the Saundes Island and Wolstenholme Island. Later, contamination of these places was confirmed [5, 8, 9].

Elevated plutonium air concentrations in the eastern direction from the Thule

Air Base were observed immediately and up to some month after the accident. Since the ^{239,240}Pu/^{90}Sr ratio was higher at Thule than in the other northern sampling stations at that time, it was concluded that this increased concentration was caused by the accident [10, 11]. The air sampling station at Thule is situated about 15 km to the east of the air base and at an altitude of 259 m. Air concentrations and global fallout data for different radionuclides at the Thule station and other northern sampling stations are available from year 1956 in the Environmental Measurement Laboratories (EML) open data base [10]. The increased plutonium air concentrations indicate that the area between the point of impact and the air sampling station (i.e. the Thule Air Base) have been exposed to debris from the accident. No reported investigations from this area are to be found in the literature, unlike for the marine environment where numerus reports and articles can be found.

The Bylot Sound has been visited by marine sampling expeditions 7 times over the past 34 years, i.e. 1968, 1970, 1974, 1979, 1984, 1991 and 1997. These expeditions have been performed during the short arctic summer (August, September) when the Bylot Sound generally has open water. However, the sampling can be difficult and sometimes even prevented by drifting ice passing Bylot Sound occasionally during the summer and severe weather with strong storms. On these expeditions water, sediment and biological samples have been collected and analyzed. The results from the expeditions between 1968–1991 can be found in e.g. [11, 12, 13, 14, 15, 16, 17, 18, 19, 20] and the results from the 1997 expedition are presented, excluding this thesis with enclosed papers, in [21, 22, 23, 24, 25].

1.3.1 Water

In the summer following accident, the average water concentration of ^{239,240}Pu in Bylot Sound was about 0.2 Bq m^{-3} [11, 20], based on about 25 samples collected between the 6th and the 21st of August. This was about twice the concentration measured on samples collected remote from the accident area, i.e. the Bylot Sound water contained about 0.1 Bq m^{-3} excess accidental ^{239,240}Pu. The filtered (1 μm millipore filters) water samples showed that these consisted of dissolved Pu, or at least attached to particles less than the filter pore size. Since the water volume of Bylot Sound is 50 km^3, it was about 5 GBq of excess accidental ^{239,240}Pu half a year after the accident. From 1970, only 3 water samples are reported [12] and the water ^{239,240}Pu concentration were only slightly above the global fallout levels. In all of the following expeditions the surface water samples have been of the same concentration as expected from the global fallout. In the bottom water there has been increased concentration due to the accident. However, the activity has been associated with particles, which most probably have been resuspended from the contaminated sediments.

1.3.2 Sediments

It has been understood that the plutonium contamination of Bylot Sound sediments mostly originates from the unrecovered fraction that was left on the ice after the cleanup operation. It has been estimated that after scraping and removal of snow from the crash area, about 220 g plutonium were not recovered from the ice surface. Additionally, in the refrozen ice (i.e. the area where the ice broke at impact) it has been estimated that about 350 g was contained within the ice [5]. The amount of ^{239,240}Pu injected through the broken up ice to the water has been impossible to estimate, but the first thoughts considered it to be a small amount. In the summer it was observed that the ice from the site of the accident was drifting to the north before melting, implicating that the plutonium contamination should mostly be found in a direction northwards from the point of impact. However, in all of the sediment investigations the highest contamination has been found beneath the point of impact, which can be an indication of that the Pu injected through the broken up ice could be considerable. The estimated inventories between 1968 and 1991 have been about 1 TBq ^{239,240}Pu, i.e. the amount that was not recovered from the ice during the clean up operation.

1.3.3 Biota

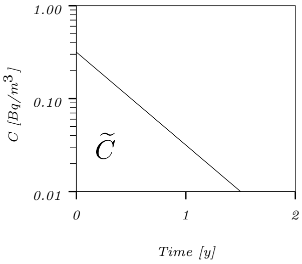
Studies of radioactivity in biota in the Bylot Sound have been used to estimate the absorbed dose commitment from consumption. The absorbed doses from consumption of marine biota from Thule were calculated from environmental analysis of Pu in bivalves, shrimps, fish, seabirds, seals and walrus collected at Thule following the accident. By assuming an annual individual consumption by the Inuits of 5 kg bivalves, 5 kg shrimps, 25 kg fish, 5 kg seabird and 30 kg of seal and walrus from the Bylot Sound the dose commitment from 1968 and 1995 becomes 143 μSv from ^{239,240}Pu and 10 μSv from ^{241}Am [20]. The total committed dose (153 μSv) corresponds to the dose received in about 3 weeks from the local background radiation, i.e. an insignificant dose from a human health point of view.

1.3.4 Some thoughts concerning the early investigations

In the literature there has been no discussion about how much of the Pu activity that has been transported out by water currents during the first 1.5 year after the accident when measurable concentrations were detected. In Bylot Sound the water current is predominantly tidal [5], pumping seawater in and out of the sound. So, by assuming that the whole volume of water in Bylot Sound is exchanged in 1 week (a guess probably near the upper limit) and that the water ^{239,240}Pu concentration in Bylot Sound has decreased exponentially since the accident, it is possible to calculate the amount of ^{239,240}Pu that has left the Bylot Sound with the water. By fitting the accidental excess ^{239,240}Pu water concentration, C = 0.1 Bq m^{-3}, at the time, t = 0.5 year, and C = 0.01 Bq m^{-3} at t = 1.5 year to an exponentially decreasing function, the intercept (initial activity concentration, C_0) and slope (decreasing rate,β) of the curve can be obtained:

$$C(t) = C_0 e^{-\beta t} \tag{1}$$

The coefficients C_0 and β are calculated to 0.32 Bq m^{-3} and 2.3 y^{-1}, respectively. The cumulated ^{239,240}Pu concentration over time, $\widetilde{C}$, is the concentration function, C(t), integrated over time,



$$\widetilde{C} = \int_{t=0}^{1.5y} C_0 e^{-\beta t'} \quad dt' \tag{2}$$

The amount of ^{239,240}Pu that left the Bylot Sound by water transport during the first 1.5 year is the cumulated concentration, $\widetilde{C}$ = 0.13 Bq y m^{-3}, multiplied by the water volume of Bylot Sound, V = $50 \cdot 10^9$ m^3, divided by the exchange time (1/52 y), which equals to 0.35 TBq. This is a rough estimate, and should only be seen as an example.

1.4 Aims of the studies in the present report

The aim of this report was to continue with the study of the Thule accidental plutonium in the marine environment. First transfer to the benthic animals, sedimentation processes and dispersion of the accidental plutonium in the Bylot Sound was studied, based on samples collected at the Thule-97 expedition, **Paper I**. The second aim was to determine if the areas to the east of the accident point have been contaminated by the debris either from close in fallout and/or from resuspended material from contaminated areas, **Paper II**. The third aim was to investigate the hot particle influence of the inventory in sediments of Bylot Sound and to study the dispersion of accidental plutonium from the point of impact, **Paper III**. The fourth aim was to investigate the source term of the Thule accidental debris, by using hot particles as they can be considered to originate from unique sources, **Paper V**. To accomplish this study, a new separation and identification method was developed for plutonium hot particles, **Paper IV**.

2 Methods

2.1 Sampling techniques

2.1.1 Water

In **Paper II** lake water samples are reported which were sampled as follows. Two-hundred litres of filtered surface lake water (filter pore size of 1 μm) were collected for the determination of ^{137}Cs, ^{238,239,240}Pu and ^{241}Am concentrations. ^{137}Cs was collected in two ways. For two of the samples, Cs was absorbed onto copper ferrocyanide ($Cu_2[Fe(CN)_6]$) formed *in situ* upon the addition of $K_4[Fe(CN)_6]$ and $Cu(NO_3)_2$ solutions. The precipitate was collected in plastic carboys for further gamma spectrometric analysis in the laboratory. The other two Cs samples were passed, at a low flow rate (approximately 5 litres per minute), through a copper-ferrocyanide-impregnated cotton wound cartridge filter [26]. In the laboratory the filters were incinerated and prepared for gamma spectrometric analysis. In both these procedures, ^{134}Cs was used as a yield determinant. To determine the possible presence of ^{134}Cs originating from the Chernobyl accident, the ^{134}Cs/^{137}Cs ratio was determined by pumping large volumes of water, more than 900 litres, through a copper-ferrocyanide-impregnated cotton wound cartridge filter. The filters were treated in the way described above.

Plutonium and americium were coprecipitated as hydroxides at $pH > 10$. First the water was acidified with concentrated HCl to a pH of about 2. The precipitation was then achieved by adding sufficient NaOH solution to the sample after adding 100 mg of $FeCl_3$ and about 5 g reducing agent ($Na_2S_2O_5$), together with the chemical yield determinants. As the lake water concentration of free ions was very low, the addition of Ca, Mg and Al ions was necessary to make hydroxide precipitation possible. The precipitates were collected in plastic carboys for further chemical separation and alpha spectrometry in the laboratory. The isotopes ^{242}Pu and ^{243}Am were used as radiochemical yield determinants for Pu and Am.

Surface and near bottom seawater samples were collected during the Thule 97 expedition, which is reported in **Paper I**. The water sampler used had a volume of 130 litres. The samples analysed at Risø were of about 180 litre unfiltered water samples. The determination of Pu was performed as described above, however, without the addition of Ca, Mg and Al ions. Several other seawater samples were collected for speciation of Pu in the water. These methods and results are published elsewhere [21].

2.1.2 Sediment


The sediment corer used in the lake survey.

The lake sediments were sampled by a kayak sediment sampler (HTH corer), with a core diameter of 6.4 cm. The sediment cores were sliced in 1 cm layers, which were stored in plastic bags. On arrival at the home laboratory the wet/dry weight ratio and loss on ignition (LOI) were determined.

Two different sediment corers were used for the marine sediments during the Thule-97 expedition. Most sediment samples were collected with the Finnish Gemini Twin Corer, new version of the Niemisteö Corer, delivering two parallel 8 cm diameter cores. Immediately after sampling, the cores were extruded and sliced, normally in 1 cm slices. In most cases, the same layer from the two cores collected simultaneously were pooled. At many sampling locations, stones hampered sediment coring. At these locations, the HAPS corer, a 13.6 cm diameter steel corer, had a better success rate. HAPS cores without too large stones were divided in 3 cm slices onboard. The samples were stored frozen in plastic boxes. On arrival at the laboratory, the wet weight was determined followed by freeze drying.

2.1.3 Biota

Shrimps and starfish were caught, occasionally, with crab-cages. However, most benthic biota samples were collected by a Sigsbee trawl and a Van-Ween grab. As far as feasible, the sampled biota were allowed to purge in clean surface seawater to reduce the importance of sediments in their guts. The seaweed (*Fucus*) samples were collected from the shore lines of the visited islands by using a Zodiac rubber boat.

2.2 Radiochemical separation techniques

When the radionuclides in the sample cannot be measured directly, it becomes necessary to do a chemical separation. This is the case for all the alpha and most of the beta emitting radionuclides. Firstly, the attenuating material must be separated from the studied nuclide and, secondly, the interfering radionuclides, with similar energy in the spectra must be removed. Separation techniques can also be used if the concentration in a sample is low, but it is then more a question of pre-concentration from a large sample volume. The final step is to prepare a source to the detector used for measurement of the radionuclide. The radiochemical analysis procedures used in the present work, with some modifications, are describe by Talvitie [27] and Holm [28]. The principal of a radiochemical chain is outlined below.

2.2.1 The use of tracers

In the chemical separation procedure some of the radionuclides studied will be lost in the different steps. To be able to determine the chemical yield, a known amount of an isotopic yield determinant (also called tracer) is added to the sample in the beginning of the procedure. At the end, the yield is determined either by radiometrical or gravimetrical methods.

Some radionuclides do not have an isotopic tracer, then a nuclide with similar chemical properties is used instead, i.e. a non-isotopic tracer. It is assumed that this non-isotopic tracer behaves in the same way as the studied radionuclide in all the different separation steps. In Table 2 the yield determinants used in the enclosed papers of this report are listed.

An ideal tracer should only contain one specific nuclide not present in the studied sample. However, often the actinide tracers contain trace amounts of impurities, usually of the same isotope or from the ingrowth from decay of the tracer to other nuclides. For that reason, in the determination of nuclide ratios in a sample, the chemical separation is often processed without any addition of tracers.

Table 2. Examples of chemical yield determinants are listed for different radionuclide separations.

Analyte	Yield determinant
^{137}Cs	^{134}Cs, measured by gamma spectroscopy
^{210}Po	^{208}Po or ^{209}Po, measured by alpha spectroscopy
^{234,235,238}U	^{232}U, measured by alpha spectroscopy
^{234,235,238}U	^{233}U, measured by alpha spectroscopy or mass spectrometry
^{237}Np	^{239}Np, measured by beta counting or gamma spectroscopy
^{237}Np	^{242}Np, measured by alpha spectroscopy or mass spectrometry
^{238,239,240}Pu	^{242}Pu, measured by alpha spectroscopy or mass spectrometry
^{241}Am	^{243}Am, measured by alpha spectroscopy

2.2.2 Sub-sampling

This is a critical step, which the result totally depends upon. Often the total sample is much larger than the amount that can be processed in the chemical separation procedures, or the sample will be used to represent a large area. To take an adequate sub-sample for the whole sample can be difficult, especially if the sample contains so called hot particles. Often the sampling regime are based on the fact that the activity is homogeneously spread in the sample or area, which makes the evaluation of the results easier. In Bylot Sound sediments the activity concentration is very heterogenous, but in the past the sampling has been performed as if the activity concentrations was homogeneous, i.e. small and few sub-samples have been used to represent large areas.

One way to avoid taking an un-representative sample in an area with hot particles is to increase the sub-sample size and/or by taking more aliquots from the samples. However, this can be difficult as there are no good methods describing total dissolution of large sediment samples.

In **Paper III** a gamma screening method for sediments is presented. It is based on that five 1 g aliquots (i.e. the normally used size of aliquots in the earlier investigations) are taken from each sediment slice in a sediment core. Further, if one core is sliced in N slices, 5^{N} permutations (different sets of core combinations) can be derived from one single core. The ^{239,240}Pu is then determined by indirect gamma measurements on ^{241}Am. By a Monte Carlo program, using replacement of the samples, the core inventory distributions were calculated. The advantages with this technique are that the dissolution problem with the hot particles is excluded and it is faster and cheaper than radiochemical determination, resulting in more samples being measured. Finally, the fluctuations in the inventory caused by the heterogenous activity concentration can be observed.

2.2.3 Solubilisation

When the sub samples have been prepared, the separation starts. The dissolution of samples containing radionuclides can be achieved either by leaching or by total dissolution. If the sample is of solid material the procedure usually begins with ashing in an oven. The ashing temperature depends on the nuclide, which is going to be studied. In the ashing procedure the organic compounds are eliminated in the sample. If the nuclide is volatile, wet ashing is preferred to minimize losses. After the ashing, leaching of the nuclides from the sample starts. Leaching is often performed with *Aqua Regia*. This step solubilizes the nuclides from the sample into the solution. In some cases the radionuclide compounds are not "opened up" by *Aqua Regia*, which is the case for refractory Pu-oxide particles . Then stronger regents must be used. An efficient mixture of hydrofluoric and nitric acid can be used to totally dissolve these particles [29]. The results from a small test (HF test) performed to evaluate how effective the *Aqua Regia* leaching technique is to dissolve Pu in Bylot Sound sediment, is presented below.

HF test

The chemical form of plutonium in the Thule debris is PuO_2. This form is known to be difficult to completely dissolve [29]. To investigate the Risø standard method (which is the method described by Talvite [27]) of dissolving plutonium in sediment samples a small test was performed. The test assumed that if any plutonium remained undissolved using the Talvitie method, it would be associated with the residue sediment after the 2 h *Aqua Regia* leaching. In the test the residue was totally dissolved in a mixture of HF and HNO_3 (1:3 ratio). After that, a new amount of tracer was added. The samples used were all low activity samples from Thule sediments, where the activity concentration can be over 3 orders of magnitude higher than the samples analyzed in the test. The maximum amount of Pu left in the residue was calculated from the chemical yield determined for the samples that had been leached with *Aqua Regia*. This amount was subtracted from the Pu activity results of the residue fraction. If the tracer in the first activity determination is equal to that in the sample Pu, then the second result should be of zero activity. The results from these experiments are seen in Figure 4. It can be seen that 8 – 31 % of the plutonium in the samples is missing when using the *Aqua Regia* method. The chemical yields were good for all the results of the *Aqua Regia* method, indicating that a minimum of Pu was lost in the chemical procedure, a conclusion that is incorrect. It is also expected that in high activity samples including hot particles, a larger fraction would be left out, and as a consequence, the activity determination would be underestimated using the *Aqua Regia* method. This is discussed in detail in **Paper III**. For samples from the Thule area, the leaching method should not be used. Preferably a total dissolving technique should be used, such as using a mixture of HF and HNO_3 or an alkaline fusion technique. The HF/HNO_3 dissolution method has been used on the samples presented in **Paper II**, **Paper V** and to some extent in **Paper III**, while in **Paper I** the *Aqua Regia* method was used.

Another efficient method of total dissolution is alkaline fusion [30]. The sample is placed, together with e.g. Na_2O_2/NaOH, in a vessel that is then placed in an oven (temperature around 900° C). The fusion melt is then dissolved in acid.

2.2.4 Concentration

After the dissolution there is a lot of bulk material that is not desired. This bulk material can be solid or liquid residue from the leaching procedure. The solid material is filtered or centrifuged so only the solution is left. Evaporation or pre-

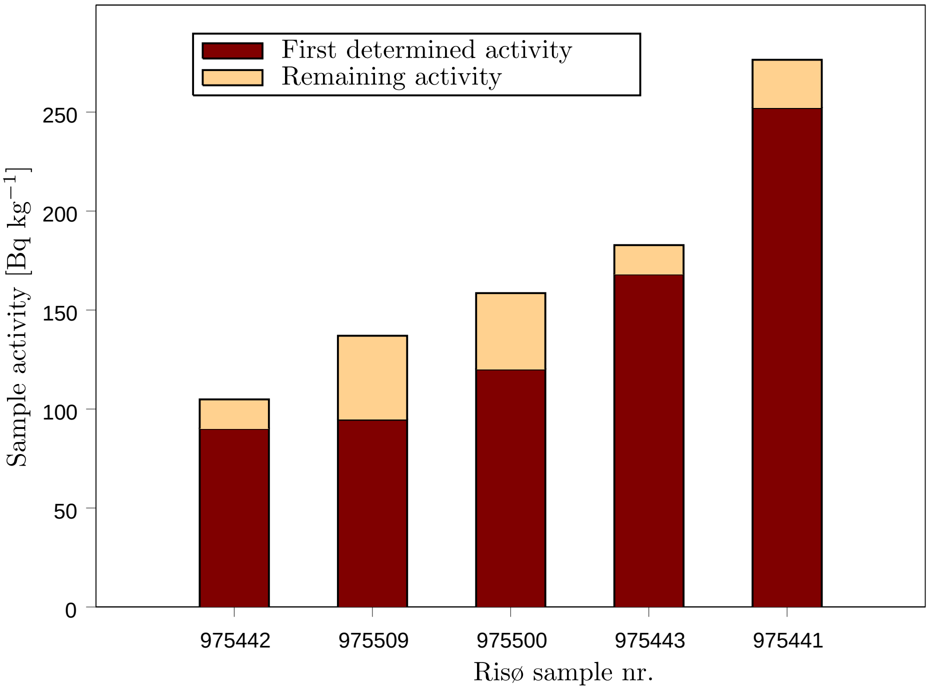


Figure 4. Residual fraction of Pu in Thule sediment samples that have been leached with Aqua Regia.

cipitation is done on the remaining solution. This concentrates the radionuclides, which is necessary for the separation and purification step.

2.2.5 Separation and purification

The first thing to do is to ensure that the radionuclides are in equilibrium with the tracer. This is performed by oxidation and reduction of the nuclides in the solution. In this way the radionuclide and the tracer end up in the same oxidation state, which is important for the subsequent procedures. For gamma emitting radionuclides no further radiochemistry is needed except for source preparation, but for alpha and beta emitters further purification is needed. This is usually done by ion-exchange or solvent extraction methods. One new method that has been introduced to radiochemical separation techniques is extraction chromatography.

Ion-exchange

There are two classes of ion-exchange resins, cation-exchange and anion-exchange. Cation-exchange resins collect cations from the ambient solution and anion-exchange collects anions. Ion-exchange is based on adsorption-desorption on the resin. It consists of small spheres made of organic polymers that have small channels with ionic sites (functional groups) within them. The sample solution is passing through the resin column to permit adsorption of the ions of interest. They are then washed out (eluted) from the resin by a selected solution. The selected solution does only elute the ions of interest. In this way it is possible to separate different radionuclides.

Solvent extraction

Solvent extraction is also referred to as liquid-liquid extraction. The organic solvent contains an organic extractant, most often high molecular amines. This extractant removes the analyte from the aqueous phase and leaves the interfering ions in the aqueous phase. The analyte forms a complex which is more soluble in the organic phase. The purified analyte is then back-extacted from the organic phase into a separate aqueous phase by adjusting the extraction conditions. The separation can also be done the other way around, i.e. the interfering ions are forming an organic soluble complex and leave the analyte in the aqueous phase. Some examples of organic extractants for Pu are thenoyltrifluoroacetone (TTA) and tri-butyl-phosphate (TBP).

Extraction chromatography

Extraction chromatography involves the use of resins of highly selective organic extractants. The resins are used as ion-exchange columns. However, due to the highly selective nature of the extractant much smaller quantities of the resin are needed and smaller volumes of the reagent which decrease the total separation time for the whole radiochemistry procedure. There are resins for some radionuclides, and for separation of americium the two resins CMPO and Aliquat-336 are used [31, 32].

2.2.6 Source preparation

Before alpha and beta measurements, the nuclides are attached to a disc or transferred to a liquid scintillation tube. When measuring the radionuclides in a scintillation device it is straight forward and no further chemical procedure is needed. In the alpha and beta device it is necessary to attach the radionnuclide to a disc. This can be performed using two methods. One of the methods is to precipitate the nuclides and filter the precipitation onto a filter. This filter can then be measured. The resolution is often poor in alpha systems when using this method, but it is sufficient for beta counting. The other principle is to deposit the radionuclides on metal discs by electrolysis [33], which was the technique used on the Pu, Am and U samples in the present report.

2.3 Detection and detection limits

2.3.1 Radiometric methods

In this section a brief explanation of how to measure the most common decay products is given. It is focused on the Alpha decay, Beta minus decay and the Internal conversion. Some disintegrations are followed by more than one radiation quantity, for example gamma-photons and beta-particle in the same disintegration.

Alpha spectroscopy

The most common technique to measure the actinide elements is by alpha spectroscopy. Every isotope has its signature in form of the disintegrating energy emitted from one or several energy levels. Most of the actinides are alpha emitters. By measuring the alpha-particles energy, the signature, the nuclide can be identified and the activity determined in a sample. The detectors used are often solid-state detectors with a good preamplifier and a linear amplifier connected to a pulse analyzer. Ionisation-chambers can also be used for alpha spectrometry. Since the resolution of alpha systems are poor compared to gamma systems using solid state detectors, it is difficult to resolve multiple peaks in the spectra. For example, the two nuclides ^{239}Pu and ^{240}Pu have similar energies and the alpha spectra appear often as one peak. This peak is a composition of five peaks. There are, however, methods to resolve them. One of the methods is by using a deconvolution technique [34, 35, 36, 37]. This technique requires a spectrum with fairly good resolution (FWHM < 20 keV) and a well-known point-spread function of the de-

FWHM, Full Width at Half Maximum

tector system. The point-spread function can either be a theoretically calculated function or a separated mono-energetic peak in the spectra. By deconvolution, it is possible to get information about the contribution of individual peaks to the total peak and thereby also the nuclide activity ratio. This method has been used for instance to determine the source term and composition of the Thule debris [38]. A typical Pu alpha spectrum is seen in Figure 5. This Pu spectrum is from a high active Thule sediment sample.

As a note, measurements of alpha emitting nuclides can also be performed by a liquid scintillation system with a pulse shape analyzer. This device can distinguish between alpha and beta particles, but the technique has rather poor energy resolution so the result gives total alpha activity in the sample [24, 39].

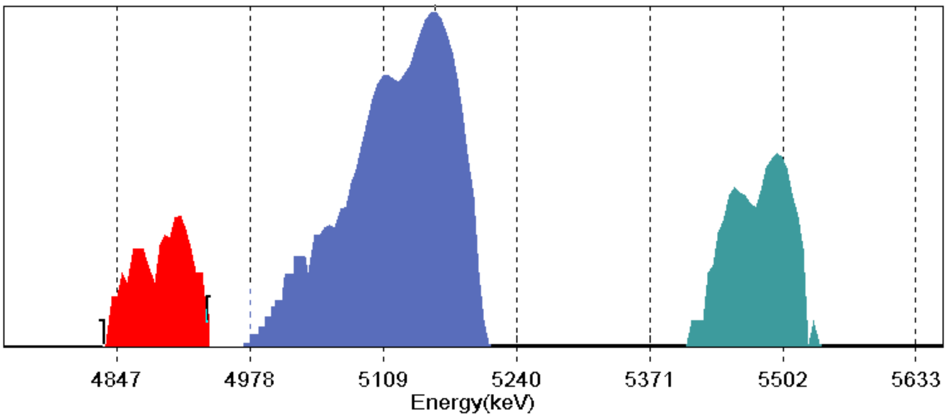


Figure 5. An alpha spectrum (log scale) from a sediment sample taken in the Thule area (Greenland), 1997. This is a Pu-sample including a so called "hot particle". To the left is the tracer ^{242}Pu peak, in the middle is the combined peak from ^{239,240}Pu and to the right is the ^{238}Pu peak.

Gamma spectroscopy

This technique to measure the disintegrating energy is the only method that usually does not need chemical separation before measurement. This is often true, but when the photon energy is low, attenuation in the sample can be significant and makes it difficult to determine the activity of the sample. Low energy photons occur for example from internal conversion decay in form of monoenergetic X-rays. Beta decays often leave the daughter nuclide in an excited mode and in the deexcitation the nucleus sends out a gamma photon. This photon can be measured and the nuclide and the activity in the sample can thereby be determined. The most commonly used detectors are solid-state detectors of the type HPGe and scintillation detectors, often of NaI type. The detectors are connected to amplifiers and a pulse height analyzer. This is the most commonly used technique for determining radionuclides and their activity in a sample. In **Paper III** a well type HPGe detector have been used for measurements on ^{241}Am in sediment samples. The well detector is suitable for measurements on samples when Pu hot particle are present, as the count-rate is less geometrical dependent of the particle position than a planar detector. Gamma spectrometric measurements combined with alpha spectrometry can be used to determine the ^{240}Pu/^{239}Pu ratios by measurements on the L X-ray for the different isotopes. This method is described in [40, 41]

Beta measurements

Some of the radioactive isotopes have no alpha or gamma emission when a disintegration occurs. These nuclides are pure β-particle emitters. The beta decay always includes a neutrino with which the disintegration energy is shared. This results in the beta particle having no discrete energy as for alpha particles and gamma photons. Instead there is a distribution from zero to maximum energy of the disintegrating energy, the so called endpoint energy. This makes it very difficult to distinguish between different beta emitting radionuclides, without doing a chemical separation before the measurements. The measurements are usually performed in a counting system, either by liquid scintillation counter, proportional counter or by a Geiger-Müller tube. ^{241}Pu, ^{99}Tc and ^{90}Sr are examples of nuclides that are radiometrically measured by these techniques.

2.3.2 Indirect measurements of ^{239,240}Pu

When it is difficult or expensive to measure a particular radioactive nuclide, measurements can be performed on the daughter nuclide or a nuclide with known ratio, to determine the activity. In **Paper III**, indirect measurements of ^{239,240}Pu have been performed by measurements of the gamma emitting ^{241}Pu daughter, ^{241}Am. The ^{241}Am samples were absolute calibrated to ^{239,240}Pu by selecting 20 of the 440 measured samples on which Pu radiochemistry were performed. This technique is promising for the Thule area, as the ^{241}Am/^{239,240}Pu activity ratio is still increasing as all of the ^{241}Pu has not decayed. The maximum ^{241}Am/^{239,240}Pu activity ratio has been estimated to take place around year 2035 in the Bylot Sound sediments [15]. This method is cheaper and faster, which means that more and larger samples can be used to determine the activity.

2.3.3 Sediment dating techniques

Sediment is an environmental and historical archive containing information about events and conditions in the past. To determine the chronology of sediments, one has to look for historical markers, such as a single injection of radioisotopes or other well defined events like ash from volcanos. It is, however, possible to use natural radioisotope ^{210}Pb for dating purposes. The purpose of using sedimentation models is often to determine the sedimentation rates and the mass flux in the water. There are basically two models used for lake sediments today, the CIC (Constant Initial Concentration) and the CRS (Constant Rate of Supply) models [42]. In this way it is possible to date a specific sediment slice in the sediment core. For instance, there may occur a peak of a radionuclide or there may be some other indication of an event that is of importance to date. These indications can also be a tool for checking the model if the time of the event is well known. The two models are based on the excess ^{210}Pb in undisturbed sediment and the half-life of this radionuclide. The difference between the two models is that the mass flux may vary in the CRS model while it is constant over the time in the CIC model. The later model (CIC) is hardly used anymore as the assumption of constant mass flux is considered to be incorrect. The CIC model gives the age of a specific sediment slice at a depth, x, as:

$$t = \frac{1}{\lambda} \ln \left(\frac{C_{Pb,0}}{C_{Pb}(x)} \right) \tag{3}$$

where $C_{Pb,0}$ and $C_{Pb}(x)$ are the excess ^{210}Pb activity concentration [Bq kg^{-1}] at the surface and the sediment slice at the depth x.

The CRS model gives the the age of a specific sediment slice at a depth, x, as:

$$t = \frac{1}{\lambda} \ln \left(\frac{A(0)}{A(x)} \right) \tag{4}$$

where A(0) and A(x) are the integrated area activity concentration [Bq m^{-2}] in all slices and below the slice at depth x respectively, i.e.

$$A(0) = \int_0^\infty \delta(x')C_{Pb}(x')dx' \tag{5}$$

and

$$A(x) = \int_x^\infty \delta(x')C_{Pb}(x')dx' \tag{6}$$

The derivation of the above equations can be found in [42].

2.3.4 Hot particle separation technique

In the Thule sediments the fission material from the accidental radioactive debris is, to a great extent, in the form of radioactive hot particles, **Paper III**. Studies on these particles are essential for determination of the physicochemical forms and the source terms, parameters that can be used in deterministic models. In order to study these particles, separation and identification is necessary. This has usually been accomplished by spreading out sediment on a photographic film, i.e. ordinary autoradiography [5, 43, 44]. Another commonly used technique is the so-called CR–39 detector [45, 46, 47, 48, 49, 50] based on etching radioactive induced weakened areas away from a plastic sheet. These two methods are time consuming (exposure time up to 30 days) and both require analysis/visualisation in a microscope.

In **Paper IV** two new methods of separation and identification of hot particles are presented. The initial step is based on gamma measurements of ^{241}Am (hν = 59.54 keV, n$_\gamma$ = 35.9%). The slices of dry powder sediment are screened until a 59.54 keV peak in the gamma spectrum appears. If a signal appears, the sample is split into equal halves and measured again. This procedure is continued until a few sediment grains are left, which equals about 25 sample splittings. The few grains are then attached to an adhesive carbon tape and introduced to the two real time digital images systems being used, the beta camera and the IDE-Bioscope 3250. The beta camera is based on a scintillation technique [51] and the IDE-Bioscope 3250 on a semiconductor detector technique [52]. These techniques are mainly used in nuclear medicine studies. The advantages with these techniques compared to ordinary autoradiography and the CR–39 detector, are that they are much faster (less than 1 day compared to exposure times of up to 1 month) and that they give real time information on a screen, see Figure 6. The beta camera is the most sensitive of these two techniques for the imaging of alpha emitting hot particles, and to produce an image with good statistics, about 15 minutes acquisition time was sufficient for the beta camera compared to some hours for the IDE-Bioscope 3250.

2.3.5 Scanning Electron Microscope, SEM

In **Paper IV** and **Paper V** a 30 kV Philips SEM 515 was used. A scanning electron microscope is most often used for morphological studies of specimens. These images are produced by the low-energetic secondary electrons emitted from the surface of the specimens produced by the scanning electron beam. However, more information can be gained by studying the high-energetic backscattered electrons. These backscattered electrons give information about density differences on the specimen's surface, since high density areas produces more backscatter electrons than low density areas, which then produce a higher signal in the detector. The scanning electron beam also produces characteristic X-ray from the elements on

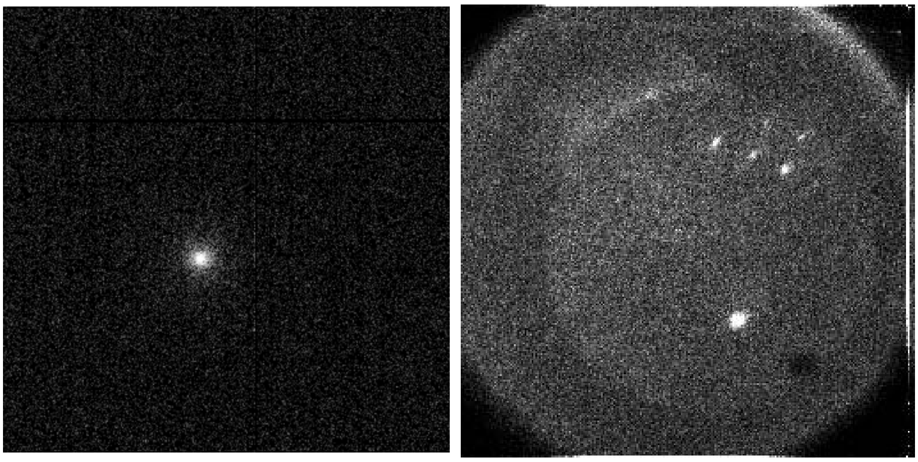


Figure 6. Real-time images of the same particle using two different systems. To the left is the image obtained after 8 hours in the IDE Bioscope, and to the right the image after 1 hour of exposure to the beta camera. The five dots in the beta camera image are the superimposed position system. The distance between the dots is 3 mm. Image from ***Paper IV****.*

the specimen's surface, which can be analysed by an energy dispersive X-ray analyser (EDX). It can, however, be difficult to determine the elemental ratios in the specimens, as, firstly, the cross sections for the same electron energy are different for different elements and the cross sections also differ for different electron shells of the element. Secondly, the fluorescence yield must be taken into account. The elements have different electron binding energies and as the electron beam, during passage into the specimens, will lose energy in collisions, the mean energy of electrons in the beam will decrease as a function of depth. This means that elements with lower Z, and thereby lower binding energies, will produce X-rays in a larger volume than the high Z elements, resulting in the ratio derived from a spectrum being biased. There is a rule of thumb; when dong an elemental ratio estimate using SEM, the mean energy of the electrons in the scanning beam must be three times higher than the binding energies of the element studied [53]. For a Pu/U hot particle, analyzed by a 30 kV scanning electron beam, one could only use the M X-ray lines in the elemental ratio determination. This, since the L_3 shell binding energies are 18.05 keV and 17.17 keV for Pu and U, respectively, i.e. about 2/3 of the mean energy of the scanning beam electrons.

2.3.6 Mass spectrometry

A method that gains more and more popularity in the measurements of actinides is mass spectrometry. Mass spectrometry is more sensitive than alpha spectrometry and is a complement to this method when the sample activity is low and in the determination of isotopic ratios. In general the principle is that the atoms are ionized, accelerated and declined by a magnet and/or passing through an electric field created by a quadrupole lens, whereby the masses are sorted out. The nuclides, sorted by mass, are then counted by a collector. A relatively new mass spectrometry technique, the so called "time of flight", uses the fact that ions of the same charge with different masses and with the same kinetic energy will have different velocities (see Equation 7), i.e. they will reach the collector at different times and thereby mass separation can be accomplished.

$$\vec{\boldsymbol{F}} = q\vec{\boldsymbol{v}} \times \vec{\boldsymbol{B}}$$

$$\vec{\boldsymbol{F}} = q\vec{\boldsymbol{E}}$$

The general physics behind the mass spectrograph is simplified by the equations 7–9.

The energy furnished by the acceleration potential is

$$V \cdot q = \frac{m \cdot v^2}{2} \tag{7}$$

where q and m are the charge and mass of the ion, respectively. When the ion enters the magnetic field, the centripetal force furnished by the magnetic field is

$$\frac{m \cdot v^2}{r} = q \cdot v \cdot B \tag{8}$$

Solving equation 7 and equation 8 simultaneously for m gives

$$m = \frac{r^2 \cdot B^2 \cdot q}{2V} \tag{9}$$

Below is a presentation of the most common techniques in this field. The difference between them is mainly how the device produces the ions that are injected into the accelerating tube.

Thermal Ionization Mass Spectrometer, TIMS
TIMS is a very sensitive mass spectrometer and some configurations can measure femtograms of one element in a sample. It is used to determine isotopic ratios of uranium, but the technique has also started to be used in transuranic studies [54]. After chemical separation the sample is either electrodeposited on the rhenium filament or the solution is loaded on the filament and then dried. The ions are produced when the filament is heated. With this technique most of the isobaric and molecular inteferences are eliminated.

Inductively Coupled Plasma Mass Spectrometer, ICP-MS
With this technique the ions are produced in a microwave tube. In this tube the microwave produces a high temperature plasma of the injected sample. For actinide studies the sample must be prepared by chemical separation to avoid molecular or isobaric interference, which is a problem with this technique. The detection limits are in the order of picogram/milliliter. By applying an ultrasonic nebuliser the limit can go down to femtogram/milliliter. The ultrasonic nebuliser produces a spray of small aerosols that are injected into the microwave tube. Cross flow nebulizers are also commonly used in ICP-MS techniques. In the cross flow nebulizer the argon gas flow also produce a spray of small aerosols but a smaller fraction reaches the plasma. In **Paper V**, two types of ICP-MS machines have been used, one Quadrupole ICP-MS (ELAN 6100) and a high resolution-ICP-MS (PlasmaTrace2).

Accelerator mass spectrometry, AMS
This is the most sensitive device today, and the mass separation is about 1000 times better than the two methods described earlier. The device is a tandem accelerator, working with MeV energies. The ion source can be of different types. Most common is a sputtering source, where a beam of Cs-ions is focused on the sample, resulting in production of multiple charge ions of the nuclide that is studied. The samples are prepared in advance with chemical separations. The technique has hardly any problems with isobaric, isotopic or molecular interference. It is the most expensive method for measuring the nuclides. At some places in the world also transuranic elements are measured with success using this technique [55, 57].

2.4 Statistics

The uncertainty limits reported in the present paper have been determined using the error propagation hypotheses where the standard deviation can be calculated as in equation 10.

$$\sigma_y^2 = \left(\frac{\partial y}{\partial a}\right)^2 \sigma_a^2 + \left(\frac{\partial y}{\partial b}\right)^2 \sigma_b^2 + \left(\frac{\partial y}{\partial c}\right)^2 \sigma_c^2 + ... \qquad (10)$$

where a, b and c are the variables of the determined quantity y (mass, activity or ratio). Typical variables are: sub sample size, tracer concentration, number of counts in the peak, etc. The uncertainty of the isotopic ratios derived from the same spectra only includes the counting statistics, as the ratio is independent of the tracer and sample size. For mean values the standard deviation (SD) and number of samples (n) are reported.

2.4.1 Distribution functions

In **Paper III** the results are given in form of distribution functions. Since the distributions are skew, the standard deviation has less meaning, and for that reason the median value, together with the first and third quartile are presented, i.e. the interval where 50% of the results, centered around the median value, are included.

In **Paper III** there is also a discussion on the particle size distribution reported for the Thule debris [5]. The particle size distribution measured was a log-normal distribution with a standard deviation of 1.7 and a mean diameter of 2 μm. This would result in that a few large particles carry most of the activity. The probability of sampling such large particles in a log-normal particle distribution is very low. This must be considered in the sampling strategy in order to obtain representative samples. In the earlier investigations a few grams of dry sediment in these activity heterogeneous sediments were extrapolated to represent an area from 0.5 km^2 to several square kilometers. The values reported can for that reason not be used for inventory estimates with good credibility.

3 Results and Conclusions

3.1 Source term

To a scientist doing investigations, the source terms are equally important to know as the fingerprints of criminals are for the court of law. By knowledge of the source terms, estimates of the excess amount of one specific source contribution within a sample can be made. The source term is often a ratio of elements that the debris consists of. The Thule debris was soon realized not to contain any fission products as no fission occurred. In the first investigations it was assumed that the Thule debris consisted of one single source, and in the first reports the isotopic ratio of ^{238}Pu/^{239}Pu was used to characterize the debris [5, 11]. Later the nuclides ^{240}Pu, ^{241}Pu and ^{241}Am were included in the characterization [12, 13, 14, 15, 17, 19]. It was, however, assumed that only one unique source term was present in the debris. One investigation in 1997 [38], using a deconvolution technique on alpha spectra derived from five sediment samples from the Thule area, received scattered ^{240}Pu/^{239}Pu activity ratios, leading to the suggestion that more than one unique source is present in the Thule debris. These samples were later, in 1998, measured in a HR-ICP-MS and the isotopic ratios were more or less confirmed [23, 58]. These results started an investigation of several Thule sediment samples to evaluate if there were more than one unique source, or if the 5 samples had been contaminated in the laboratory, not from fallout but rather from hot samples collected in the Mayak area (Russia). About 50 one gram aliquots from sediment samples close to the impact point, i.e. fallout inventory is insignificant, were measured in a HR-ICP-MS instrument. The results indicate that more than one source was present in the debris **Paper I**, [23]. The ^{240}Pu/^{239}Pu ratios were scattered, but the high activity samples were split into two groups, see Figure 7. These results are based on bulk sediment samples which probably contain fractions of all the sources present. It is probable that other elemental and isotopic ratios would vary between different sources. In **Paper I** the correlation between the ^{238}Pu/^{239,240}Pu and ^{241}Am/^{239,240}Pu to the ^{240}Pu/^{239}Pu ratio were examined. There was a weak correlation, which could partly be explained by the fact that the counting statistics of ^{238}Pu for some samples were low and the interference in the peak from ^{228}Th could be of significance. The ^{241}Am/^{239,240}Pu ratio, on the other hand, had scattered ratios partly because the nuclide activity concentrations were sometimes determined from different aliquots, which is a fatal procedure as the activity concentration is heterogenous in the Thule sediments (see discussion below). A report on scattered ^{241}Am/^{239,240}Pu activity ratios in Thule sediments have been presented, in which the suggestion of different sources were addressed [24].

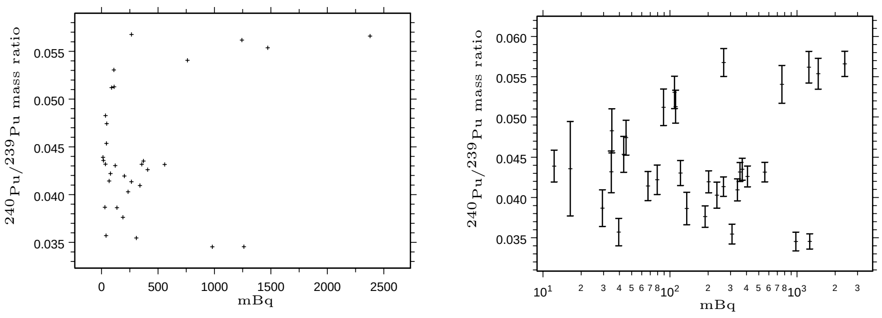


*Figure 7. The two plots show the $^{240}Pu/^{239}Pu$ mass ratio in bulk sediment samples. The two plots consists of the same data and the ratios are plotted against the activity in the sub sample. To the left is a linear scale and to the right a logarithmic scale for the sub sample activity. The mass ratios are grouped in two groups around 0.056 and 0.035. From **Paper V**.*

As mentioned above, the measured ^{238}Pu/^{239,240}Pu ratio was scattered, which can be an indication of different sources. In **Paper V** the ^{238}Pu/^{239,240}Pu ratio was obtained from samples collected during the last three Thule expeditions in 1984, 1991 and 1997. The mean ratio from 328 samples close to the point of impact, i.e. the global fallout plutonium is insignificant, was 0.014 ± 0.004 (decay corrected to 2002). However, by applying certain criteria to the samples studied to ensure that the activity originated from one source, some valuable information was gained. One criteria was that sub-samples with the highest activity would most probably originate from one source. The second criteria was that an abnormal activity concentration peak should appear in the sediment depth profiles. About 20 of the 328 samples satisfied these two criteria. The interesting observation is that none of these samples had the mean ratio of 0.014, instead the ^{238}Pu/^{239,240}Pu activity ratios were grouped around 0.016 and 0.010.

At the time when the results discussed above were reported, limited attention had been paid to hot particles present in the sediments of the Bylot Sound. One optimal procedure to confirm if the debris consists of different sources, would be to study single isolated hot particles, which most probably would originate from one unique source. One such study has been performed in **Paper V** on five particles sampled at different years. It was shown that these hot particles originated form one source, which agreed with one of the two ^{240}Pu/^{239}Pu mass ratios described above (0.0551 ± 0.0008, 1 SD, n = 5). The ^{238}Pu/^{239,240}Pu (0.0161 ± 0.0005, 1 SD, n = 5) and ^{241}Am/^{239,240}Pu (0.169 ± 0.005, 1 SD, n = 5) for these 5 particles also showed almost identical activity ratios which strongly indicates that they are all from the same source. It is interesting that the ^{241}Am/^{239,240}Pu activity ratio is constant even though the particles have been exposed in the sediment for different amounts of time. This indicates that these two elements have not leached from the particles or that they have the same leaching rate. To the date of this report no particles from a most probable second source have been analysed. This can mainly be explained by the fact that the separation method described in **Paper IV** used the daughter nuclide of ^{241}Pu, ^{241}Am. If the none-sampled source contained less ^{241}Pu the probability of detecting these particles would be lower. Moreover, the samples from which the ^{238}Pu/^{239,240}Pu ratio have been determined, indicate that the highest activity samples originate from the source from which the 5 particles originate. This can indicate that the sources have been disintegrated into different particle size distributions and for that reason the analysed particles would originate from the source that disintegrated with the largest size fractions. It cannot be concluded wether these sources originate from different parts of the same weapon or from different weapons.

The first separation and identification of one single hot particle from the Thule sediments was done in late 1997 at Risø. The preliminary results for the SEM studies performed on this particle were presented in 1999 [25]. X-ray spectra from the surface of this particle, derived by the EDX device connected to the SEM, clearly showed that the particle contained uranium. The fact that the Thule debris contained uranium had never been reported before, and came as a surprise. Later, in 2001, a similar observation was reported for a Thule hot particle [44]. In **Paper V** the uranium isotopic ratios are reported. The ^{235}U/$^{235+238}$U mass ratios were in good agreement for all particles, (0.502 ± 0.040, 1 SD, n = 5). This ratio is easily biased by contamination from naturally occurring uranium, which would lower the ratio. However, one of the most interesting results in this thesis is that the mass ratio ^{235}U/^{239}Pu is decreasing with the time that the particles have been present in the sediment, i.e. uranium has a higher dissolution rate than plutonium.

Dissolution of uranium from nuclear fuel have been widely studied. Most of these studies have been performed as laboratory experiments and for that reason it cannot easily be applied to environmental (U,Pu)O_2 hot particles from the Bylot Sound. De Pablo *et al.* [59] has studied uranium dissolution from nuclear fuels in bicarbonate environments. He have derived a dissolution model which explains the bicarbonate promoted oxidative dissolution in three steps:

1. Initial oxidation of the UO_2 surface.
2. Binding of HCO_3^- at the U(VI) sites of the oxidized layer
3. De-attachment of the U(VI)-carbonate surface complex

The model has been applied to spent/unspent fuel with good agreement with experimental results.

Another study has investigated uranium dissolution under oxidized, anoxic and reducing conditions. The dissolution rate has been in the order of a few mg d^{-1} m^{-2} [60]. Applying this dissolution rate to a particle with a diameter of 120 μm (similar size as for a particle collected in a Bylot Sound sediment 1997) would result in that about 1 μg of uranium has left. This is considerably less than observed. The particles are, however, not perfect spheres so the specific surface area is much larger, which would result in that more uranium has left. Also, the dissolution rate might depend on how the (U,Pu)O_2 matrix is produced [29]. Keller lists three main production procedures that form more or less homogeneous (U,Pu)O_2 bindings with some presence of UO_2 and PuO_2 fragments. For that reason, the particles formed at Thule should be treated as site-specific particles and be regarded as a unit of their own. Knowledge on their dissolution and corrosion rates may only be derived from experiments conducted with the very same material.

3.2 Seawater

The plutonium in the debris was in the unsoluble chemical form PuO_2 and the earlier reported data on unfiltered surface water have not detected any significant activity concentrations above the fallout levels [12, 15], confirming that Pu is fixed to the sediment. The first study in Bylot Sound, performed during the summer following the accident, observed higher Pu seawater concentrations, about twice the global fallout level. In near bottom water close to the point of impact, elevated Pu concentrations compared to the fallout level have been observed. Since the analysis have been performed on unfiltered water this has been understood as an effect of that resuspended sediments have been included in the samples, **Paper I**. As the water samples only reflect the concentration of Pu at the sampling dates, bio-indicators such as brown-alga, *Fucus*, can be used to reflect the time integrated water concentration. There have been significantly higher Pu concentrations than the global fallout levels in these [15], indicating that Pu water concentrations could be temporarily elevated, e.g. after storms.

Plutonium speciation in seawater has shown that 43% of the activity from sampling sites near the point of impact was particulate, i.e. resuspended from the contaminated sediments [21]. Plutonium in the dissolved phase was to 68%± 6% (n=6) in the Pu(V-VI) oxidation states. However, it is concluded that the dissolved plutonium has a global fallout origin, as the ^{238}Pu/^{239,240}Pu activity ratio (0.06±0.02) is similar to the global fallout ratio at this latitude ($\sim$ 0.04).

3.3 Sediments

The Bylot Sound sediments, as has been mentioned above, are highly contaminated by fissile material from the accident. To model the fate of this material it is necessary to know the input function, i.e. the total released amount of material which sank to the sea floor in this area. In order to determine the input function, estimates of the total amount of plutonium have been reported [12, 15, 17, 19, 25]. The inventory of ^{239,240}Pu shows a range from 1 to 1.8 TBq. However, these estimates can be considered as underestimates because the sample dissolution method used does not dissolve all the plutonium in the sample (Section 2.2.3), and none representative samples have been used (Section 2.2.2). A weakness in these estimates are that no uncertainty limits of the calculated total inventory can be given, more than guesses. The activity concentrations have been scattered, and replicate aliquots from the same sample have shown differences of up to 2 orders of magnitude and not unusually 1 order of magnitude differences in the ^{239,240}Pu activity concentrations. This is, however, a problem close to the point of impact (within a radius of $\sim$ 10 km). The variation is due to the presence of hot plutonium particles, although they have not been considered to influence the total inventory. For that reason small sub-samples have been used for activity determination in an area with homogeneous activity concentration. Techniques for determining activity concentrations in samples with gamma emitting hot particles have been reported, e.g. [61, 62, 63].

In **Paper III** a comparison is performed between the conventional analytical technique of determining the ^{239,240}Pu activity concentration used on the Thule sediment and a non destructive technique, measuring Pu indirectly, as described earlier. The differences between the two activity determination methods is most pronounced closed to the point of impact where the gamma measurements show higher concentrations. This is explained by that the conventional technique used at Risø do not totaly dissolve the plutonium in the samples and that too few sub-samples in the activity determination were used. The gamma measuring technique used five times more samples than the conventional technique. More sub-samples should, however, be used for the two sites V2 and P as no even inventory distributions were obtained. Instead, the inventory distributions are highly dependent on some hot particles, see Figure 8. At the sampling sites Hnø and C, 6.4 km and 17 km from the point of impact respectively, either of the activity determination methods can be used, while at the sampling site Ny-3 the alpha spectrometric method should be used. One interesting observation is that location P is situated in the same direction as the maximum tidal current (0.4 knots to the south-west), and the particles found at this location were all of similar activity, i.e. around 2 Bq. At location V2 (the point of impact) the dominating particles had considerably higher activity (50 and 153 Bq). This could be an indication of that the tidal current has transported the smaller particles, with low sedimentation velocity in the water column, to greater distances than the lager particles.

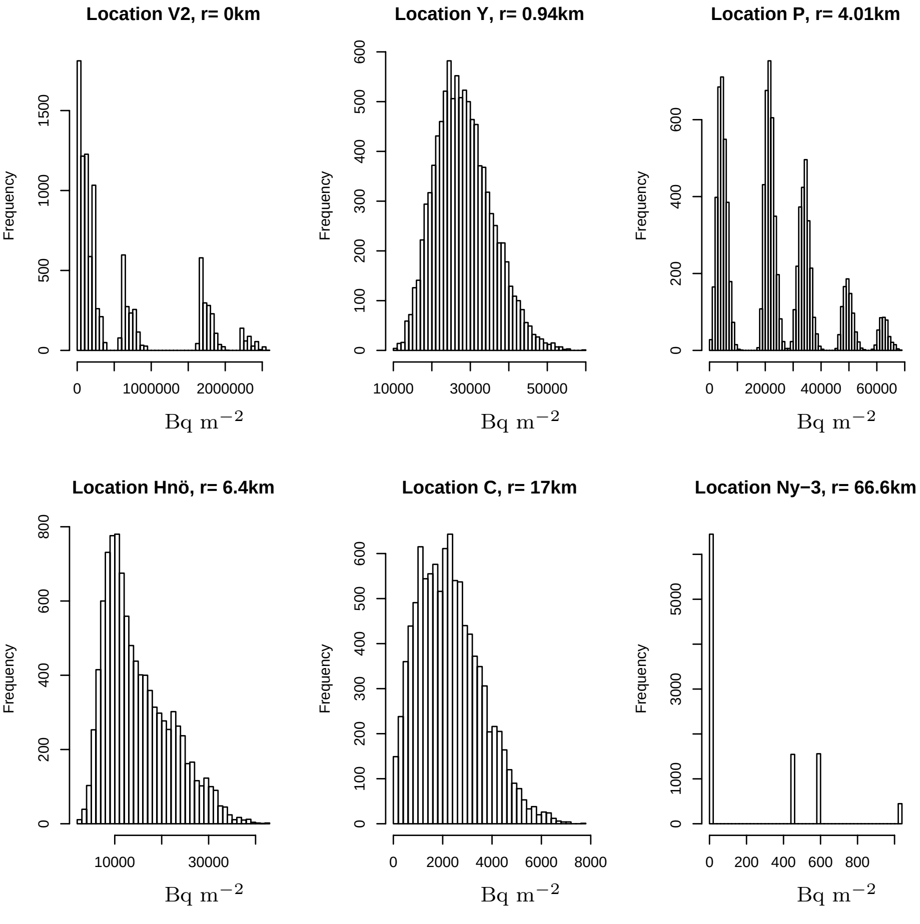


*Figure 8. ^{239,240}Pu inventory distributions calculated from 10 000 sediment core combinations (permutations). It is clear that the distributions for locations V2 and P are highly influenced by hot particles. From **Paper III***

Of the three different fits applied to the conventional determined activity at each location, the bi-exponentially decreasing function resulted in the best fit to the data. The fast component is probably describing the initial dispersion (the debris which went into the water at the accident and also the dispersion of the debris that occurred when the contaminated ice was drifting from the accidental site and melted). The slow component reflects, probably, resuspension of the contaminated sediment in Bylot Sound out to uncontaminated areas. In order to calculate the total accidental Pu inventory in the sediments, integration of the fitted function was performed. The upper integration limit (dispersion distance) was determined from the ^{239,240}Pu/^{137}Cs equalling the global fallout ratio. The estimated dispersion distance determined for samples collected at the Thule-97 expedition is 99.3 km, i.e. the dispersion rate is about 3.4 km y^{-1} (99.3 km/29 y).

The total accidental Pu inventory determined by the conventional method is higher than earlier estimates, 3.9 TBq ^{239,240}Pu compared to about 1–1.7 TBq. This is explained by that in this estimate a high resolution alpha spectroscopic set up was used, enabling accurate activity determination of high activity discs. Secondly, the integration was performed on a lager area, as a bi-exponentially function was used to describe the dispersion. However, the inventory of 3.9 TBq is underestimated, since the radiochemical technique do not totaly dissolve the Pu in the samples and only one 1 g sub-sample have been used in the activity determination. Additionally, at some sampling stations, the sampled sediment core have not been sufficient long, i.e. have not sampled down to zero accidental levels in the sediment. This is the fact for 4 of the 16 sites (see Figure 2 in **Paper I**), all close to the point of impact. The activity concentrations in these cores are almost constant down to a depth of 15–20 cm.

The new total accidental inventory is about 10 TBq (6.7 TBq, 1st quartile, 13.2 TBq 3rd quartile) or about 3.8 kg ^{239,240}Pu derived from the screening investigation in **Paper III**. This might, refereing to the discussion above concerning the sampled core length, be an underestimation. The estimation is based on cores from six sites, and to include more sites would be preferable. Development of this technique should be done and this technique should be used for determining the total inventory in upcoming expeditions.

A consequence of the new estimate must be that a considerable amount of Pu must have entered through the broken up ice at impact, as it was estimated that only about half of a kg was unrecovered from the ice during the decontamination operation.

3.4 Resuspension on land

When the B-52 bomber crashed and exploded on the sea ice of Bylot Sound, a cloud with some of the fissile material rose up in the sky. This cloud drifted south with the wind and contaminated an area around the settlement of Narsarssuk [8, 9]. In air samples collected to the east of the point of impact, elevated plutonium concentrations, probably originating from the accident, were observed [11, 10]. Another land area that was contaminated was the so called "Tank Farm", where the contaminated snow and debris were loaded into large tanks. In **Paper II** a survey in the area east of the Thule air base is reported. The aim was to determine if there was any contamination originating from the Thule accident, either from close-in fallout or from resuspension from other contaminated areas, in this eastern area. The study focused on the undisturbed lake sediments, as they have a well-defined chronology. However, the time resolution, determined by the CRS-model, was too low to separate a possible accidental peak in the sediment depth profile from the global fallout peak [64]. The ^{239,240}Pu/^{137}Cs ratio was in good agreement with the global fallout ratio, so the conclusion was that the contamination was small, if any at all.

3.5 Biota

The Bylot Sound has a rich animal life with a food web that includes, in the lower parts of the food chain, plankton and benthic biota, through fish, seabirds, seals, walrus, whales up to the top predator of the food chain, the Inuits. In the sediments of Bylot Sound the biomass of benthic biota is high, about 450 g m^{-2}, including over 150 species of lower animals [65]. The main concern has been to study if there is a bio-magnification of Pu from the sediments up through the food chain causing a radiation hazard for native Inuits in the Thule area. Earlier investigations showed that transfer of plutonium to higher trophic levels was very small, that no bio-magnification has occurred [11, 12, 14, 15] and that no radiation hazard from food to native people exists. The highest Pu levels were found in benthic species feeding on sediment. The Pu concentrations in these species were about 1–2 orders of magnitude lower than the concentrations in the sediment, **Paper I**, which was a confirmation of earlier studies [11, 12, 13, 14, 15, 17]. It has also been observed that ^{241}Am had a higher concentration ratio to the biota than ^{239,240}Pu. However, the reported concentration ratios, CR, (Bq kg^{-1}_{biota}/Bq $\mathrm{kg}^{-1}_{sediment}$) are probably overestimated since the sediment concentrations are underestimated due to exclusion of hot particles, as described above.

4 Concluding Remarks and Future Research

I think it is sad that still after 33 years, such information as the source term and the amount of debris dispersed in the accident is classified, as this information is essential for all model work and predictions. If this information was available the Thule area could be a very interesting experimental area where a lot of valuable knowledge could be gained. Instead, today, the area is a sad memory of the cold war era and an accident where limited knowledge has been gained.

However, in my opinion, some future subjects to focus on in the Thule area could be to continue the study of hot particles. First of all these studies could provide an answer to the source term question. When such a determination is done, the inventory can be estimated more easily and cheaply. This would also mean that the resuspension rate/translocation of the sediment in Bylot Sound to uncontaminated areas could be determined.

Another interesting subject to study would be the particle surface chemistry (i.e. oxidation state on surface in synchrotron radiation facilities using the XPS-technique) so solubility conditions could be determined. Experimental studies of the isotopic ratios in the interstitial sediment water and bottom water could show if corrosion of the transuranic elements in the Thule debris is of importance.

Investigations of radioactive particle transport through the ice have not been reported. However, this could also be a subject of importance, as it took over a month between the accident and the removal of contaminated snow on the ice. As the evaluation of the effect of the decontamination operation was performed with gamma and X-ray detectors, the result could easily be biased by the fact that ice was attenuating the radiation from activity in the ice. As an example the 59.54 keV radiation intensity from ^{241}Am is attenuated to 50% if the activity is situated at a depth of 3.9 cm in the ice. An evaluation of hot particle transport in ice could give some interesting information.

My hope is that this report has highlighted some interesting subjects that can be studied in further research in the Thule area, and that a more accurate source term has been provided. One can say, with some help from Churchill: This is not the end of the investigation of the Thule accident, it is not even the beginning of the end, but perhaps it is the end of the beginning, and the start of some very interesting science.

To be a scientist is to have doubts about everything and to have a childs curiosity of the unknown. If not, you are a scientific marionette.

Best Regards, Mats Eriksson

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Paper I

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Plutonium in the marine environment at Thule,
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PLUTONIUM IN THE ENVIRONMENT
A. Kudo (Editor)

Plutonium in the marine environment at Thule, NW-Greenland after a nuclear weapons accident

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Abstract

In January 1968, a B52 plane carrying 4 nuclear weapons crashed on the sea ice ~12 km from the Thule Air Base, in northwest Greenland. The benthic marine environment in the 180–230 m deep Bylot Sound was then contaminated with ~1.4 TBq ^{239,240}Pu (~0.5 kg).

The site was revisited in August 1997, 29 years after the accident. Water and brown algae data indicate that plutonium is not transported from the contaminated sediments into the surface waters in significant quantities. Sediment core data only indicate minor translocation of plutonium from the accident to the area outside Bylot Sound. The present data support an earlier quantification of the sedimentation rate as 2–4 mm per year, i.e. 5–12 cm during the 29 years since the accident. Biological activity has mixed accident plutonium much deeper down, to 20–30 cm, and the 5–12 cm new sediment has been efficiently mixed into the contaminated layer. In addition to the classical bioturbation mixing the upper ≈5 cm, the plutonium data indicate the existence of a deeper bioturbation gradually decreasing with depth. Transfer of plutonium to benthic biota is low leading to 1–2 orders of magnitude lower concentrations in biota than in sediments. Some biota groups show a somewhat higher uptake of americium than of plutonium.

Sediment samples with weapons plutonium from the accident show a significant variation in ^{240}Pu/^{239}Pu atom ratios in the range 0.027–0.057. This supports the hypothesis that the Thule plutonium originates from at least two sources of different quality. The radioecological implication of the observed variations is that the use of plutonium isotope ratios in quantitatively determining the influence of different plutonium sources is a very complex affair requiring substantial data sets.

Keywords: Environmental radioactivity; Plutonium; Americium; Isotope ratios; Nuclear weapons; Accident; Arctic; Greenland; Marine environment; Marine sediments; Marine biota; Transfer factors; Excess Pb-210; Sedimentation rate; Bioturbation

Introduction

In January 1968, a B52 plane from the US Strategic Air Command caught fire and crashed on the sea ice in Bylot Sound ~12 km from the Thule Air Base, Northwest Greenland. The plane carried 4 nuclear weapons. Part of the weapons plutonium was distributed over some square kilometres of the ice in the explosive fire that followed. Plutonium-contaminated ice was recovered with large machines and shipped back to the US, as was the plutonium-contaminated wreck. The underlying sea sediments received a fraction of the weapons plutonium when the sea ice melted the following summer and probably also during the accident, as the impact caused part of the ice to break up (U.S. Air Force, 1970).

It has been estimated from earlier sample collections (1968, 1970, 1974, 1979, 1984, 1991) (Aarkrog, 1971, 1977; Aarkrog et al., 1981, 1984, 1987, 1988, 1997) that the pollution remaining in the seabed in Bylot Sound by 1968 amounted to approximately 1.4 TBq ^{239,240}Pu (~0.5 kg), 0.025 TBq ^{238}Pu, 4.6 TBq ^{241}Pu and 0.07 TBq ^{241}Am.

The Thule Air Base is located at 76°30′N in NW Greenland (Fig. 1) near the former main living area for the Thule culture, an indigenous Inuit society surviving mainly through hunting marine mammals and birds. The main part of the Inuit population was forced to move further north, to Qaanaq, in 1953, because of intensified 'cold war' base operations. However, they still use the area for hunting marine mammals and birds and as a residence area for a small part of the population. The rich marine benthic fauna, the basis for the important walrus population, was intensively studied in 1939–1941 (Vibe, 1950). Selected data from the Thule-1997 sampling have been given at recent conferences (Dahlgaard et al., 1999a, b; Eriksson et al., 1999; McMahon et al., 2000).

Materials and methods

In August 1997 we took a new set of marine samples from the contaminated area in Bylot Sound as well as background samples from the Greenland west coast. The sampling was performed onboard the Greenland fisheries investigation vessel 'Adolf Jensen' and was focused on water, sediments and biota. Two different sediment corers were used. Most samples were taken with a Finnish 'Gemini Twin Corer' delivering two parallel 8-cm diameter cores. Immediately after sampling, the cores were extruded and sliced with sophisticated sectioning equipment — normally in 1 cm slices. An earlier version of the Gemini Corer, the Niemistö Corer, has been described in the literature (Niemistö, 1974). The Niemistö Corer only takes single cores, but the slicing equipment is similar. In most cases, the same layers from the two cores taken simultaneously were pooled. At many locations, stones hampered sediment coring. In these cases, the 'HAPS' corer (Kanneworff & Nicolaisen, 1973), a 13.6 cm diameter steel corer used during earlier sampling cruises, had a better success rate. HAPS cores without too large stones were divided in 3-cm slices onboard. Longline fishing — aiming at halibut and other large fish — with 4500 squid-baited hooks distributed at 3 locations overnight was unsuccessful. Some shrimp and starfish were caught with baited crab-cages. Most benthic biota samples were taken by

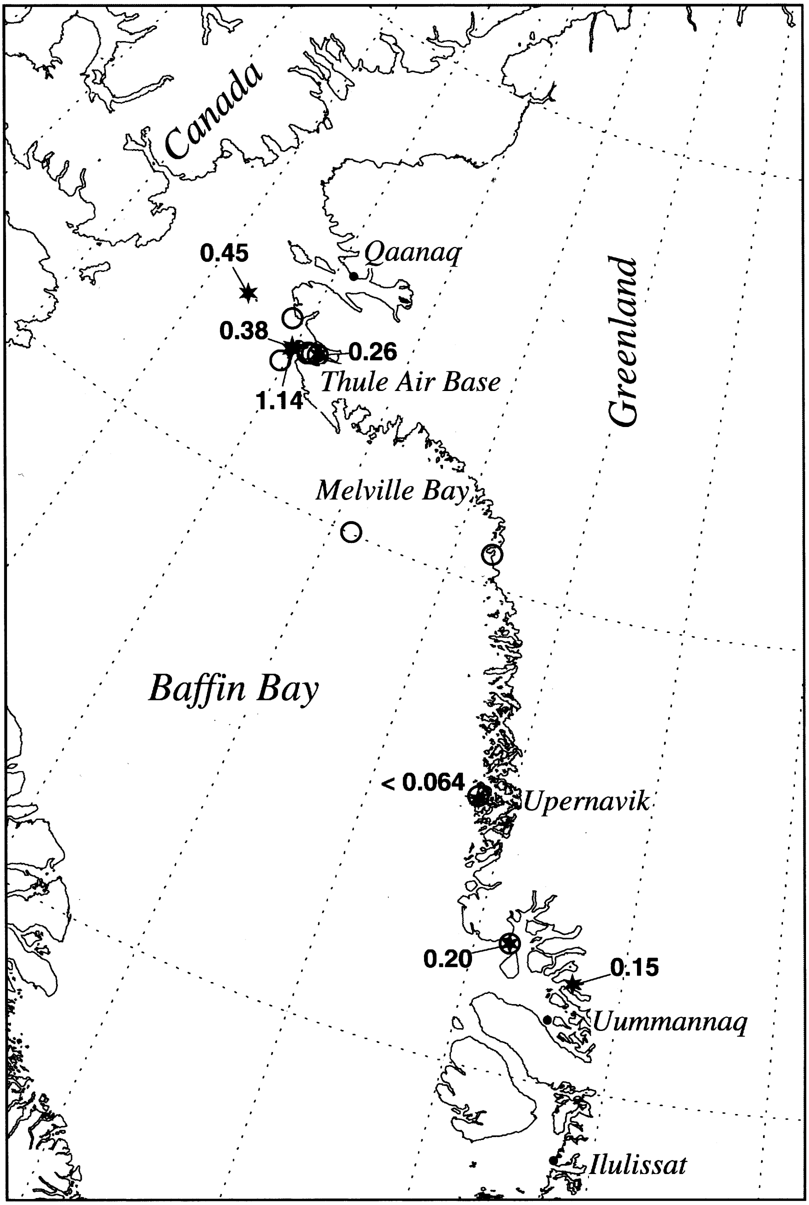

Fig. 1. Thule 1997. Map of NW Greenland with sampling locations for seawater (O) and seaweed (✱). Numbers are concentration of ^{239,240}Pu, Bq kg^{-1} dry, in Fucus (brown algae).

a Sigsbee trawl and a Van-Ween grab. As far as feasible, the sampled biota were allowed to purge in clean surface seawater to reduce the importance of sediments in their guts.

Plutonium and americium was analysed by alpha-spectrometry after radiochemical separation and electrolysis on stainless steel discs (Talvitie, 1971; Holm, 1984). For sediment samples, analyses were performed on 1 g aliquots except for background samples taken outside Bylot Sound, where 5 g aliquots were used. For biota, up to 10 g dry weight aliquots or the whole sample was used. Pb-210 was analysed by (HP)Ge semiconductor gamma-spectrometry on 10–15 g aliquots. All data referred to here are excess ^{210}Pb calculated by subtracting the *in-situ* supported ^{210}Pb level based on ^{226}Ra calculated from the same gamma spectrum.

Results and discussion

Plutonium in water and seaweed

The concentrations of ^{239,240}Pu in *Fucus disticus* (a brown alga) around Thule and 750 km south near Uummannaq are given in Fig. 1. The source of most of this plutonium is global fallout. One of the samples taken near the accident site had a slightly higher concentration than the other samples, 1.14 Bq kg^{-1} dry weight.

With the exception of a near-bottom water sample taken at the point of impact which shows a total concentration of 30 mBq ^{239,240}Pu m^{-3}, 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) 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 ^{239,240}Pu m^{-3} unfiltered surface water (Fig. 2).

The water and brown algae data thus indicate that plutonium from the contaminated sediments is not transported into surface waters in significant quantities. Plutonium speciation in water has been reported elsewhere (McMahon et al., 2000).

Sediments

Examples of ^{239,240}Pu and excess ^{210}Pb concentration profiles versus sediment depth are given for two contaminated sediment cores, locations 20 and P (Fig. 3). An apparent exponential decrease in concentration with depth is observed for both excess ^{210}Pb and ^{239,240}Pu. A set of further plutonium sediment profiles is given in Fig. 4 — for contaminated cores from Bylot Sound as well as for assumed background cores taken outside Bylot Sound (ny-3, 1410 and Schades Øer). In all cases, plutonium seems to be well mixed in the upper 3–5 cm sediment layers. In the first 8 examples in Fig. 4, the 1968 plutonium pulse then shows gradual decreasing activity concentrations, down to 20–30 cm sediment depth in some cases. However, in some of the cores, a uniform contamination level was seen throughout the whole column. This indicates that in these cases the corer has not managed to penetrate the sediment sufficiently deeply to account for the total contamination and furthermore that some of the cores are from sediments that may have undergone atypical mixing. Many explanations could be given for this, e.g. penetration in

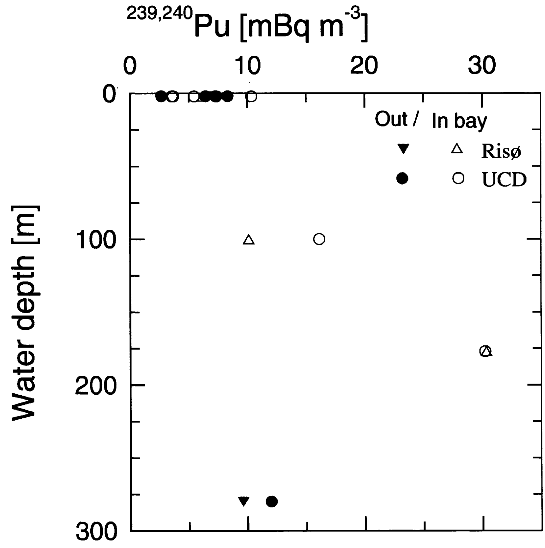

Fig. 2. Thule-1997. Plutonium concentration in water, mBq ^{239,240}Pu m^{-3}, measured in Bylot Sound (△, ○) and outside the Sound (▼, ●). Data measured at Risø (▼, △) are on unfiltered water. UCD data (●, ○) (McMahon et al., 2000) are filtered and either 10% or the actually measured particulate fraction is added.

an area where previous trawling or dredging has disturbed the layering or maybe the effects of sediments sliding along submarine slopes.

It should be noted that the concentration axis in Figs 3, 4 is logarithmic. In spite of this, the large variation of observed plutonium concentrations is obvious. This is caused by hot particles. In several cases reanalysing a second aliquot, where orders of magnitude differences are sometimes observed, supports this. In an ongoing study, the frequency and the analysis of these hot particles is being further studied.

If the deeper part of the high-concentration layer is assumed to correspond with the accident in 1968, 29 years before the sampling, a sedimentation of 5–12 cm, i.e. 2–4 mm per year, has occurred since then. This corresponds well with ^{210}Pb dating of earlier cores (Smith et al., 1994). The penetration of plutonium to much deeper layers and the absence of very low concentrations in the top layers are both thought to be caused by biological mixing processes driven by the rich benthic community. The apparent penetration of accident plutonium far deeper than the assumed 1968 depth plus the depth of the surface mixed layer could have implications for the use of ^{210}Pb as a sedimentation rate chronometer in coastal environments with rich biological activity. If the explanation is a small but significant deep biological mixing in addition to the fast bioturbation of the surface layer, this should be accounted for when comparing the slope of the excess ^{210}Pb depth distribution with its 22.3 year physical half-life. Bioturbation in the upper mixed layer was included in the earlier sedimentation modelling (Smith et al., 1994). Data from the present sampling have not yet been finally evaluated concerning sedimentation rates.

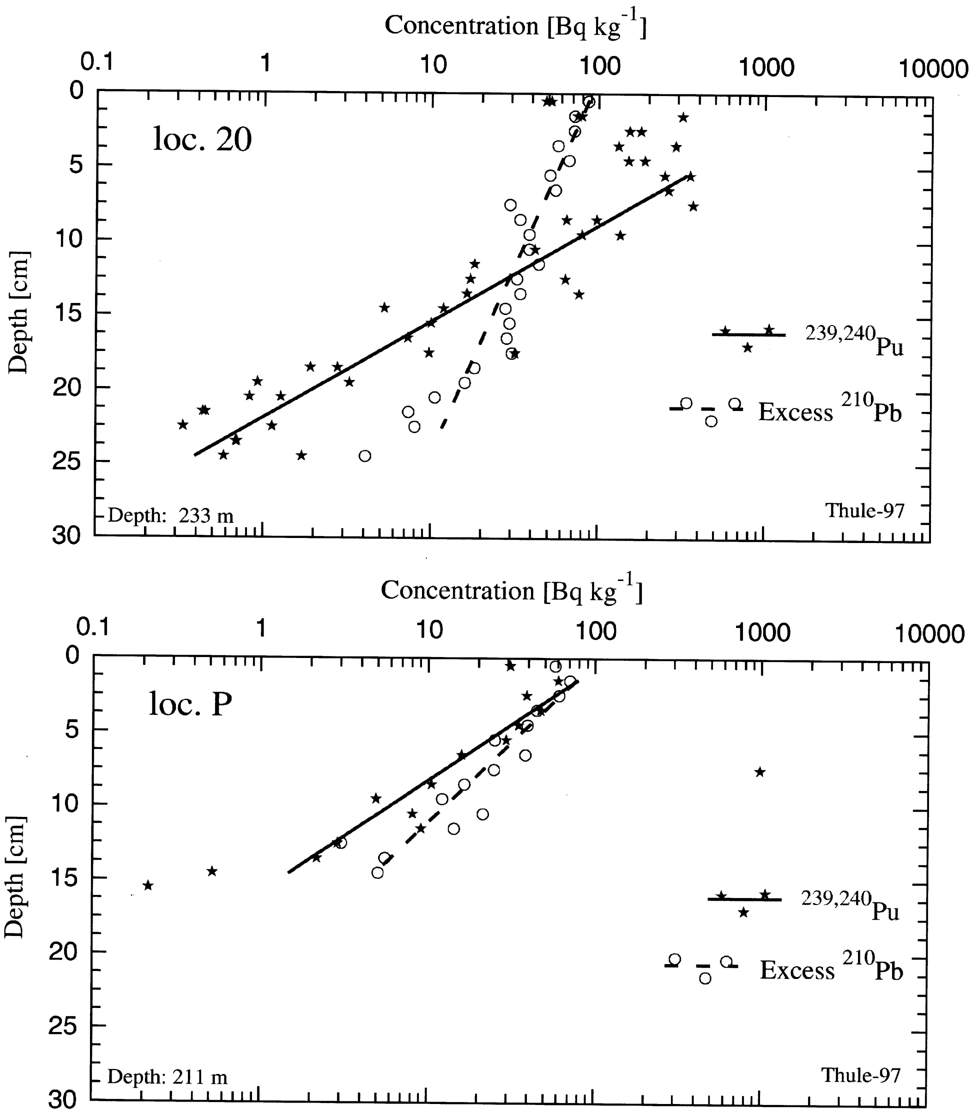

Fig. 3. Thule-1997. Two different sediment ^{239,240}Pu and ^{210}Pb concentration (Bq kg^{-1}) profiles with sediment depth (cm). Loc. 20 and loc. P. The regression lines are:
Loc. 20: $\ln(^{210}\mathrm{Pb}\ [\mathrm{Bq\,kg^{-1}}]) = 4.52 - 0.091d$, 0–23 cm, $r^2 = 0.84$.
Loc. 20: $\ln(^{239,240}\mathrm{Pu}\ [\mathrm{Bq\,kg^{-1}}]) = 7.77 - 0.35d$, 5–25 cm, $r^2 = 0.90$.
Loc. P: $\ln(^{210}\mathrm{Pb}\ [\mathrm{Bq\,kg^{-1}}]) = 4.66 - 0.21d$, 1–15 cm, $r^2 = 0.86$.
Loc. P: $\ln(^{239,240}\mathrm{Pu}\ [\mathrm{Bq\,kg^{-1}}]) = 4.81 - 0.30d$, 1–15 cm, $r^2 = 0.89$.
d is mean depth of sediment layer in cm.

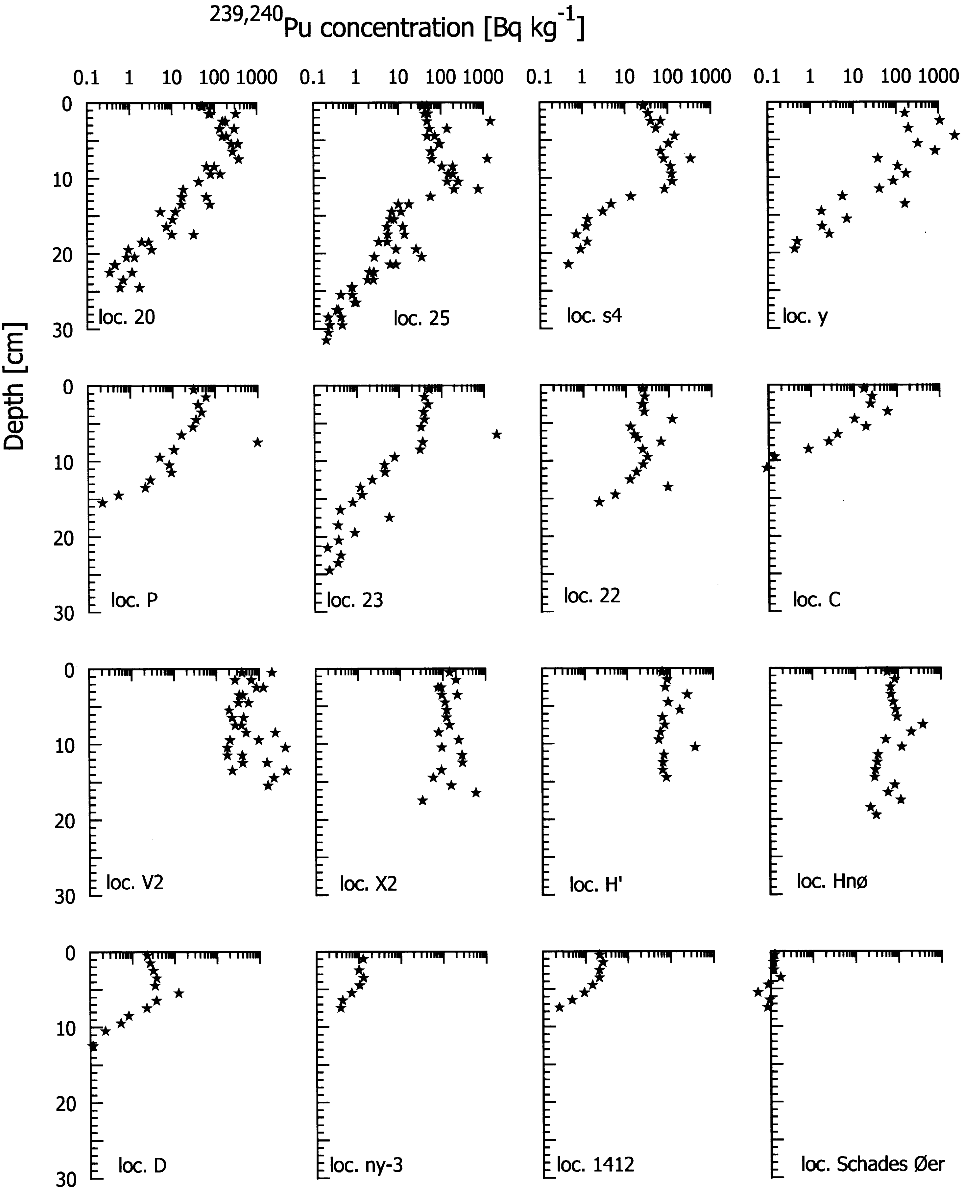

Fig. 4. Thule-1997. Sediment ^{239,240}Pu concentration (Bq kg^{-1}) profiles with sediment depth (cm).

Plutonium concentrations in 0–3 cm surface sediment are shown in Fig. 5. 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 background

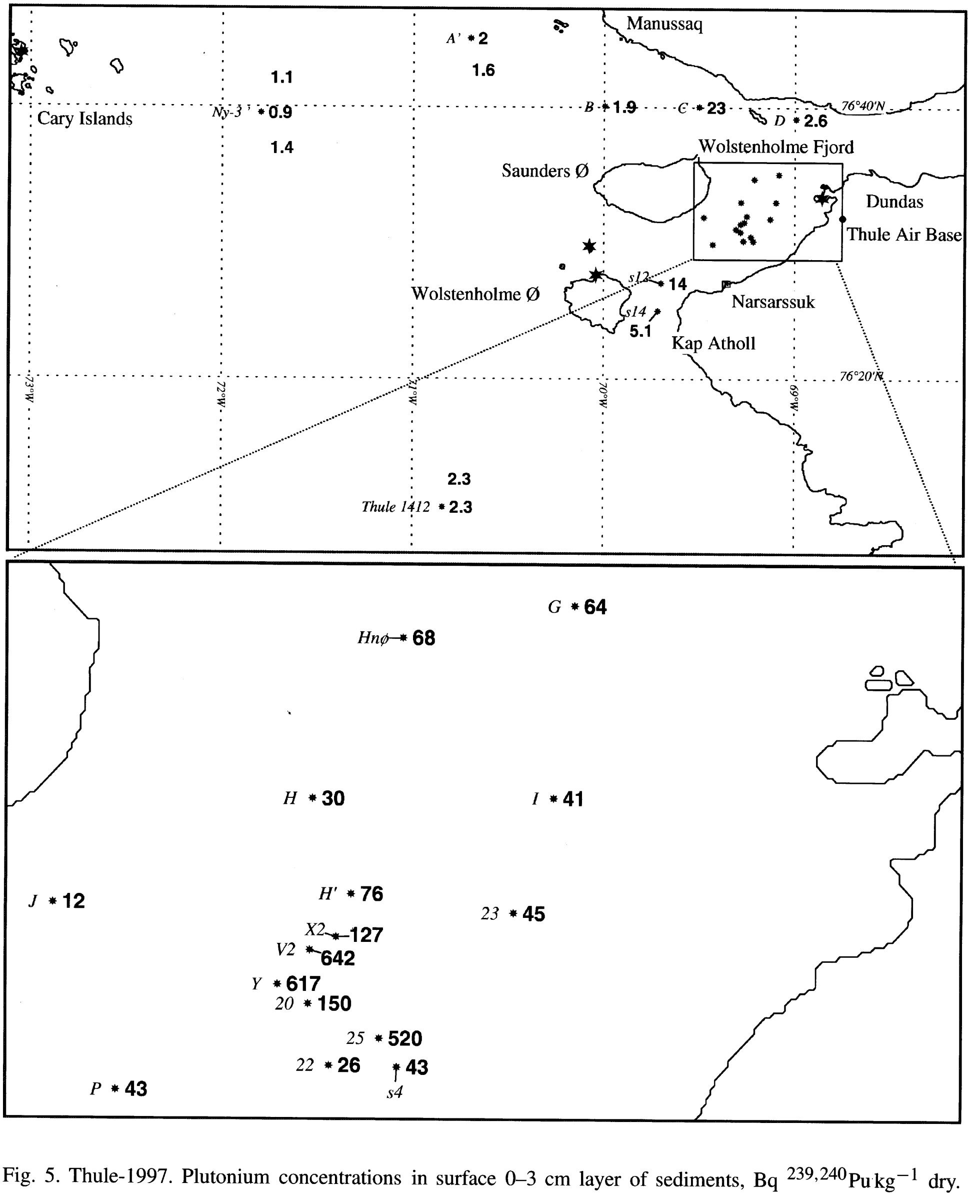

Fig. 5. Thule-1997. Plutonium concentrations in surface 0–3 cm layer of sediments, Bq ^{239,240}Pu kg^{-1} dry. Location names in italics, concentrations in bold. The point of impact was on the sea ice 180 m above the location marked V2.

fallout concentrations prevail outside Bylot Sound. The accident site — around location V — with the highest concentrations is situated at a depth of 180–230 meters.

It was not possible to obtain sediments in areas shallower than 100 m due to rocky bottoms. The two "background sites" outside Bylot Sound, Ny-3 and 1412, are from 500 and 640 m. A surface 0–3 cm concentration of 0.12 Bq ^{239,240}Pu kg^{-1} dry was observed at Shades Øer (Fig. 4) 750 km further south — between Upernavik and Uummannaq (Fig. 1). The surface concentrations outside Bylot Sound, locations 1412 and ny-3, are an order of magnitude higher (Figs 4, 5). It is not clear whether this is caused by accident plutonium or it is a natural perturbation caused by differences in sedimentological parameters. During the sampling expedition, much effort was devoted to obtaining additional sediment samples from Upernavik, Melville Bay and the area between Cary Islands and the mainland. The success rate for this effort was very low due to stones in the sediments — even far from land and at large depths. The stones are probably dropped from the numerous icebergs in the area.

Plutonium inventories integrated over the full sediment columns taken, expressed as Bq ^{239,240}Pu m^{-2}, are given in Fig. 6. A preliminary integration of the data in Fig. 6 gives a total inventory estimate of 1.8 TBq (Eriksson et al., 1999). This is not considered significantly different from previous estimates (cf. Introduction). A possible error in the inventory estimates caused by the lack of quantitative knowledge of the hot particles is currently being investigated.

Benthic biota

Where possible, plutonium concentrations in biota samples have been compared with concentrations in 0–3 cm surface sediments (Fig. 5) to give a "concentration ratio", CR, Bq ^{239,240}Pu kg^{-1} dry biota/Bq kg^{-1} dry 0–3 cm sediment (Table 1). It is noted that, although

Table 1
Thule-1997. Plutonium Concentration Ratios, CR, Bq ^{239,240}Pu kg^{-1} dry biota/Bq kg^{-1} dry sediment between various groups of benthic biota and upper 3 cm of sediments. Average values, dry weight basis

Class	Species	CR, Bq kg^{-1} biota/Bq kg^{-1} sediment (0–3 cm)		
		Average	SD	*n*
Mollusc	Bivalves	0.025	0.024	13
Mollusc	*Macoma calcarea*	37[a]		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	0.052	4
Annelida	var.	0.023	0.033	10
Annelida	Tube	0.28	0.29	6
Fish	*Liparis sp.*	0.00035		1

[a] Outlier, probably caused by hot particle.

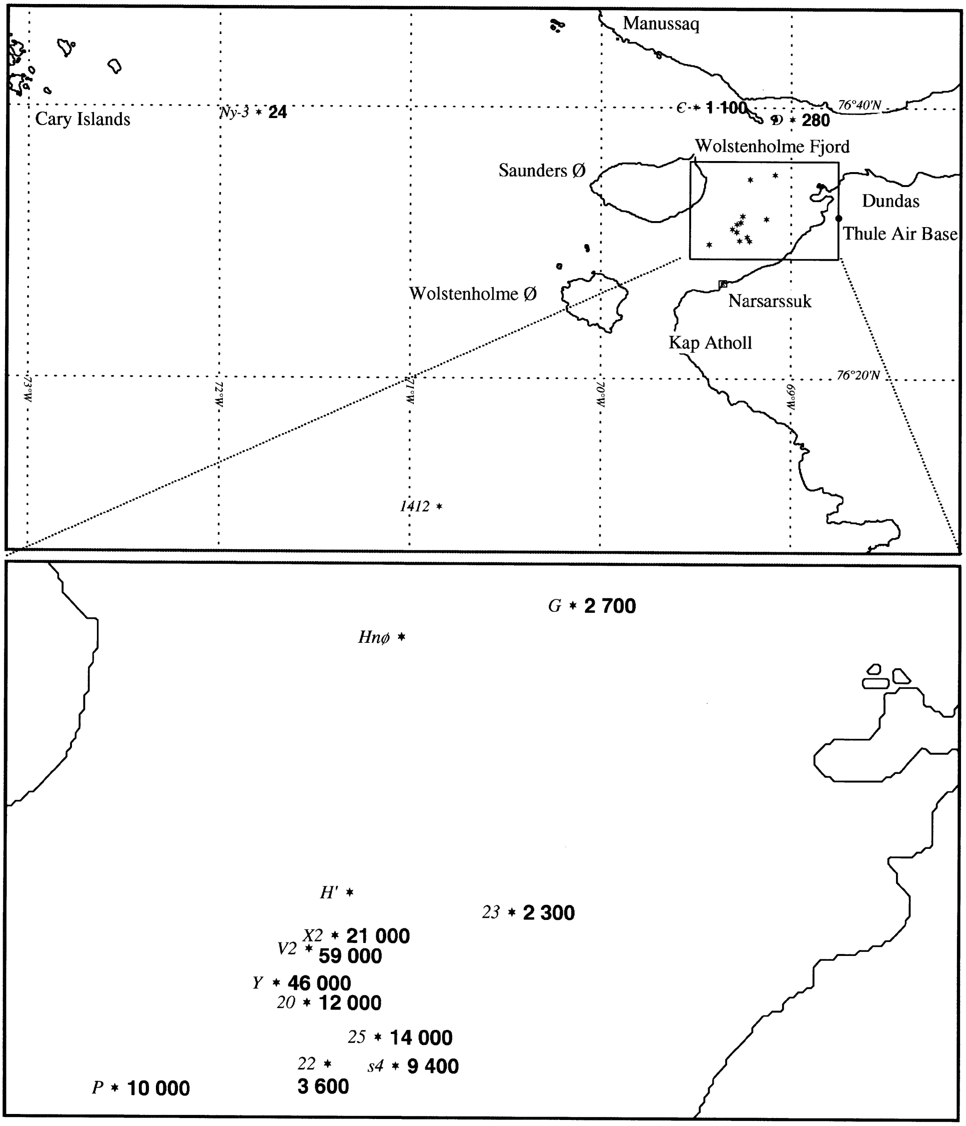

Fig. 6. Thule-1997. Plutonium inventories integrated over the full sediment column taken, expressed as Bq ^{239,240}Pu m^{-2}. Location names in italics, inventories in bold. The point of impact was on the sea ice 180 m above the location marked V2.

most of the biota is living buried in the sediments or on the sediment surface, the CR values indicate that the weapons plutonium is not readily transferred to biota. 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,

Table 2
Thule-1997. Average concentrations of plutonium in benthic biota samples and radiation dose[a] expressed as the number of kg to be consumed to obtain 1 mSv from ^{239,240}Pu

	Bq kg^{-1} fresh	SD%	*n*	kg/mSv	%dry
Bivalves	0.29	205	13	1.40E+04	18.2
Snails	0.13	97	9	3.17E+04	23.2
Starfish	0.94	254	9	4.24E+03	25.8
Brittle stars	0.29	88	4	1.38E+04	45.7
Feather stars	0.07	30	4	5.77E+04	35.0
Sea Urchins	1.57	114	4	2.54E+03	23.8
Sea cucumber	0.05	108	4	7.60E+04	14.9
Shrimp	0.06	141	4	6.90E+04	23.5
Crustaceans	0.18	47	4	2.17E+04	23.5
Pectinaria	4.92	149	4	8.13E+02	29.1
Annelida	0.34	107	10	1.19E+04	26.4
Bivalve, outlier	83.14		1	4.81E+01	18.2
Squid, *Rossia sp.*	0.0047		1	8.49E+05	19.0
Fish, *Liparis sp.*	0.0363		1	1.10E+05	16.2

[a] Dose factor for ^{239,240}Pu: 2.5 E-07 Sv/Bq.

a significant part of this plutonium is probably not metabolised but rather associated with particles in the guts and adhering to the surface structure of the animals.

One single bivalve sample showed a much higher level, which was probably due to a hot particle. In Table 2, average concentrations of plutonium in different groups of biota samples are given on a fresh weight basis. Furthermore, radiation doses from a highly hypothetical consumption are given as the number of kg (fresh weight) to be consumed to obtain 1 mSv from ^{239,240}Pu. In this calculation, a dose factor of 2.5×10^{-7} Sv/Bq ingested is assumed (ICRP 68, 1994).

Isotope ratios

A number of Thule sediment samples from the present 1997 sampling as well as a few hot ones taken in 1979 and 1991 have been analysed for ^{240}Pu/^{239}Pu atom ratios at Risø's HR-ICPMS facility (Stürup et al., 1998; Dahlgaard et al., 1999a). These samples show ^{240}Pu/^{239}Pu atom ratios in the range 0.027–0.057 (Fig. 7 and Table 3). The calculated uncertainties on most of the samples are 2–10%. In Fig. 7, it is seen that the samples with highest activity — which have all been identified as "hot particles" — show a significant variation in the ^{240}Pu/^{239}Pu atom ratios, i.e. there is a variation in plutonium isotope ratios in the Thule debris significantly above measurement errors. This supports the earlier conclusion (Mitchell et al., 1997) that the Thule plutonium originates from at least two sources of different quality. Hot particles analysed from the environment contaminated by the Palomares accident are comparable to or even higher than the highest ^{240}Pu/^{239}Pu atom ratios in the present Thule material (Mitchell et al., 1997), whereas several environmental samples contaminated with Russian weapons material show a lower ratio (Dahlgaard et al.,

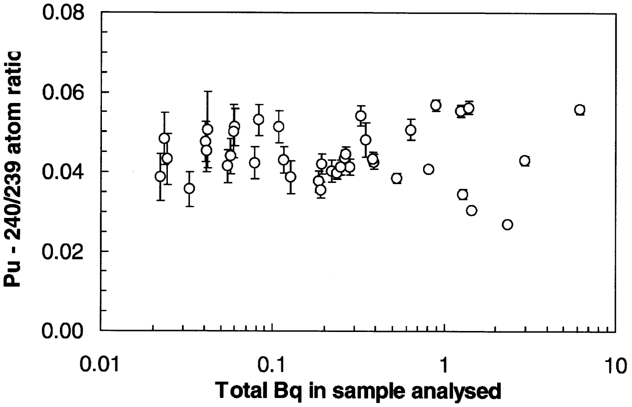

Fig. 7. Thule-1997. $^{240}Pu/^{239}Pu$ atom ratios in Thule sediment samples measured by HR-ICPMS.

Table 3
Thule-1997. Isotope ratios in sediment samples containing more than 20 Bq $^{239,240}Pu\,kg^{-1}$. Reference date: August 1997

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

1999a). Plutonium concentrations in the samples used for this work are dominated by the Thule weapons accident. Therefore, the higher $^{240}Pu/^{239}Pu$ atom ratio observed in global fallout, approx. 0.18 (Mitchell et al., 1997), will not affect the result. Any influence of the higher $^{240}Pu/^{239}Pu$ atom ratios in Sellafield discharges, up to around 0.25 (Kershaw et al., 1995), is even more unlikely, as the Sellafield contribution to the Arctic Ocean plutonium concentration is supposed to be less than global fallout (Kershaw & Baxter, 1995).

In Figs 8 and 9, $^{238}Pu/^{239,240}Pu$ and $^{241}Am/^{239,240}Pu$ activity ratios are shown as a function of $^{240}Pu/^{239}Pu$ atom ratios in sediment samples from the present 1997 sampling. Linear regressions indicate that the relationship between the $^{238}Pu/^{239,240}Pu$ and the $^{240}Pu/^{239}Pu$ ratios is probably significant ($P > 95\%$; $r^2 = 0.17$) and the relationship between the $^{241}Am/^{239,240}Pu$ and the $^{240}Pu/^{239}Pu$ ratios is significant ($P > 99\%$; $r^2 = 0.30$). This further supports the hypothesis that the Thule plutonium is not a homogeneous source. The data furthermore indicate that the Thule plutonium on average was of a higher 'quality' than the plutonium lost at the similar accident in 1966 in Palomares, Spain (Mitchell et al., 1997). The radioecological implication of the observed variations is that the use of plutonium isotope ratios in quantitatively determining the influence of different plutonium sources is a very complex affair requiring substantial data sets.

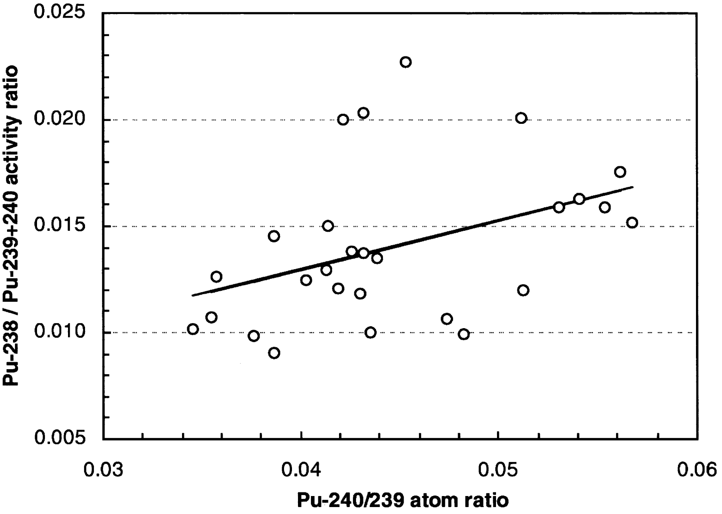

Fig. 8. Thule-1997 sediments. ^{238}Pu/^{239,240}Pu activity ratios shown as a function of ^{240}Pu/^{239}Pu atom ratios. The regression line: $y = 0.0038 + 0.229x$ is probably significant ($P > 95\%$; $r^2 = 0.17$).

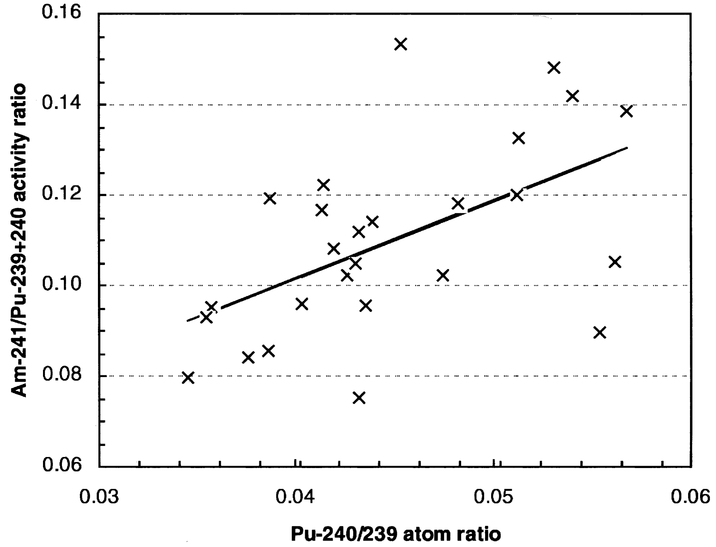

Fig. 9. Thule-1997 sediment samples. ^{241}Am/^{239,240}Pu activity ratios shown as a function of ^{240}Pu/^{239}Pu atom ratios. The regression line: $y = 0.0327 + 1.72x$ is significant ($P > 99\%$; $r^2 = 0.30$).

Table 4
Thule-1997. ^{241}Am/^{239,240}Pu activity ratios in various groups of sediment dwelling benthic biota

Type	Sub-type	^{241}Am/^{239,240}Pu activity ratio		
		Mean	SD%	*n*
Benthos	All	0.39	76	84
Molluscs	All	0.63	62	24
Annelida	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

Average isotope ratios, ^{240}Pu/^{239}Pu atom ratios and ^{238}Pu/^{239,240}Pu and ^{241}Am/^{239,240}Pu activity ratios for sediment samples containing more than 20 Bq ^{239,240}Pu kg^{-1}, i.e. at least an order of magnitude above the fallout background, are given in Table 3. The reference date is the sampling date, i.e. 1997. By comparison of the ^{241}Am/^{239,240}Pu activity ratios for the sediments (Table 3) with data for the benthic biota samples (Table 4), it is seen that some of the biota groups seem to have a higher uptake of americium than of plutonium. This appears to be the case for molluscs — bivalves as well as snails — and for the echinoderm groups brittle stars (*Ophiuroids*) and sea stars (*Asteroids*), but not for sea urchins (*Echinoids*) and sea cucumber (*Holothuriods*). The differences between the different animal groups could indicate differences in the importance of direct sediment contamination as compared to metabolic uptake of the transuranics. A higher affinity for americium than for plutonium in some biota groups is not new. Thus IAEA, for example, reported higher CF values for Am than Pu in molluscs (IAEA, 1985). Furthermore, it is generally seen that the K_d values for Am are higher than for Pu in coastal sedimenting material (IAEA, 1985). Both observations may be related to the fact that the main source of americium is *in-situ* production from the decay of ^{241}Pu.

Conclusions

- Plutonium from the contaminated sediments is not transported into the surface waters in significant quantities. This is deduced from analytical results of surface sea water and brown algae. However, plutonium-bearing sediments seems to be resuspended near the bottom.
- The low near-background plutonium concentrations indicate that only minor, if any, translocation of plutonium takes place to the area outside Bylot Sound.
- The present data support an earlier quantification of the sedimentation rate at 2–4 mm per year, i.e. 5–12 cm during the 29 years since the accident. Biological activity has mixed accident plutonium much deeper, down to 20–30 cm, and the 5–12 cm of new sediment have been efficiently mixed into the contaminated layer.

- Transfer of plutonium to benthic biota is low leading to lower concentrations in biota than in sediments.
- Thule sediments containing weapons plutonium show a significant variation in ^{240}Pu/^{239}Pu atom ratios in the range 0.027–0.057. This indicates that Thule plutonium originates from at least two sources of different quality.
- The radioecological implication of the observed variation is that the use of plutonium isotope ratios in quantifying different plutonium sources requires substantial data sets.

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Paper II

Eriksson M., Holm E., Roos P. and Dahlgaard H.:
Flux of ^{238,239,240}*Pu,* ^{241}*Am,* ^{137}*Cs and* ^{210}*Pb to High Arctic Lakes in the Thule District (Greenland)*
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Flux of ^{238}Pu, ^{239,240}Pu, ^{241}Am, ^{137}Cs and ^{210}Pb to High Arctic Lakes in the Thule District (Greenland)

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Abstract

Environmental samples (soil, sediment and lake water) in the Thule area (NW Greenland) have been studied to assess the contamination of radionuclides originating from a nuclear weapons accident (the Thule accident in 1968).

Four lakes were chosen at different distances from the point of impact with the Thule air base community situated in between.

The sedimentation rates in the lakes varied from 0.4 mm a^{-1} (5 mg cm^{-2} a^{-1}) to 1.6 mm a^{-1} (82 mg cm^{-2} a^{-1}). With these sedimentation rates it is not possible to resolve the ^{239,240}Pu global fallout peak from a possible ^{239,240}Pu "accident" peak in the sediment depth profiles. However, the ^{239,240}Pu to ^{137}Cs ratio and the isotopic ratio of ^{238}Pu to ^{239,240}Pu agreed well with the global fallout ratios, indicating that plutonium originating from the accident had not reached these lakes. This also indicates that the Thule air base community has probably only been exposed to radionuclides from the accident to a very limited extent.

A limited study showed that ^{210}Pb could not be used as a normalizing nuclide for the transport of transuranic elements from the catchment area to the lake, i.e. ^{210}Pb has a different transport mechanism from that of the transuranic elements studied in this investigation. Our study also indicates that americium is more mobile in the catchment area of the lake than plutonium.

Key words: Plutonium; Americium; Radiocesium; Radio-lead; Sediments; Lakes; Catchment; Thule; Thule accident; Remobilization; Fallout; Arctic; Radionuclides

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1 Introduction

On January 21, 1968, a B-52 aircraft accident occurred in the Thule district, NW Greenland (76° 33 N, 68° 54 W). The accident started with a fire in the aircraft, and the pilot tried to make an emergency landing at the Thule air base but failed, and the plane crashed about 11 km from the shore off the base. The aircraft was carrying 4 nuclear fusion weapons, which underwent a chemical explosion on impact. An area of approximately 2.23×10^5 m^2 was contaminated by about 3.5 ± 0.7 kg (8.8 TBq) of plutonium (Strand, Balonov, Aakrog, Bewers, Howard, Salo, et al., 1998), which can be compared with the fallout contamination of 2.1 MBq (Hanson, 1980) in this specific contaminated area. A few weeks after the accident, a clean-up operation, "Crested Ice", was started to recover the debris and the contaminated ice. The operation lasted for about 6 months. During this operation, about 85 % of the plutonium was recovered from the sea ice (USAF Nuclear Safety, 1970).

There was reason to believe that the Thule air base community could have been contaminated with radionuclides originating from the accident, as it took some weeks before the clean-up operation started (USAF Nuclear Safety, 1970). During this time, the debris and the contaminated ice were exposed to severe weather with several storms that could have spread the contaminated material around the area. Air sampling measurements, performed by the Environmental Measurement Laboratory (EML) at the Thule air base showed indications of higher air concentrations of ^{239,240}Pu directly after, and up to some months after, the accident (EML, 1999; Aarkrog, 1971). Hanson (1980) found plutonium originating from the accident on Saunders Island (west), Wolstenholme Island (west) and in soil samples south of the point of impact. Another area that was probably contaminated, is the so-called "Tank farm" (USAF Nuclear Safety, 1970). This was a large area on the seashore where the debris and the peeled contaminated ice were loaded into tanks for further transport to the USA. Under the hard working conditions, windy and cold in combination with rough equipment, spillage was possible which would have contaminated the ground. Resuspension of radioactive elements from these contaminated areas has now been going on for 30 years and could be a possible source of radiation exposure for employees and Inuits at the Thule air base.

Since the Thule accident in 1968, there have been regular expeditions (1968, 1970, 1974, 1979, 1984, 1991) to the area. Many investigations of the distribution and transfer of radionuclides in the surrounding environment, almost exclusively in the marine environment, have been performed (Aarkrog, 1971, 1977; Aarkrog, Dahlgaard, Holm, Hanson, Lippert, & Nilsson, 1981; Aarkrog, Dahlgaard, & Nilsson, 1984; Aarkrog, Boelskifte, Dahlgaard, Duniec, Holm, & Smith, 1987; Aarkrog, Buch, Chen, Christensen, Dahlgaard, Hanson, et al., 1988; Aarkrog, Chen, Clausen, Christensen, Dahlgaard, Ellis, et al., 1997).

During the Thule '97 expedition, an investigation of the terrestrial land area east and north east of the point of impact, was carried out for the first time.

One objective of the present study was to investigate whether any of these land areas had been contaminated following the accident, and whetter these areas are now/were exposed to resuspended material from contaminated areas closer to the point of impact. If we could identify a signal from the accident in these selected lakes, it is probably that the Thule air base community has also been affected by material from the accident. Another objective was to study the general behavior of radionuclides in these high arctic lakes. While the transport mechanisms of atmospheric deposited contaminants to lakes in the temperate zones is governed, in general, by drainage from the drainage basin, this is not the case in arctic desert lakes. The low precipitation in this area combined with strong winds makes resuspended material an important contributor to the mass load to the lakes and they may therefore act as large-area integrators to a greater extent than lakes in temperate zones. Lakes with a well-developed, undisturbed, sediment archive would thus be valuable, not only as sensors for the drainage basin, but on a wider scale for the region and, of course, not only for the purpose of observing radioisotope fluxes but also other fluxes of contaminants to the arctic region.

2 Materials and Methods

2.1 Area studied

The Thule area (Pituffik) is a high arctic landscape containing wetlands with several lakes. The area has been a cultural centre used by Inuits from the Thule culture for about 4000 years.

The lakes in the area are, in general, oligotrophic, small and shallow and some of them contain fish (arctic char). There is some vegetation (lichen and moss) in places around the lakes, but most of the area between the inland ice and the sea is stoney, and can be described as a cold desert. One estimate is that only about 1 % of the land is covered by some sort of vegetation. The annual precipitation is low (130 mm a^{-1}) (EML, 1999) and the ground is temporarily covered by snow from September to June. The Thule area is shown in Figure 1. The lakes from which samples were taken are indicated in the figure.

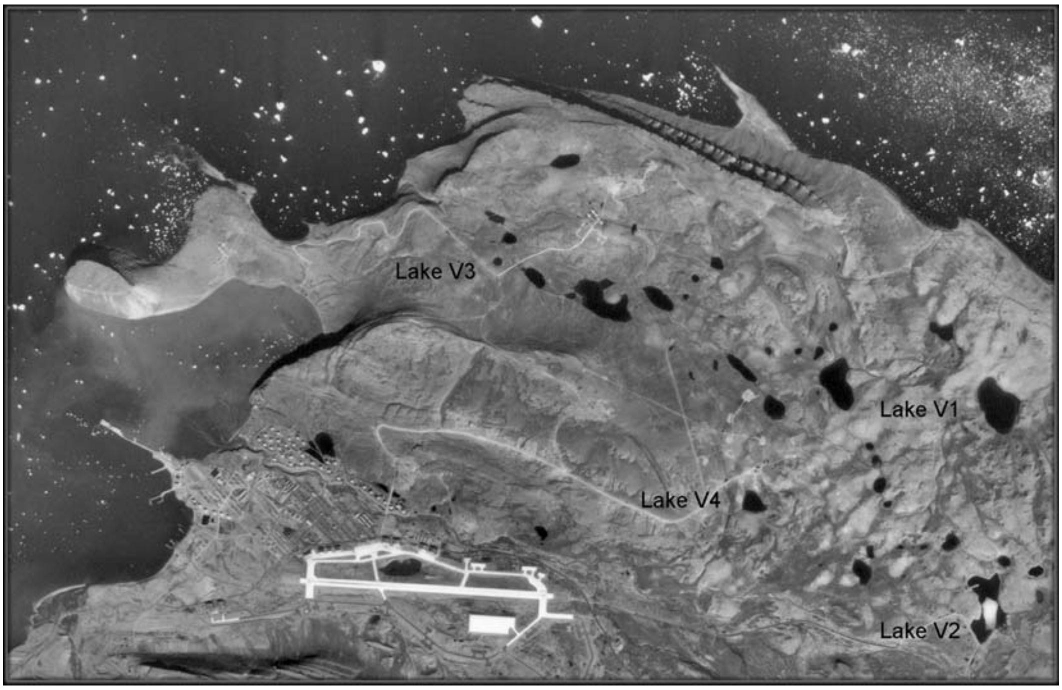

Fig. 1. Aerial photograph of the Thule air base. The sampling stations are shown in the figure. The point of impact is located about 15 km west of the base. The runway (the white strip) is 3.1 km long. The white patch on lake V2 is an unmelted ice floe and the white spots on the Wolstenholme Fjord (North) are icebergs. ©Kort & Martikelstyrelsen (A. 23–99)

2.2 Field sampling

Samples from 4 lakes, denoted V1 to V4, and soil samples were collected during the (land-based) Thule '97 expedition. The lakes were partly chosen so there were different distance to the B-52 impact point, but the depth of the lake was also considered important due to the need to obtain undisturbed sediment profiles. At the start of the expedition the lakes were open, but the winter came early in 1997 and the lakes froze over during the expedition. When samples were due to be taken from lake V4, the ice was too thin to walk on and too thick to use a boat as a sampling platform, so only near-shore water samples were collected from this lake. Three days after the first ice formation, the lakes were covered with 7 cm of crystal-clear ice. For sampling from lake V3 we used the ice as a working platform. In lakes V1 and V2 a small boat was used.

Sediment samples were collected from three of the four lakes using a kayak sediment sampler with a tube diameter of 64 mm. Two sediment cores were taken from lake V1 and three sediment cores each from lakes V2 and V3. The maximum depth was found with an echo sounder, and from the deepest area of the lake the sediment cores were collected. The sediment cores were immediately sliced into 1 cm sections at the sampling stations and packed in small plastic bags. On arrival at the laboratory, the sediment sections were weighed and dried at 80°C for 48 hours.

The soil was extremely difficult to sample, firstly because most of the area has no vegetation, and consists only of gravel and stones, secondly because of the permafrost. During these conditions we were only able to sample soil cores from the catchment area of lake V1. The soil sampler used has an inner diameter of 70 mm. The soil cores were stored in plastic tubes. On arrival at the laboratory, the soil cores were sliced into 1 cm sections and treated in the same way as the sediment samples.

Two-hundred litres of filtered water (filter pore size of 1 μm) were collected from each lake for the determination of ^{137}Cs, ^{238,239,240}Pu and ^{241}Am concentrations. ^{137}Cs was collected in two ways. For two of the samples, Cs was absorbed onto copper ferrocyanide ($Cu_2[Fe(CN)_6]$) formed *in situ* upon the addition of $K_4[Fe(CN)_6]$ and $Cu(NO_3)_2$ solutions. The precipitate was collected in plastic carboys for further gamma spectrometric analysis in the laboratory. The other two Cs samples were passed, at a low flow rate (approximately 5 litres per minute), through a copper-ferrocyanide-impregnated cotton wound cartridge filter (Roos, Holm, & Persson, 1994). In the laboratory the filters were incinerated and prepared for gamma spectrometric analysis. In both these procedures, ^{134}Cs was used as a yield determinant. To determine the possible presence of ^{134}Cs originating from the Chernobyl accident, the ^{134}Cs/^{137}Cs ratio was determined by pumping large volumes of water, greater than 900 litres, through a copper-ferrocyanide-impregnated cotton wound cartridge filter. The filters were treated in the way described above.

Plutonium and americium were coprecipitated as hydroxides at pH > 10, achieved by adding sufficient NaOH to the sample after adding 100 mg of $FeCl_3$ and about 5 g reducing agent ($Na_2S_2O_5$), together with the chemical yield determinants. As the lake water concentration of free ions was very low, the addition of Ca, Mg and Al ions was necessary to make hydroxide precipitation possible. The precipitates were collected in plastic carboys for further chemical separation and alpha spectrometry in the laboratory. The isotopes ^{242}Pu and ^{243}Am were used as radiochemical yield determinants for Pu and Am.

2.3 Laboratory treatment

All the analysis were carried out at the Dept. of Radiation Physics in Lund, Sweden and at Risø National Laboratory in Roskilde, Denmark. High purity germanium (HPGe) detectors with low background were used for gamma analysis in order to detect the low-energy gamma-emitting nuclide ^{210}Pb, used to date the sediment cores. To be able to determine the supported ^{210}Pb, which were performed by measurements on the short-lived ^{226}Ra daughters, ^{214}Pb and ^{214}Bi, the samples were left for 3 weeks before being analysed in the counting geometry to ensure radioactive equilibrium. This is necessary as the packing procedure causes the radon to be exhaled from the sample and the determination of ^{214}Pb and ^{214}Bi activity will thus be underestimated. The final ^{210}Pb data include corrections for different densities of the sediment samples. The copper-ferrocyanide-impregnated filters were incinerated before being analysed in a well-calibrated geometry. The Cs precipitates were dried before gamma counting. The analytical procedures used for Pu and Am are described by Talvitie (1971) and Holm (1984), although with small modifications. For Pu and Am analysis about 5 g (d.w.) of sediment were incinerated overnight at 550°C to determine the organic content. To ensure that any PuO_2 particles, originating from the accident in 1968, would be dissolved we used HF/HNO_3 (1:10) repeatedly. The hydroxide precipitates of filtered lake water were dissolved in HNO_3 and coprecipitated with iron hydroxide by adding ammonia to $pH \approx 10$. The precipitates were dried overnight, dissolved in 8 M HNO_3, followed by the methods mentioned above (Talvitie, 1971; Holm, 1984). Alpha-particle spectroscopy was performed using solid state silicon detectors.

3 Results and Discussion

3.1 Caesium, plutonium and americium concentrations in the high arctic lakes

The lakes (V1, V2, V3 and V4) are small and shallow with small depth gradients. The maximum depths of lakes V1, V2 and V3 are 4, 9 and 2 metres respectively. Lake V1 has the largest catchment area and the lake area is equal in size to that of lake V2. Lake V2 is a dammed lake which was influenced by anthropogenic activity during construction of the dam, so that gravel and stones are present in the sediment. This lake also serves as a drinking water reservoir for the Thule air base.

Sediments

The area activity concentrations (Bq m^{-2}) of caesium, plutonium and americium for the sediment profiles are shown in Figure 2 for each lake (the concentrations are decay corrected to the reference date 1997–09–01). It can be seen that the isotopes exhibit maximum at the same depth, and this corresponds to the global fallout peak (assumed to represent the year 1963). The rather well shaped sediment profiles of fallout activity and the chronological

Table 1. The inventory in the sediment cores from the lakes studied. V in combination with a number represents the lake and S in combination with number represents the sediment core. The final row of numbers gives the inventory for the soil sample taken in the catchment area of lake V1.

Lake and Core	^{137}Cs inventory [Bq m^{-2}]	^{239,240}Pu inventory [Bq m^{-2}]	^{238}Pu inventory [Bq m^{-2}]	^{241}Am inventory [Bq m^{-2}]
V1S1	1193 ± 27	31.6 ± 0.8	1.80 ± 0.06	–
V1S2	1091 ± 27	28.3 ± 1.5	1.14 ± 0.15	11.3 ± 0.5
V2S1	–	5.14 ± 0.35	–	3.18 ± 0.23
V2S2	363 ± 9	8.72 ± 0.26	0.25 ± 0.01	3.98 ± 0.25
V2S3	496 ± 18	11.6 ± 0.54	0.33 ± 0.04	–
V3S1	578 ± 16	21.8 ± 1.1	0.51 ± 0.04	6.86 ± 0.34
V3S2	1085 ± 14	25.6 ± 0.8	0.58 ± 0.04	10.8 ± 0.1
V3S3 [a]	343 ± 9	5.51 ± 0.37	0.12 ± 0.03	3.54 ± 0.19
Soil				
V1M2	474.5 ± 13	17.5 ± 0.8	0.18 ± 0.03	4.89 ± 0.25

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[a] Top (0∼1 cm) sediment lost during sampling

agreement with the ^{210}Pb data indicate that the sediments have only been disturbed to a limited extent, in spite of the very low sedimentation rate. This is particularly true for lake V3. This indicates that the sampling locations in the lakes are not seriously affected by bottom freezing, which may be anticipated, especially in lake V3, where the sampling depth was only about 2 m. The integrated activities are presented in Table 1 for each core. In lake V1 the two cores have almost the same inventory although the peaks appear one cm apart, suggesting different sedimentation rates at these sampling sites; these two cores were taken about 200 meters apart. Lake V2 has the lowest inventory of all radionuclides studied which may be explained by the smaller catchment area. Lake V3 shows the greatest variability in the inventories of these nuclides, differing by a factor of 3 for ^{137}Cs and ^{241}Am, and a factor of 5 for Pu (cores V3S2 and V3S3). In core V3S3 the top (0∼1 cm) was lost during sampling, which explains some of the variability.

Sediment core 2 in lake V2 (marked with "+" in Figures 2–4), was taken from a site in the lake which was the lake shore before the construction of the dam. In this core there is a layer (sediment depth 3–7 cm) which consists partly of moss and lichen from the period before the dam was built. This explains the LOI (Loss On Ignition) curve, i.e. the ratio between the ash weight to the dry weight decreases because there is a substantial amount of organic matter in the sediment. It can also be seen from the LOI curves in Figure 3 that most of the other sediment cores consist of inorganic material, i.e. eroded particulate matter from the bedrock in the area around the lakes, which has probably been transported by wind resuspension.

Water

The ^{238,239,240}Pu, ^{241}Am and ^{137}Cs concentrations in the water were very low. Both the ^{241}Am and ^{137}Cs concentrations were below the detection limit, despite the fact that 200-litres samples were analysed. ^{239,240}Pu concentrations in the filtered water were between 3 and 6 μBq l^{-1}. The low concentrations indicate that all these radionuclides are effectively scavenged from the water column down to the sediment in this type of lake. This was expected, as there is hardly any water movement in the lakes when they are covered by ice, about 10 months per year, which permits suspended particles to settle in the sediment. The freezing process also causes the radionuclides to leave the frozen water phase. This can be an important mechanism in the high arctic lakes as some of these shallow lakes may become almost completely frozen. However, it may also be expected that redox-sensitive actinides might become remobilised to some extent, from the sediments to the water column under anoxic conditions (Sholkovitz, Carey & Cochran, 1982), which can occur after a long period of ice coverage. The oxygen consumption in the sediment is, however probably very low, due to the very low organic matter concentrations (the LOI is of the order of 5 %, except for lake V3, where the LOI is of the order of 20-30 % for the upper 5 cm). Also, the dissolved Fe and Mn concentrations are probably low, so even if reducing conditions would occur the carrier phases would not become affected. However, to see such effects, sampling should be carried out shortly before the ice breaks up. In this particular case, sampling was performed at the end of the open-water season.

As the ^{137}Cs was not detectable in 200-litres water samples, it would require water samples of at least some 12,000-litres to be able to detect ^{134}Cs from pure Chernobyl fallout, assuming a ^{134}Cs/^{137}Cs ratio of 0.017 in 1997. The large water samples (900–1200 litres) filtered through a $Cu_2[Fe(CN)_6]$ filter thus contained no detectable ^{134}Cs.

Soil

The soil core (Figure 2, bottom row) was sampled from the catchment area of lake V1. The inventories of the nuclides can be seen in Table 1. The inventories in the soil are lower than the inventories in lake V1, which is an indication that the catchment area is a source of radionuclides to the lake. The inventories of ^{137}Cs and ^{241}Am in the soil are 42 % and 43 %, respectively, of the inventories in the lake, while for ^{239,240}Pu the difference in the inventory is less (58 % of the inventory in the lake). The integrated (Bq m^{-2}) ^{241}Am/^{239,240}Pu ratios in the lake sediments are generally higher than in the soil, although the spread is rather large. There are, however, indications that Am is somewhat more mobile than Pu. The integrated ^{241}Am/^{239,240}Pu ratio in global fallout should be around 0.35 by 1997. However, as these conclusions are only based on a single core they should be treated with caution. These indications are, however, interesting and further studies are in progress on samples collected in similar areas in the Canadian high arctic.

3.2 ^{210}Pb data and sediment chronology

We used the Constant Rate of Supply (CRS) model (Appleby & Oldfield, 1978) to determine the sediment chronology. The choice of the CRS model is based on the following arguments:
-The CRS model is more flexible than the Constant Initial Concentration (CIC) model, and will give the same results as the CIC model if the initial concentration is constant over time.
-The atmospheric input of ^{210}Pb is assumed to be constant from year to year and the ^{210}Pb in these inorganic sediments is considered to be immobile.

There is no reasons to believe that the flux of ^{210}Pb would have changed significantly over time during the past decades. Such changes would require a change in the amount of precipitation or in the general air mass transport in the region. Such drastic regional changes have not been reported. The large

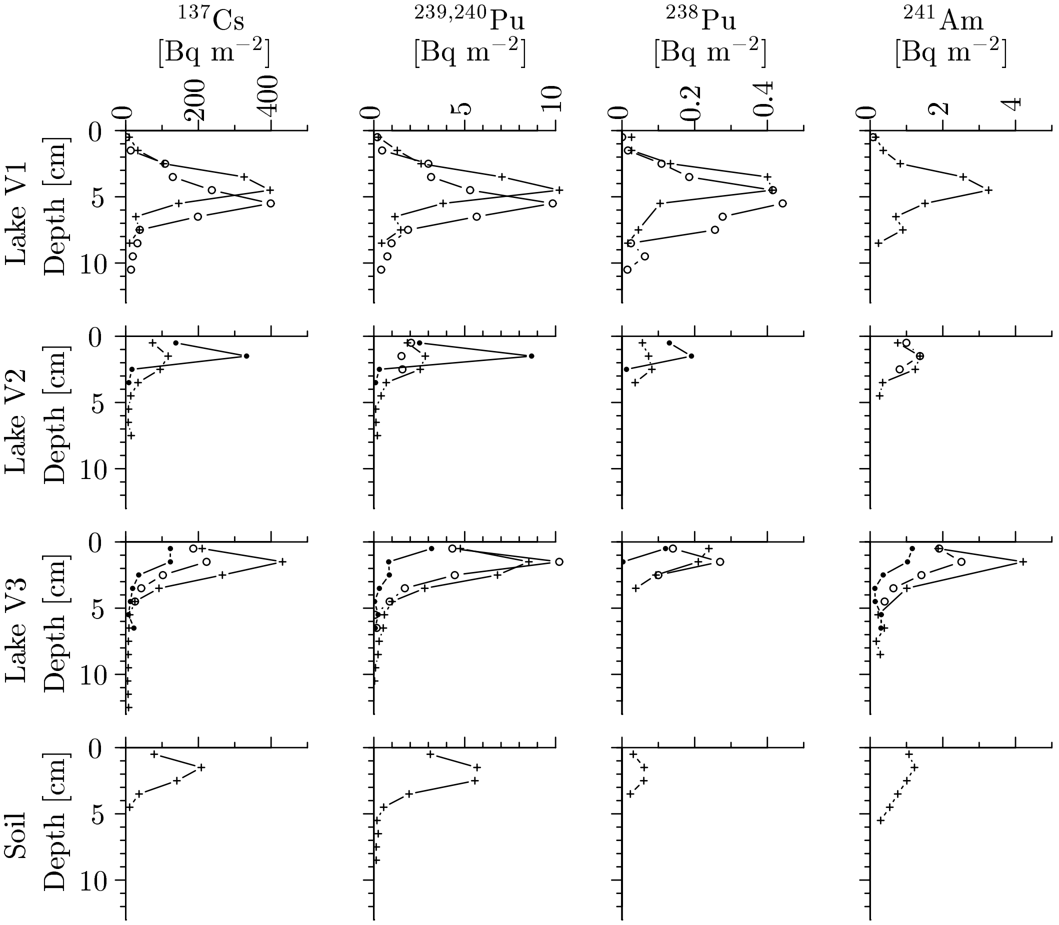

Fig. 2. Depth profiles. The first row of figures represents lake V1, the second row lake V2 and the third row lake V3. The columns represent individual nuclides with the activity concentrations plotted versus depth. In each graph the individual sediment cores can be distinguished, "○" represents core 1, "+" represents core 2 and "●" represents core 3 in each lake. The top (0∼1 cm) sediment in core V3S3 was lost during the sampling procedure. Uncertainties have been omitted from the figure to make it legible, and are for ^{137}Cs ∼ 3 %, for ^{239,240}Pu ∼ 8 %, ^{238}Pu ∼ 15 % (but at low activity levels up to 100 %) and for ^{241}Am ∼ 10 %.

variation in ^{210}Pb flux during each year, which is due to the long period of ice cover, does not affect the CRS model as long as the overall yearly flux is the same. Since some construction work has obviously occurred around lake V2 there is reason to believe that the suspended matter concentrations and thus the mass flux to the sediment has changed over time. Due to this, the CRS model was used, rather than the CIC model. To be consistent the CRS model was used for all sediment cores collected.

Air concentrations of ^{210}Pb were taken from the EML-database EML (1999). The data show air concentration maxima of ^{210}Pb in the winter and minima in the summer, although the exhalation of ^{222}Rn from the ground is assumed to reach a maximum in the summer. The same annual cyclic ^{210}Pb air concen-

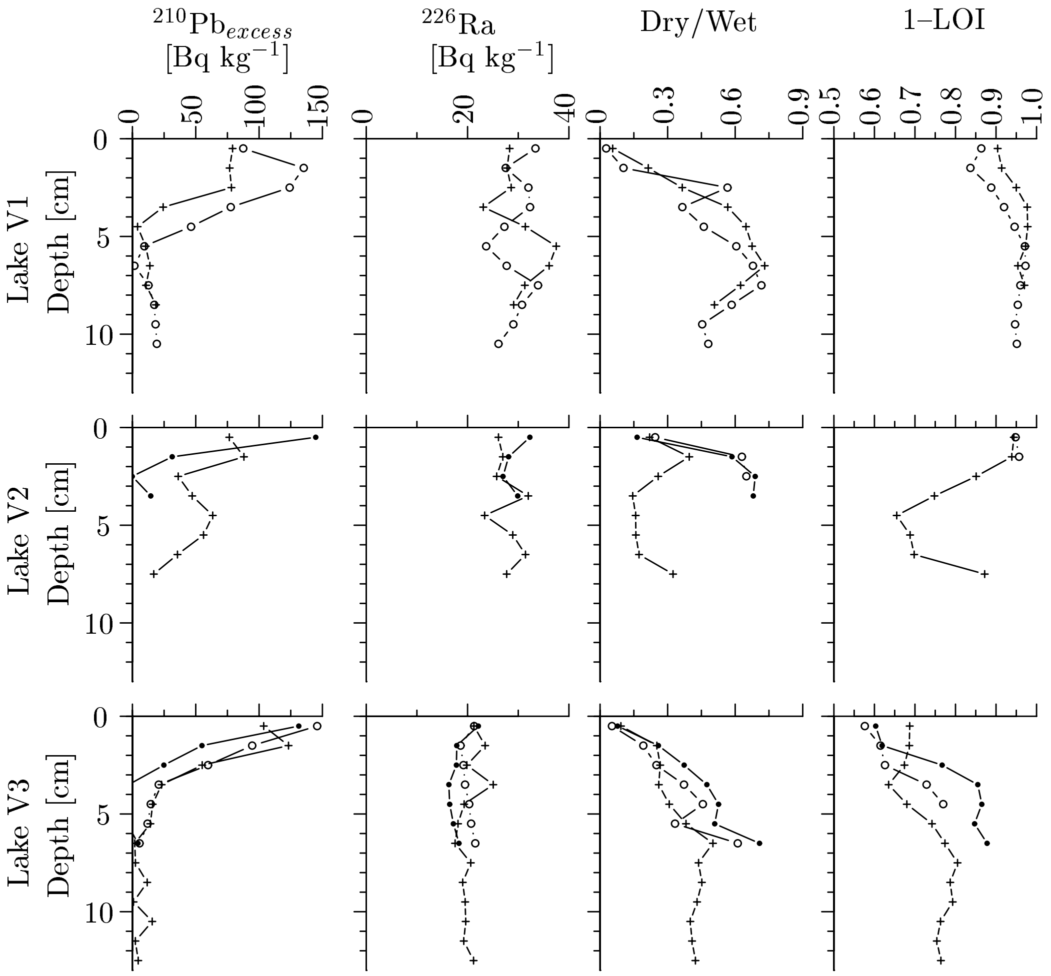

Fig. 3. Depth profiles. The first row of figured represents lake V1, the second row lake V2 and the third row lake V3. The two first columns represent the activity concentration versus depth for excess ^{210}Pb and ^{226}Ra. The third column shows the ratio between dry weight and wet weight and the fourth column gives the ration of the ash weight to dry weight. In each graph the individual sediment cores can be distinguished, "∘" represents core 1, "+" represents core 2 and "•" represents core 3 in each lake. Uncertainties have been omitted from the figure to make it legible, and are for ^{210}Pb $\sim$ 5 % and for ^{226}Ra $\sim$ 5 %.

trations was observed by Paatero, Hatakka, Mattsson & Viisanen (1998) in northern Finland. The explanation for this, according to Paatero et al. (1998), is that the mixing height of the lower atmosphere is much lower during winter when there is no light to heat the ground, and the activity concentration therefore increases. Typical winter air concentrations in Thule are 0.6 mBq m^{-3}, while summer air concentrations are less than 0.1 mBq m^{-3}. The annual geometrical mean value is about 0.25 mBq m^{-3} (16 years of monthly measurements), which was the value we used to determine the ^{210}Pb deposition velocity.

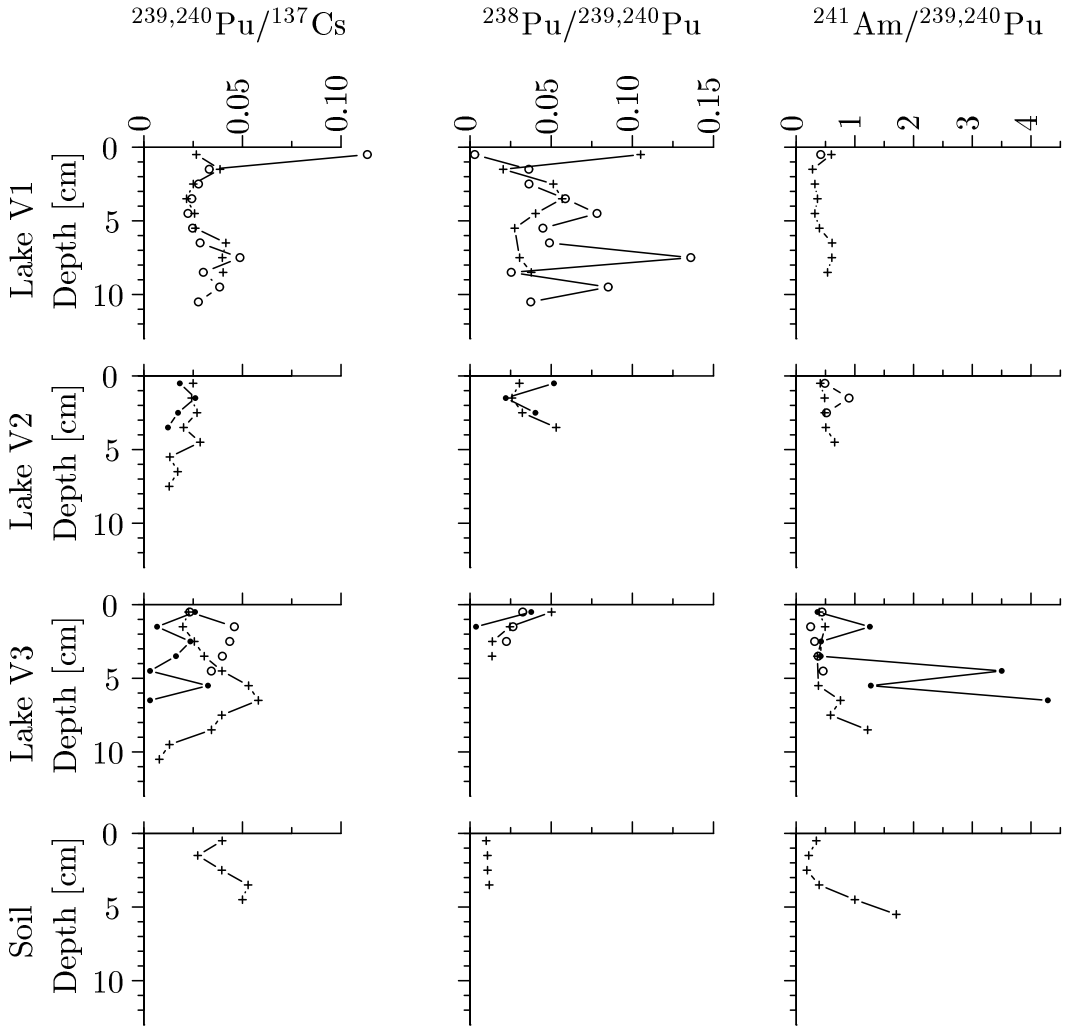

Fig. 4. Depth profiles. The first row of figures represents lake V1, the second row lake V2 and the third row lake V3. The columns represent the nuclide ratios versus depth. In each graph the individual sediment cores can be distinguished, "○" represents core 1, "+" represents core 2 and "●" represents core 3 in each lake. Uncertainties have been omitted from the figure to make it legible, and are for ^{239,240}Pu/^{137}Cs ∼ 10 %, for ^{238}Pu/^{239,240}Pu ∼ 25 % (but at low activity levels up to 100 %) and for ^{241}Am/^{239,240}Pu ∼ 15 %.

Determination of unsupported ^{210}Pb was performed using gamma spectrometry. Supported ^{210}Pb was assumed to be in equilibrium with ^{226}Ra and the short lived daughters, ^{214}Pb and ^{214}Bi, after the sample had been stored for 3 weeks. The activity of these nuclides were also measured using gamma spectrometry and the geometrical mean value represents the supported level. The counting jars used in the gamma spectroscopy measurements were not completely gas-tight, so there may have been some loss of radon. If this was the case, the supported level would be underestimated and the slices would be determined to be younger than they actually are. It seems that we did loose some ^{222}Rn, as the excess ^{210}Pb tails do not reach zero at great depths in the sediment profiles. This loss, however, makes no significant difference in the chronology of the upper 5–10 cm of the sediments, which in this case was the important part.

The flux of ^{210}Pb from the atmosphere was found to be 72 Bq m^{-2} a^{-1}, which was calculated from the integrated area concentration in the soil core times the decay constant ($\lambda = 0.03108$ a^{-1} for ^{210}Pb). The total deposition velocity, which relates the total ^{210}Pb flux to the ^{210}Pb activity air concentration, was found to be 0.92 cm s^{-1}. These values were calculated from a single soil core and might not be representative of the whole catchment area, especially as the ^{210}Pb seems to have a higher affinity to moss and lichen than the mineral soil.

The excess ^{210}Pb profiles for the sediments are shown in Figure 3. The sedimentation rates were determined to 1.3–1.6, 0.4 and 0.26–0.47 mm a^{-1} in lakes V1, V2[2] and V3, respectively, and the corresponding mass fluxes were found to be 75–82, 13 and 5–12 mg cm^{-2} a^{-1}. The slice in the sediment cores where the fallout peaks were observed corresponds well with the CRS model, but the CRS results systematically gave a slightly younger age of these slices. This is probably due to radon losses when determining the supported level (see above).

In Figure 3 it can be seen that the $^{210}\text{Pb}_{excess}$ profile for core 2 in lake V1 shows an even activity concentration in the top 3 cm. This is not an effect of mixing, as the depth profiles of the other radionuclides indicate no mixing. A mixing profile (mixing depth 2.5 cm and rapid mixing constant, such as the $^{210}\text{Pb}_{excess}$ profile indicates) of these other nuclides would give a much higher concentration in the top sediment, as was shown by Robbins, Mudroch & Oliver (1990). There is also no reason to believe that ^{210}Pb has a high mobility in the sediments since the amounts of redox-sensitive carriers (Fe, Mn or organic matter) are very low in the sediment. At present, we have no satisfactory explanation of this behaviour and measurement artifacts can not be ruled out.

The annual fluxes of excess ^{210}Pb to the sediments were 26.3–51.9 (lake V1), 18.7–31.1 (lake V2) and 15.2–26.0 Bq m^{-2} a^{-1} (lake V3). In the catchment area the flux was calculated to be 72 Bq m^{-2} a^{-1}. This result is difficult to explain as the fluxes should be at least the same or higher in lake V1 than the fluxes in the catchment profile from this lake. As mentioned before, the soil core might not represent the whole catchment area, and for this reason care should be taken not to draw too broad conclusions. As can be seen from the lake V2 data, moss and lichen probably contributes a substantial amount of the ^{210}Pb

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[2] In lake V2 only core 3 was used as core 2 was sampled at a site which had been on land before the damming of the lake, and the CRS model is not valid for such a core.

to these lakes; the more organic matter transported to the lake, the more ^{210}Pb will also be transported. It is important to keep in mind that the lakes are deposition zones for areas not necessarily represented by their drainage basins, but for a much wider area. Wind-blown dust and moss and lichen are carried far beyond the drainage basin borders, and therefore sediment inventories and ratios may very well differ from what is found in the soil profiles in the close vicinity of the lake.

The results for the lake V1-area are interesting, as there are higher inventories of anthropogenic nuclides in the lake V1 than in the catchment area (a factor of 2 higher). This means that ^{210}Pb can not be used as a normalising nuclide for transport of transuranic elements from the catchment area to the lake, i.e. ^{210}Pb has a different transport mechanism than the transuranic elements studied in this investigation. ^{210}Pb probably has an active uptake mechanism in vegetation, which the transuranic elements do not have, which prevents ^{210}Pb from leaving the catchment area. Alternatively, the difference may be due to the fact that we are comparing a transient input with a steady state input. Perhaps the ^{210}Pb flux may be used to normalize the inputs for each year, if they could be measured (e.g. by sediment traps). Or perhaps by now (some 30–35 years after the fallout period) the main part of the anthropogenic fallout isotopes are residing in a different compartment than the main part of the ^{210}Pb and, therefore, there has been a gradual shift in isotope ratios (e.g. ^{210}Pb to ^{239,240}Pu ratios) transported to the lakes.

3.3 Indications of radionuclides originating from the Thule accident and isotopic ratios

The EML air concentration measurements of ^{239,240}Pu shown in Figure 5 indicate that in January 1968 there was an increase in concentration that remained reasonably constant ($\sim 2\ \mu$Bq m^{-3}) until September. This may be due to early annual mixing of the stratosphere and the troposphere, but it is also apparent from Figure 5 that the annual mixing reaches maximum levels in March and April during the 9 years of monitoring ^{239,240}Pu. The ^{239,240}Pu/^{90}Sr ratio increased in the air sample in January at Thule (ratio = 0.056) compared with the other northern sampling stations (ratio = 0.021) during the same time period (Aarkrog, 1971), and this again is an indication of plutonium from the accident. Kudo, Zheng, Koerner, Fisher, Santry, Mahara et al. (1998) performed radioisotope measurements on ice cores from the Agassiz ice cap of Ellesmere Island (some one hundred kilometres north-west of the Thule air base). They found a Pu peak in these depth profiles, which they dated to 1968. This peak is probably from the People's Republic of China's nuclear test programme during which, an atmospheric test detonation of fission yield equivalent to 3 Mton TNT was performed in June 1967 (Perkins & Thomas,

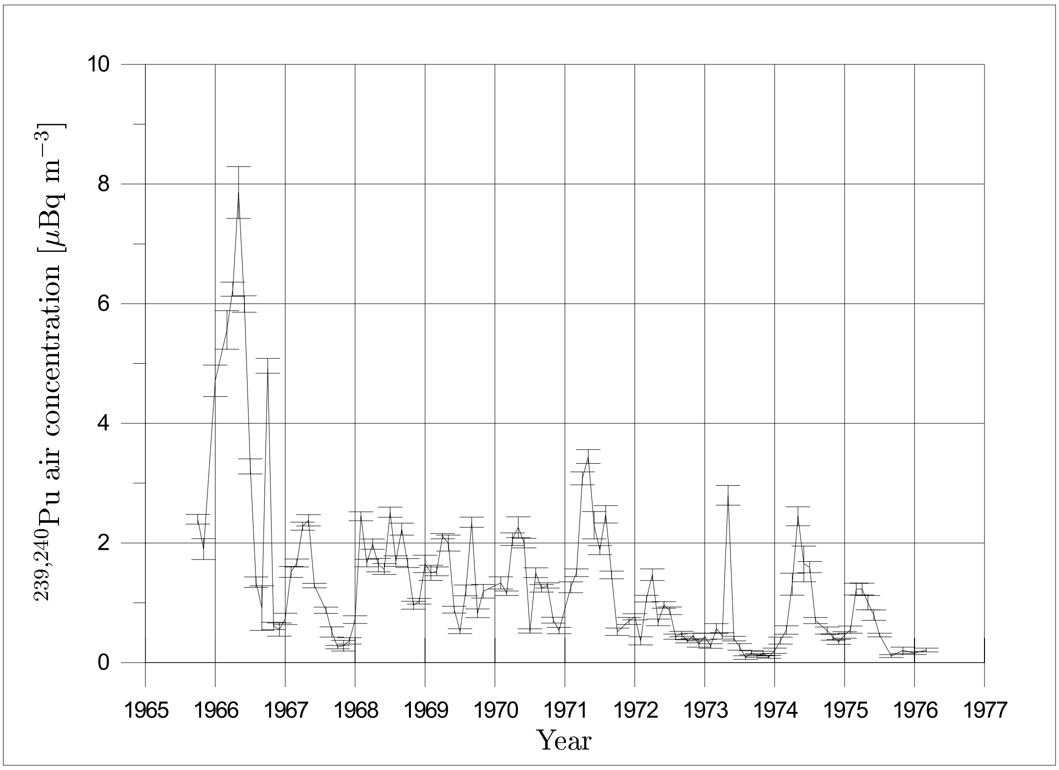

Fig. 5. EML measurements of the air concentration of ^{239,240}Pu at the Thule air base (EML, 1999).

1980), and not from the Thule accident, since the ^{137}Cs and the ^{239,240}Pu profiles in the ice follow each other. In Figure 5 it can also be observed that the air concentrations were much higher before the Thule accident and of the same order of magnitude some years after. The conclusion is that, if radionuclides from the accident are present in these lakes, they should not be very pronounced. However, the air sampling station is situated further to the east and at a higher altitude than the lakes studied, so the values might not be representative for the actual activity concentrations of the lakes studied.

In the debris from the accident the activity ratio of ^{238}Pu to ^{239,240}Pu is 0.014 (decay-corrected to the reference date 1997-09-01), (Eriksson, Dahlgaard, Ilus, Ryan, Chen, Holm et al., 1999). Fallout data have been reported from the Thule area by Hanson (1980). The ratios were 0.027 and 0.026 for ^{239,240}Pu/^{137}Cs and ^{238}Pu/^{239,240}Pu, respectively, (decay-corrected to the reference date 1997-09-01). As the explosion was not a fission explosion, no caesium would be expected from the accident. If the lakes contain plutonium from the accident the ratios would be higher for ^{239,240}Pu/^{137}Cs and lower for ^{238}Pu/^{239,240}Pu. In Figure 4 and in Table 2 it can be seen that our measurements agree with the global fallout ratios. Due to the very low sedimentation rates it is impossible to resolve a possible ^{239,240}Pu peak in the depth profiles shown in Figure 2. The ^{239,240}Pu/^{137}Cs ratio is not noticeably higher in the post-accident period (Figure 4) in any of the lakes. Our results indicate that resuspension in the eastern direction from the location of the accident point of impact and the contaminated areas have been minute. This is an important result as this means that the population at the Thule air base has not been exposed to any great extent to resuspended debris from the accident during the past 29 years. The ^{241}Am/^{239,240}Pu ratios vary between 0.40 and 0.61 (mean values for the sediment cores in the lakes). In the soil the ratio is lower (0.28) and this may indicate that americium is more mobile than plutonium, and is therefore transported to the lake more quackery. Data reported by Sokolik, Ivanova, Leinova, Ovsiannikova & Kimlenko (2001), showed that in all three soil types investigated (two mineral and one organic soil type) there was a much higher fraction of Am than Pu in the pore solution. The distribution coefficient, K_d, for Am in the solid phase-pore solution of the soil was more than twice as high as the K_d for Pu. In Figure 2 it can be seen that ^{241}Am has a broader peak than the other nuclides in the soil profile. This also gives an indication that Am is more mobile in the soil than the other nuclides studied.

4 Conclusions

No remobilization of radionuclides from the accident to the lakes has been observed. This indicates that the inhabitants of the Thule air base have been only very slightly exposed to resuspended nuclides originating from the accident, if at all. The sedimentation rates were too low to resolve a possible Thule accident peak from the global fallout peak in the sediments. However, there was no detectable plutonium contamination originating from the accident in the lake sediments, as the ^{239,240}Pu/^{137}Cs, ^{238}Pu/^{239,240}Pu and ^{241}Am/^{239,240}Pu ratios agreed with the global fallout values. Plutonium, americium and caesium are effectively scavenged from the water to the sediment. In this study it was observed that americium is more mobile in soil than plutonium, which is in agreement with the findings of Sokolik et al. (2001), however, our observation is based on one single soil core. The CRS dating agreed well with the fallout peaks in the sediment. In this study, it was also observed that ^{210}Pb in this area cannot be used as a normalised nuclide for the transport of actinides from the catchment area to the lake sediments.

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Table 2
The isotopic ratios in lake sediments and the soil core. The mean values are the geometrical mean of each slice in the cores. V in combination with a number represents the lake and S in combination with a number represents the sediment core.

Lake and Core	^{239,240}Pu / ^{137}Cs	^{238}Pu / ^{239,240}Pu	^{241}Am / ^{239,240}Pu
V1S1	0.0265 ± 0.0009	0.0571 ± 0.0024	–
V1S2	0.0259 ± 0.0015	0.0403 ± 0.0058	0.400 ± 0.028
Mean	0.0262 ± 0.0018	0.0487 ± 0.0063	0.400 ± 0.028
V2S1	–	–	0.619 ± 0.061
V2S2	0.0240 ± 0.0009	0.0284 ± 0.0014	0.456 ± 0.031
V2S3	0.0234 ± 0.0014	0.0287 ± 0.0037	–
Mean	0.0237 ± 0.0017	0.0286 ± 0.0040	0.538 ± 0.068
V3S1	0.0376 ± 0.0021	0.0234 ± 0.0021	0.315 ± 0.022
V3S2	0.0236 ± 0.0008	0.0226 ± 0.0016	0.419 ± 0.014
V3S3	0.0160 ± 0.0011	0.0223 ± 0.0052	0.642 ± 0.055
Mean	0.0258 ± 0.0025	0.0228 ± 0.0059	0.459 ± 0.061
Total Mean	0.0253 ± 0.0035	0.0318 ± 0.0095	0.475 ± 0.096
Soil			
V1M1	0.0369 ± 0.0020	0.0100 ± 0.0016	0.279 ± 0.019

BOK–2 programme.

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Paper III

Eriksson M.:
Plutonium Inventory Calculations in Sediments when Hot Particles are Present
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Plutonium Inventory Calculations in Sediments when Hot Particles are present

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Abstract

The inventory of plutonium in marine sediments, originating from the aircraft accident in 1968, in Thule (Greenland) has been calculated. Two different methods have been used for estimating the plutonium inventory in these activity heterogenous sediments containing hot particles. One of the methods assumes homogenous activity distribution and the activity is determined based on radiochemical separation followed by alpha spectrometry (conventional method). The other method is based on a non destructive technique, measuring the gamma emitting ^{241}Pu daughter ^{241}Am for the determination of ^{239,240}Pu. The design of the method makes it possible to evaluate how hot particles effect the inventory.

Plutonium from the accident has been dispersed to a distance of 99.3 km from the point of impact with a dispersion rate of 3.4 km y^{-1}. The Pu activity concentration in the sediment is best described by a bi-exponentially decreasing function of the distance from the point of impact.

The differences between the two total ^{239,240}Pu inventory estimation methods are significant, 9.6 TBq compared to 3.9 TBq. The lower estimate can be partly explained by the method assuming homogenous activity distribution, not using a representative sub-sample and also using an inadequate dissolution method not totally dissolving PuO$_2$-complexes.

1 Introduction

It is difficult to calculate an accurate inventory of plutonium in sediments when hot particles are present, as samples are heterogeneous and cannot be homogenised in terms of their activity concentrations. The main problems are outlined below.

1.1 Sampling treatment used previously for Thule sediments

There are several problems when determining activity concentrations of radionuclides in samples containing Pu hot particles. Due to poor resolution in the alpha spectra, the ^{239,240}Pu low energy tail will grow into the yield determinant peak (^{242}Pu) if a hot particle is included in the analyzed sub-sample, which prevented activity determination. In such cases in past studies, replicate samples were taken until a resolvable spectrum was obtained. Often only one such replicate sample was needed. This procedure inevitably results in an underestimation of the total activity.

Another problem (uncertainty) is that small sub-samples are used because the sediments are highly contaminated. Typically 0.5–1 g of $\sim$ 140 g has been used in determining the activity concentration in the Thule sediment samples. Such a small sub-sample is not representative of the whole sample when the activity is heterogeneously distributed in the slice, which is the case when Pu-hot particles are present.

A third problem is that the particles in the Thule sediments are present as PuO_2 [1]. Plutonium in this chemical form is difficult to dissolve using common chemical dissolution techniques, such as leaching with *Aqua Regia* [2]. Tests have shown that up to 40 % of the Pu activity remains undissolved when the plutonium is in this form [3]. The method used at Risø National Laboratory has been the one described by Talvitie [4], using *Aqua Regia* for leaching plutonium from samples. Therefore we know that the Pu activity in the Thule samples has been underestimated and for that reason the inventory is higher than published. Two of the problems described above (poor alpha resolution and leaching instead of using a total destruction technique) give a maximum measurable activity level of about 0.8 Bq ^{239,240}Pu per sub-sample. The hot particles therefore give rise to an uncertainty when the inventory is calculated.

There is also a fourth problem; sediment mixing caused by bioturbation, which has buried the plutonium deep down in the sediment [5]. The sediment corers used, Gemini and Haps, do not sample to depths below the mixing depth, and so will also result in an underestimate of the inventory. This is mainly a problem in close vicinity to the point of impact, where the plutonium originating from the accident is buried to depths greater than 20 cm. In Figure 2, data from Dahlgaard *et al.* (2001) [6], show depth profiles from the Thule-97 expedition where this effect can be seen.

To avoid the problem of small sub-samples, all of the sediment in each section could be totally dissolved and a small aliquot from the homogeneous activity solution could be used to determine the activity by ordinary alpha-spectrometry or by ICP-MS. However, this can be difficult as the dissolution problem of the PuO_2-complexes still remains and there are no radiochemical procedures reported of how to totally dissolve 140 g of sediment. It is important to keep in mind that the chemical yield determinant is in another chemical form, often Pu-nitrate. The chemical yield can therefore be very good even though some fractions from the PuO_2 particles may remain undissolved, for that reason the chemical yield calculated can be misleading.

There are relatively few hot particles in the Thule sediments, however, they carry most of the activity, as will be shown later. A method to get a more accurate estimate of the Pu-inventory could be to focus on measuring these. This could be done by gamma-measurement on the gamma emitting ^{241}Pu daughter ^{241}Am in the whole sediment slice sample. By this method the dissolution problem of the PuO_2-particle is excluded, and fairly large sub-samples could be used to determine the activity, which gives a more representive sub-sample. However, applying this technique to determine the plutonium activity requires that the activity ratios (^{241}Am/Pu and ^{241}Pu/Pu) are known in the whole sampling area. In addition, precautions must be taken as the ^{241}Am gamma energy is fairly low (E_γ = 59.6 keV) and self attenuation in the sample can be a problem. There are methods describing activity determinations when γ-emitting hot particles are present, i.e. Bunzl [7] and Kashparov *et al.* [8]. They stress the importance of measure the samples several times, mixing the sample between the different measurements, when hot-particles are present and a planar measurement geometry is used. As, if a hot-particle has a geometrically close position to the detector in the measurement geometry, it would overestimate the activity in the sample, and if the particle has a position "far away" one would underestimate the activity. Bunzl [7] also defines that a sample contains a hot particle if the different measurements of the same sample exceed a certain deviation. The magnitude of the deviation depends on the number of mixings performed and on the precision of the activity measurement. A similar study is also presented by Kashparov *et al.* [8]. Nageldinger *et al.* [9] define a hot particle as a material particle of any chemical and radionuclide composition with a size of up to 100 μm and an activity of not less than 4 Bq per particle. Nageldinger *et al.*'s [9] definition is less appropriate for Pu-alpha emitting hot particles as, in any environmental sample 4 Bq Pu would be considered a very high activity. Usually activity levels are 3–6 orders of magnitude lower (mBq–μBq) per sample. The most convenient definition of Pu hot particles in sediment is the one described by Bunzl [7].

1.2 Brief overview of the Thule accident

In January 1968 an aircraft accident involving four nuclear weapons took place in N.W. Greenland. A B-52 bomber, HOBO 28, caught fire and crashed on the sea ice in Bylot Sound, 11 km west of Thule Air Base. Both the aircraft and the four unarmed weapons disintegrated on impact and caused contamination of the surroundings. The non-nuclear explosions were due to the conventional explosive material in the detonators of the weapons. The fissile materials in the weapons were pulverized in the explosion, forming PuO_2 particles. Most of the plutonium was recovered during the clean up program "Crested Ice". However, approximately 3 kg of plutonium was not recovered according to USAF Nuclear Safety report [1] and Strand *et al.* [11]. More detailed descriptions of the accident are published elsewhere, [3, 6, 10].

On the Thule-97 expedition, which is the latest of a series of expeditions, a comprehensive sampling program was performed involving taking 56 double sediment cores, 30 water samples and 134 biota samples. Some of the results are reported elsewhere [6, 13, 14, 15].

Earlier studies in the Thule marine environment have assumed that the few hot particles observed in the sediment do not contribute significantly to the total inventory in the Bylot sound. In this paper, the influence of the hot particles on the plutonium inventory has been studied, based on samples from the Thule-97 expedition, using two different methods. One method assumes a homogenous activity distribution and uses high resolution alpha spectrometry and the other is based on a non destructive screening technique.

2 Material and Methods

2.1 Area studied

The Bylot Sound is located outside the Thule air base, 76°33N and 68°40W (NW Greenland). The sound is ice covered for about 10 months of the year. The maximum water depth is about 250 meters. The current in the Bylot Sound is predominately tidal [1] and there are two depressions, where fine grained sediments accumulate. The studied area and the sampling stations are indicated in Figure 1. The point of impact is denoted by V2 in the figure.

2.2 Field sampling

A 5 week international sampling cruise to the Thule area took place in August and September 1997.The sediments were mostly sampled by a Gemini corer from the research vessel Adolf-Jensen, but at locations with stony sediment the HAPS sediment corer was used. The sediment cores sampled by the Gemini were sliced into 1 cm slices and the cores sampled by the HAPS into 3 cm thick sections. The slices were frozen and stored in a cold room (-18°C) on the ship in plastic boxes. At some locations it was hard to sample the sea floor because of stones, most likely dropped from passing icebergs and/or because the fine sediment had been washed away by tidal bottom water currents.

2.3 Laboratory treatment

2.3.1 Preparation for alpha spectrometry

In the laboratory, the samples were weighed before freeze drying. The dry weight to wet weight ratios were determined. A one gram sub-sample was taken from every slice for Pu and Am determination. Plutonium and americium were separated using a method described by Talvitie and Holm [4, 16]. The sub-samples were ashed at 700°C for 2 hours, followed by wet ashing with *Aqua Regia*, ion-exchange was then used (AG 1×4, 100–200 mesh, BIO RAD). ^{242}Pu and ^{243}Am were used as yield determinants. The samples were electrodeposited onto stainless steel discs and measured by passivated implanted planar silicon (PIPS)-detectors. Discs with an activity higher than ~ 0.8 Bq were measured by a special high resolution setup (FWHM < 20 keV) in order to resolve the spike-peak (^{242}Pu) from the ^{239,240}Pu-peak.

Twenty of the samples were wet ashed in a microwave-oven with HF and HNO_3 in order to ensure that the Pu-oxide particles were totally dissolved. These samples were used for absolute calibration of the gamma measurements used in the screening experiment, which is described below.

2.3.2 Preparation for gamma spectroscopy

For the gamma screening experiment, sediment cores from 6 sites were selected. The sites were chosen on the basis that the activity concentration in Bylot Sound decreases exponentially with distance from the point of impact, [17, 18, 19]. The depth of the sediment cores varied between 7 and 20 cm, and they were split into one centimeter slices on board the research vessel Adolf-Jensen. From every sediment slice five aliquots were taken. In order to compare the results

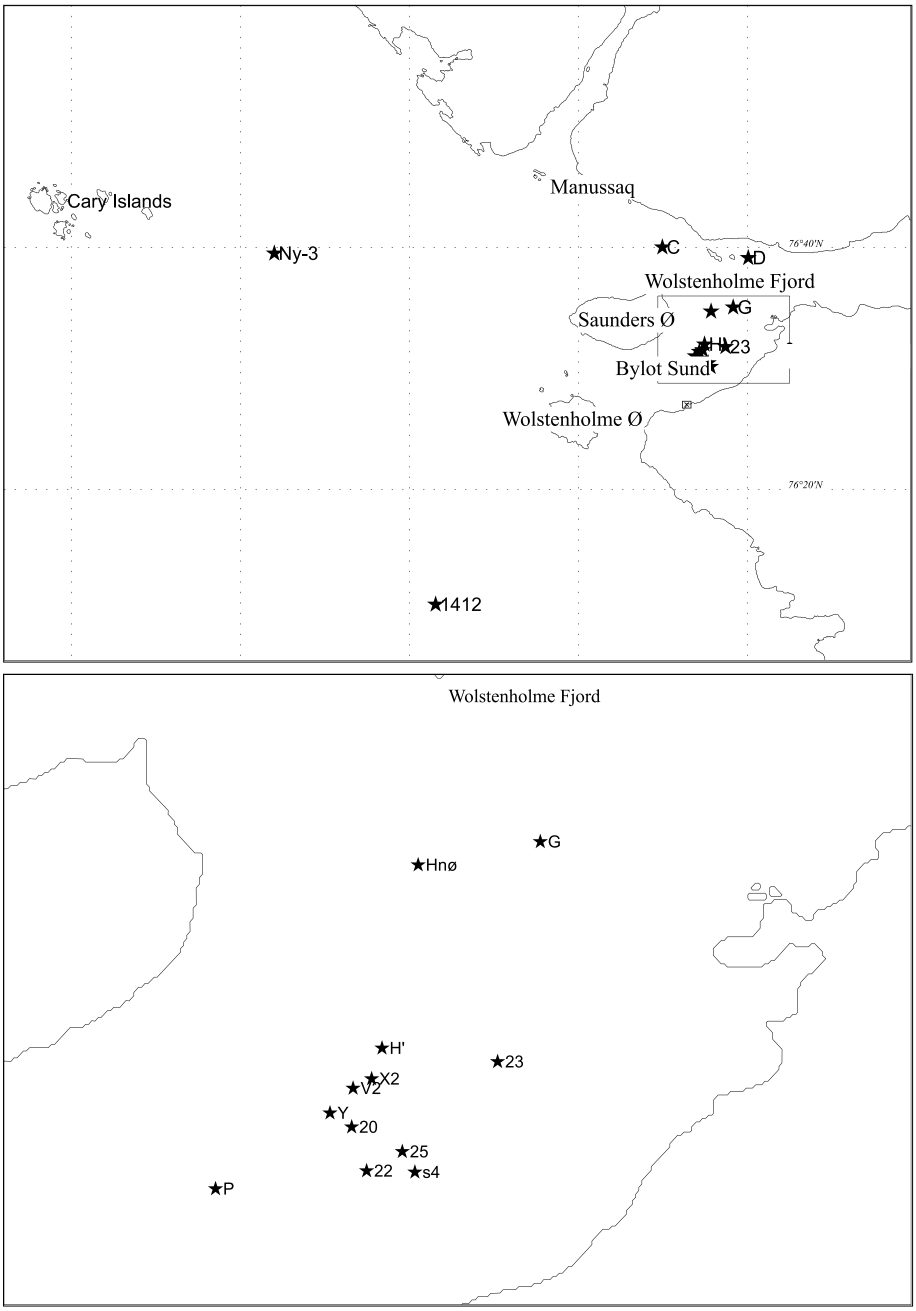

Figure 1: Sampling locations visited at the Thule-97 used in the present paper. Further information of the locations in Table 2. Point of impact is denoted V2.

with earlier expeditions, where the plutonium activity concentrations were based upon 1 g aliquots, and to be able to get an estimate of the variance of the activity concentration, 1 g sub-samples were taken. In total 440 samples were measured. The measurements were performed on a High Purity Germanium (HPGe) well-type detector and the acquisition time was about 3600 seconds. This gives a detection limit of $\sim$ 0.01 Bq ^{241}Am or 0.05 Bq ^{239,240}Pu, assuming ^{241}Am/^{239,240}Pu = 0.17. Advantages of using a small cylindrical geometry (Ø = 9 mm) are that self attenuation is small and that the count-rate is only slightly dependent on the position of the particle in the measured geometry.

The concentrations of ^{137}Cs and ^{210}Pb were determined on large sub-samples (10–15 g). Determination of ^{210}Pb was only performed for cores sampled by the Gemini corer. The measurements were done on HPGe-detectors with efficiencies between 25–40% and a low backgrounds.

2.4 Particle size distribution

The particle size distributions was investigated by autoradiography soon after the accident and the results are presented in the report "Crested Ice" [1]. In the snow sample the geometric mean diameter was 5.6 μm and for the ice sample the geometric mean diameter was 2 μm. The distributions were log-normal[1]. As the activity of a particle is proportional to the volume of the particle we have calculated the activity distribution of these particles, by the relationship described in Equation 1.

$$A_{particle} = \left(\frac{d}{2}\right)^3 \times k \tag{1}$$

where d is the diameter and k is a constant of proportionality.

2.5 Calculations of activity concentrations in the sediment

2.5.1 Conventional determination of Pu activity concentrations in the Thule sediments

For every sediment slice in a core the activity concentration was determined using a 1 g sub-sample from the well-mixed dry powder of the slices, i.e. :

$$A_{\text{slice}} = \frac{A_{\text{sub-sample}}}{m_{\text{sub-sample}}} \quad [\text{Bq kg}^{-1}] \tag{2}$$

where A_{slice} is the activity concentration, $A_{\text{sub-sample}}$ is the activity of the sub-sample and $m_{\text{sub-sample}}$ is the mass of the sub-sample. This activity concentration is then converted to activity per unit area. All the slices are then summed to obtain the inventory at the location:

$$A_{\text{Inventory, core}} = \sum_{i=1}^{N} A_{\text{activity in slice i}} \quad [\text{Bq m}^{-2}] \tag{3}$$

Here, $A_{\text{activity in slice i}}$ is the activity per unit area of slice i, and N is the number of slices in the core.

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[1] The notation "log" is in this paper refers to the natural logarithm

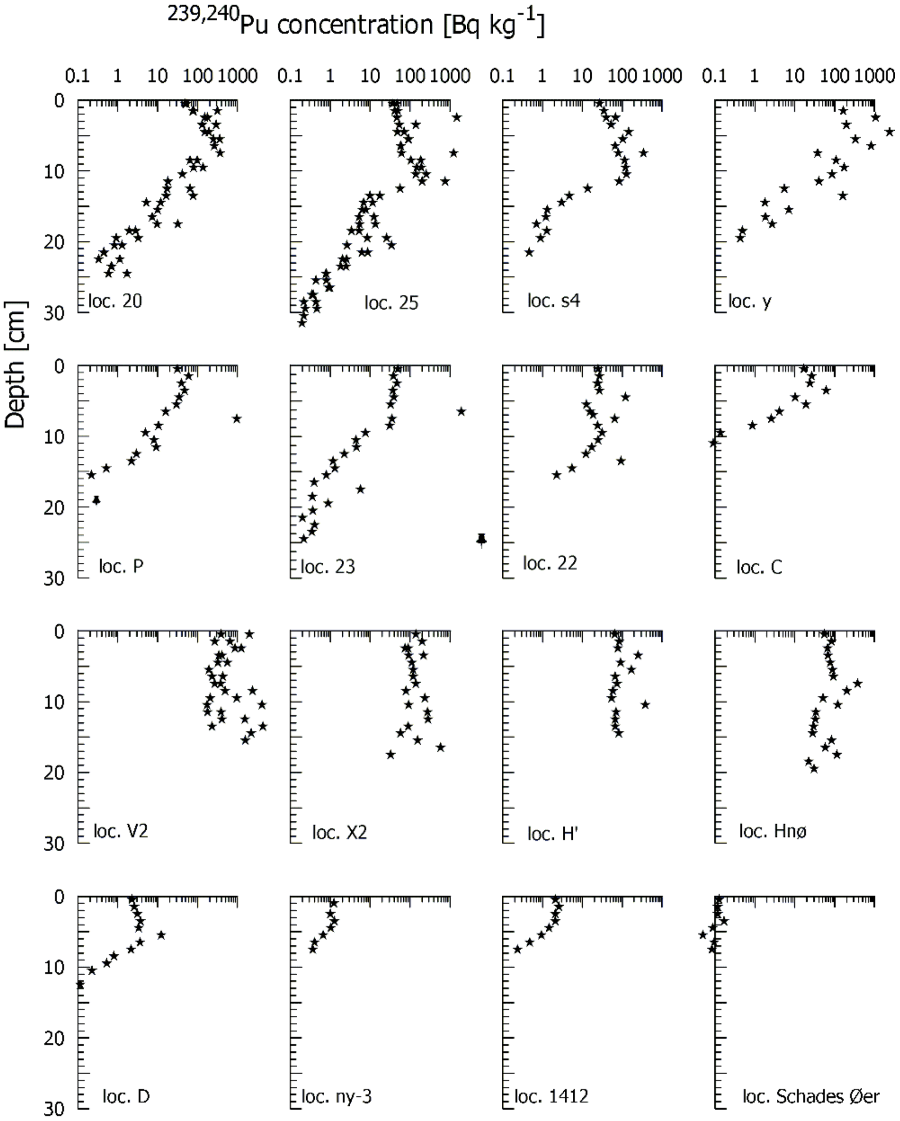

Figure 2: ^{239,240}Pu sediment profiles in sediment cores collected on the Thule-97 expedition. Figure from Dahlgaard et al. [6]

This is the conventional technique for calculating inventories. The technique is trouble-free when the activity distribution is homogeneous in the samples, which is not the case in the Bylot Sound. As an example of the biased evaluation using this technique; In Figure 2 a depth profile from location P (loc. P) can be seen. The calculated inventory at this location is 10 321 Bq m^{-2}, when assuming a homogeneous activity distribution. In this profile, a Pu-peak can be observed at a depth of 7.5 cm. This peak is due to a hot particle in the sub-sample of the sampled slice. When the activity concentration is calculated as in Equation 2, it is assumed that every equal amount of sub-sample contains a particle of this activity. Therefore, using this equation for the slice 7–8 cm at location P results in this slice containing 163 particles (dry weight of the slice = 163.6 grams, $m_{\text{sub-sample}} = 1.000$ g, $A_{\text{sub-sample}} = 1$ Bq) and that the other slices contain no particles.

It is obvious that this method does not give a proper picture of the situation and for that reason the inventory calculations are hard to evaluate. The result could also be understood as the total core having 163 particles, and this assumption is only based on one single particle. Particles are found in the sediments across most of the Bylot Sound and for that reason another calculation method of the inventory must be used in order to give a more accurate estimate of the total inventory of the plutonium from the accident. The conventional method only gives an uncertainty estimate from the measurement statistics for the alpha activity determination, and this uncertainty will not give the uncertainty of the number of particles. Also, as has been discussed before, there has been a cutoff in the measurable alpha activity of about 0.8 Bq and the chemical dissolution of Pu from the samples has not been complete, as a fraction will not dissolve.

2.5.2 New method for calculating activity concentrations in sediments when hot particles are present

In this study a screening experiment has been performed with gamma measurements, determining the gamma-emitting ^{241}Am in sub-samples as an indicator of Pu in the sediments, as described in section 2.3.2. The activity concentration, after conversion of Am to Pu, was calculated according to Equation 2 and 3. If the sediment core is sliced in N number of slices and 5 sub-samples from every slice are selected and measured, there are 5^N permutations (different sets of data) of core sets which the inventory can be calculated from, see Figure 3. The design of this survey allows an evaluation of the effect of hot particles on the inventory.

The selection of the core combinations was performed by a monte carlo program written in the statistic-program R [12]. From each site 10 000 core combinations were selected. Each combination includes one of the five gamma measured sub-samples from every sediment slice. This program was also used for calculating the local inventory of each of the six sites and the total inventory in the Bylot Sound.

The advantages of using this method for estimating the inventory are firstly that very high activity samples can be measured, without any cutoff limit in activity concentration as for the alpha measurements. More samples can be measured with a lower cost and a better estimate can be derived with uncertainties of this estimate.

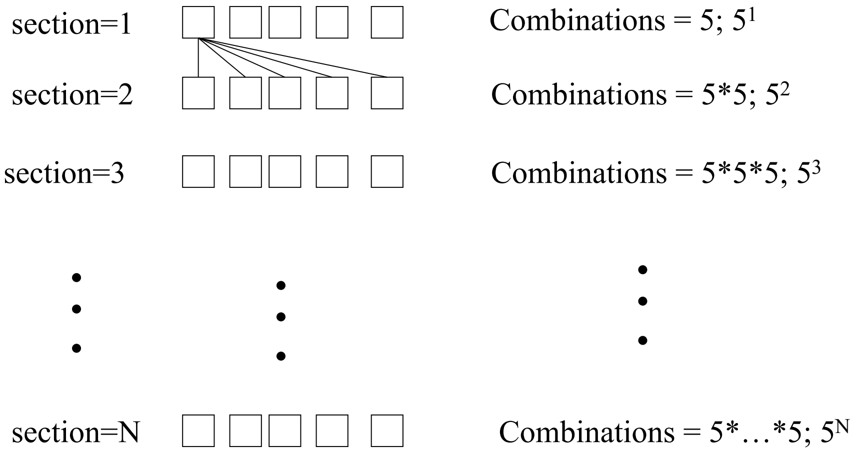

Figure 3: Illustration of the number of core combinations (permutations) that can be derived from a sediment core with N sections which have five measured sub-samples in every section.

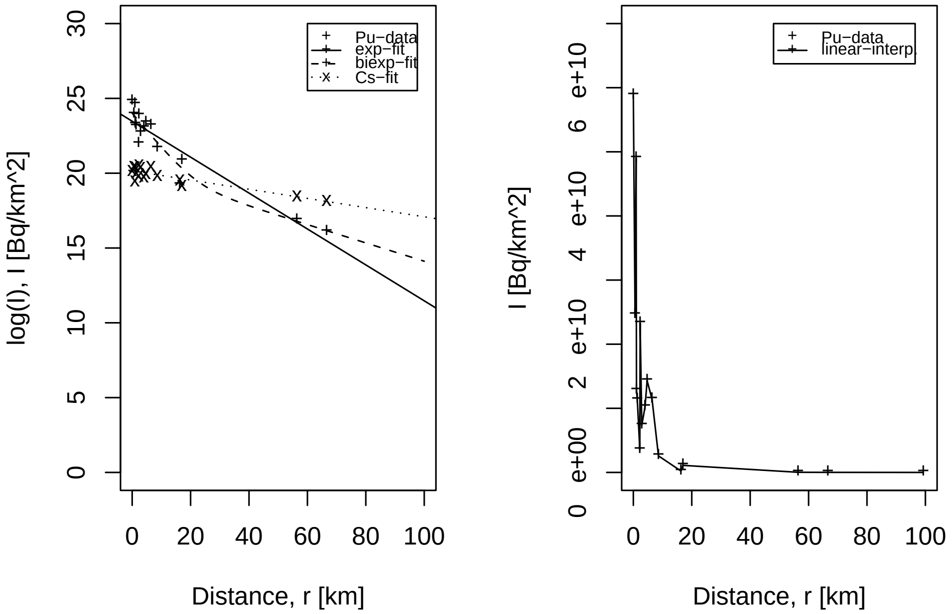

Figure 4: Illustration of the three different fits that have been applied to the local inventories, I [Bq/km^2], versus the distance, r [km]. ^{239,240}Pu data are symbolized with + and the ^{137}Cs data with ×. In the left diagram, which shows the natural logarithm of I, the bi-exponential and exponential fits are shown. To the right the discreet linear interpolated fit is shown.

2.5.3 Calculation of the total Inventory

Total inventory has been calculated using both methods described above. The total accidental plutonium inventory in the sediment has been calculated by integrating a fitted function, $A(r, \theta)$, to the local inventory, see Equation 4. It is assumed that we have equal dispersion of plutonium in all directions. The function, $A(r, \theta)$, is therefore independent of the direction, θ, and depends only on the distance, or radius r, from the point of impact. This assumption has also been applied to earlier estimates of the total inventory, [17, 18]. When the radius, r, is greater than 7.5 km it is estimated that the integrating area, $\Omega^{\star}_{r>7.5km}$, is covered by 60 % land, resulting in 40 % of seafloor to integrate over.

$$\text{Inventory} = \iint\limits_{\Omega} A(x, y)dxdy = \iint\limits_{\Omega^{\star}} A(r, \theta)rdrd\theta \tag{4}$$

The upper integration limit, r_{limit}, is determined by the ratio $^{239,240}\mathrm{Pu}/^{137}\mathrm{Cs}$ equaling the global fallout ratio. In these high arctic sea sediments, a fallout ratio of 0.18 has been applied. This is the decay corrected value, to 1997, as Aarkrog et al. [18] have applied in earlier estimates. The integration limit, or dispersion distance, r_{limit}, was derived from the exponentially fitted functions for $^{239,240}\mathrm{Pu}$ to $^{137}\mathrm{Cs}$. This means that Equation 4 can be written as:

$$\text{Inventory} = 2\pi \int\limits_{r=0}^{7.5km} A(r)rdr + 0.4 \cdot 2\pi \int\limits_{r>7.5km}^{r_{limit}} A(r)rdr \tag{5}$$

3 Results and Discussion

3.1 Particle size distribution

In Figure 5 the particle activity distributions can be seen in the peak to the left. This is the distribution that occurs if a log-normal distribution of the particle diameter with a mean of 2 μm and with a log standard deviation of one is applied. The constant, k, is set to 0.001 Bq $\mu\mathrm{m}^{-3}$. The calculation of k is derived from studies on single hot particles which will be published elsewhere. From the distributions it can be derived that only 1.3 % of the particles have an activity over the cutoff activity level of 0.8 Bq (equal to a diameter of about 18.5 μm), however these particles carry about 79 % of the total activity.

These distributions were only valid for the particles found in the contaminated ice area after the accident in 1968. Therefore, they can not simply be applied to all the sediment in this area. It is not clear from the cited references if these particle size distributions were measured before or after the clean up program. If the distributions were valid after the clean up program, it still can not simply be applied to the sediments, as the particle transport through the ice may depend on the size and activity. Also, the sedimentation rate through the water column depends on the size and density of the particles. It is expected

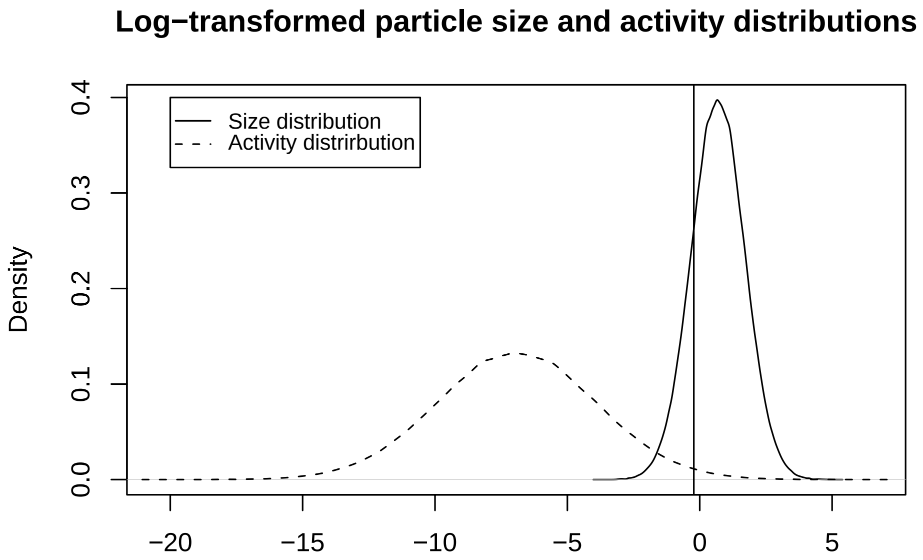

Figure 5: Particle distribution. The solid line shows the log-normal distribution function of the particle diameter (deduced from Project Crested Ice [1]), in μm, of the particles, mean diameter of 2 μm and with an log standard deviation of one. The dashed line is the particle activity distribution derived from the size distribution by Equation 1. The mean activity is 0.001 Bq with a log standard deviation of 3. The two distributions are log-transformed.

though, that the largest particles would have settled fastest and thereby also settled closest to the point of impact. Smaller size fractions may have been transported further away by the tidal current and settle to the sediment at greater distances. Therefore, it may be expected that the particle size distribution would be a function of distance from the point of impact and probably the size distribution may have a higher mean value at the point of impact compared with the distribution on the ice. These considerations are important because the few large hot particles carry most of the activity, and for that reason they are very important when inventory estimations are carried out. It is clear, from the results from the Thule-97 expedition as well as earlier expeditions, that the hot particles are mostly found within a 6 km radius from the point of impact.

3.2 Results from the conventional method of calculating the total plutonium inventory in the Bylot Sound, based on alpha spectroscopy.

Table 2 gives inventories of ^{239,240}Pu, based on alpha spectroscopy measurements, and of ^{137}Cs determined by γ-spectroscopy. The excess ^{239,240}Pu is derived by subtraction of the expected global fallout plutonium calculated from the ^{137}Cs data and the global fallout ratio. The global fallout ratio ^{239,240}Pu/^{137}Cs was set to 0.18. It is assumed that Pu has a similar transport mechanism to Cs in the sedimentation process, i.e. near shore sediments have the same global fallout ratio as sediments far from the shore. The ^{137}Cs concentration seems, as has also been observed in earlier investigations [18, 19], to decrease exponentially as a function of distance from the point of impact. This can be explained by the fact that the crash occurred over one of the depressions in the Bylot Sound where the sedimentation rate may be higher. The fitted exponential function to the ^{137}Cs data in Table 2 is:

$$A(r,\theta) = 567.16 \cdot 10^6 \cdot e^{-0.0308 \cdot r}.$$

The excess Pu data is best fitted to a decreasing bi-exponential function of the distance from the point of impact, instead of a mono-exponential function as have been used in earlier studies. This can be seen in the left diagram in Figure 4, where the excess ^{239,240}Pu is plotted against the distance in a log-diagram. In a study of bioturbation, mixing and resuspension using a bioturbation model, which will be published elsewhere, it is shown that the sampling stations D, 1412 and Ny–3 have mainly been contaminated by recent input of plutonium which originated from the accident. For the other stations it seems as the main contamination occurred soon (until the ice broke up) after the accident. It was observed that when the ice broke up in the summer following the accident, the ice drifted to the north and out of Bylot Sound [1, 10].

These observations may explain the bi-exponential decrease in concentration as a function of distance from the point of impact. The fast decreasing component in the function would then reflect the ice drift where the contaminated ice melted, resulting in the release of particles which sank to the seafloor during the ice drift. The slow component could represent the resuspension from the initially contaminated areas. There is also another compartment, which can be considered to be included in the fast component. This was the very first moment at impact (4:39 p.m. Atlantic Standard Time, 21 January 1968) where an area of about 2500 m^2 was broken up by the momentum of the impact of the aircraft on the ice and the exploding weapons. Through this hole, which was refrozen quickly, debris from the aircraft and an unknown amount of plutonium were transported to the seawater and the seafloor. The plutonium particles could at this moment have been transported some kilometers away from the impact site as there is a tidal current with a maximum speed of 0.40 knots to the south-south-west and at spring tide, 0.10 knots to the north-north-east.

One explanation that no such bi-exponential function has been observed in earlier studies could be that there has been limited sediment investigations of sites outside the Bylot Sound and that the ^{239,240}Pu and ^{137}Cs data from sampling stations outside the Bylot Sound could not be compared as the nuclides were measured in different sections of the core. As an example, on the Thule-91 expedition measurements were performed to a distance of 8.7 km from the point of impact [19], resulting in one fast decreasing mono-exponential function. There were measurements further away, but the ^{239,240}Pu/^{137}Cs ratios could not be determined as measurements were performed on different sections of the core.

The first investigations performed in 1968 on accidental plutonium in the Bylot Sound sediments, used a somewhat different method for estimating the total Pu inventory. In that study it was assumed that most of the activity was dispersed within a 30 km^2 elliptical area centered around the point of impact [10]. From the mean ^{239,240}Pu concentration in this area the total inventory was calculated. The result from this calculation was 3 Ci (0.15 TBq). In addition, the ^{239,240}Pu concentration was based on the uppermost centimeter (0–2 cm) of the sediment. In the second reported investigation [17], the activity concentration was assumed to follow either a mono-exponential function or a power function of distance, i.e. $A(r,\theta) = A_0 \cdot r^{-k}$. These functions were integrated out to a radius of 45 km. The calculated inventory from these two integrated functions were 29 and 32 Ci (1.4 and 1.5 TBq) respectively.

Eriksson et al. (1999) [15] reported an inventory of 1.7 TBq. This estimate was based on some of the Thule-97 data. However, there were fewer sampling stations included and the electroplated Pu disks with an activity higher than 0.8 Bq had not yet been analyzed in the high resolution alpha spectrometric device. Also, the upper integration limit, r_{limit}, was less than the limit used in the present study as the global fallout ratio used was higher. The inventory calculation was based on a exponential function ($A(r, \theta) = 20.813 \cdot 10^9 \cdot e^{-0.2296 \cdot r}$), which will be shown later in this article to give an under estimation of the total inventory.

As mentioned before, in the present investigation three different functions have been fitted to the ^{239,240}Pu concentration data. Firstly a bi-exponential function, which is assumed to be the most correct, where the ^{239,240}Pu concentration at different distances is given by:

$$A(r, \theta) = 25.945 \cdot 10^9 \cdot e^{-0.2303 \cdot r} + 0.616 \cdot 10^9 \cdot e^{-0.0489 \cdot r}$$

Secondly a single exponential function, to be able to compare the total inventory with earlier estimates, where the ^{239,240}Pu concentration is given by:

$$A(r, \theta) = 14.035 \cdot 10^9 \cdot e^{-0.109 \cdot r}$$

In addition, one discreet function that assumes that the concentration varies linearly between two neighbouring (referring to the distance from the point of impact) sampling stations as:

$$A(r, \theta) = \sum_{i=1}^{15} A_i + k_i r_i$$

The values of A_i, k_i and r_i can be seen in Table 1. The reason for including such a function is that the local inventories at the sampling stations close to the point of impact, r < 5 km, do not follow an exponential nor a perfect biexponential curve. This is because of the heterogenous activity concentrations the data shows. Therefore, in this inner area, the activity concentration can be explained just as well by a linear variation between sampling stations.

The upper integration limit, r_{limit}, was determined from the slowly decreasing component ($\ldots 0.616 \cdot 10^9 \cdot e^{-0.0489 \cdot r}$) from the bi-exponential function describing the ^{239,240}Pu concentration and the function describing the ^{137}Cs concentration. Using the global fallout ratio of 0.18 results in that r_{limit} equals to 99.3 km, i.e. the dispersion rate may be estimated to 3.4 km y^{-1} (99.3 km/29 y).

The inventory derived by the alpha measurements can be seen in Table 2 and the inventory integrated to different distances from the point of impact can be seen in Table 5. The three different integrated functions turn out to about 3.9 TBq. This is considerably higher than the inventory reported earlier. This is because the sampling stations Loc 1412 and Ny–3 are included in the calculations, as they have excess plutonium originating from the accident, resulting in that the fitted functions decrease much more slowly. Another explanation of this higher estimate is that a high resolution alpha spectrometry was used, so that re-sampling was not needed. It can be seen in the table that the older estimates of about 1.5 TBq are obtained somewhere between 6.4–7.5 km from the point of impact. The 3.9 TBq estimate could be considered an underestimate for three reasons. Firstly, the radiochemical technique used is insufficient to completely dissolve the Pu-oxide matrices, resulting in that hot particles to a great extent

Table 1: The coefficients A_i and k_i valid in different intervals r_i

i	1	2	3	4	5	6	7	8
$r_i[km]$	0–0.58	0.58–0.94	0.94–1.07	1.07–1.36	1.36–2.21	2.21–2.33	2.33–2.89	2.89–4.01
$A_i[Bq]$	5.88E+07	2.46E+07	4.90E+07	1.28E+07	1.13E+07	3.52E+06	2.33E+07	7.35E+06
$k_i[Bq/km]$	-5.91E+07	6.79E+07	-2.78E+08	-5.20E+06	-9.19E+06	1.65E+08	-2.85E+07	2.59E+06
i	9	10	11	12	13	14	15	16
$r_i[km]$	4.01–4.71	4.71–6.40	6.4–8.6	8.6–16.3	16.3–17	17–56.4	56.4–66.6	66.6–99.3
$A_i[Bq]$	1.03E+07	1.43E+07	1.14E+07	2.58E+06	2.23E+05	1.10E+06	2.11E+04	9.78E+03
$k_i[Bq/km]$	5.80E+06	-1.71E+06	-4.02E+06	-3.06E+05	1.25E+06	-2.74E+04	-1.11E+03	-2.99E+02

are excluded. Secondly, as can be seen in Dahlgaard et al. [6] Figure 4 of Pu depth profiles, that the sediment sampled at stations V2, X2, H' and Hnø do not reach zero activity by the deepest sediment section. In fact these profiles show a constant concentration all throughout the sampled sediment core, i.e. the inventory is underestimated. The third reason is that only one aliquot was used and that this single 1 g aliquot cannot be considered as a representative sub-sample in these activity heterogenous sediments.

3.3 A new calculation of the total plutonium inventory in the Bylot Sound, based on γ-spectrometry.

To be able to compare the γ-screening experiment with earlier estimates and to confirm that hot particles play an important role for the total inventory, two calculations were performed. The first was when all the data obtained were included, and secondly, the sub-samples with an activity concentration over 1.8 Bq/sample (which was the highest activity measurable by the alpha spectrometric measurements) were set to this value, i.e. exclusion of hot particles. By doing this, the inventory result would be in the same order as the data obtained from the alpha spectrometric measurements.

In Figure 6 the results from the 10 000 calculations of the local inventory from each of the selected 6 sites can be seen.

One would expect to see a log-normal type distribution as several sub-samples were measured which would be expected to include most of the particle sizes. However, as can be seen for the inventory distributions for location V2 (the point of impact) and location P (4.01 km from the point of impact), the inventory distribution is very dependent on the hot particle. Location V2 has several hot particles, 9 of the 70 sub-samples measured have an activity over 1 Bq, but the calculated inventory distribution is dominated by two of these hot particles. One particle is of 50 Bq in slice 10–11 cm and the other is of 153 Bq in slice 4–5 cm depth. In Figure 6 where the inventory distribution at location V2 can be seen, the first peak in the histogram is the distribution when neither of these large hot particles is included in the calculation and the second peak is when the 50 Bq particle is included but not the 153 Bq particle. The third is when the 153 Bq particle is included but not the 50 Bq particle, and the fourth peak is the distribution with both particles included. The probability that one of the particles is included is 1/5, as there are 5 sub-samples in each sediment slice, and the probability of including both is 1/25. The inventory distribution at location P is somewhat more difficult to explain. There are 4 particles that dominate the inventory distribution. Three of these are located in the sediment slice 5–6 cm (1.61, 1.62 and 2.79 Bq respectively) and there is one hot particle in the slice 10–11 cm of 2.37 Bq. The first peak is for combinations excluding all of these particles. The second peak is when one of the two particles with activities of 1.61 and 1.62 Bq is included. The third peak is when one of the higher activity particles (2.79 and 2.37 Bq) is included. As three of the particles are in the same sediment slice none of these can be combined and summarized in the inventory calculations but all of them can be combined with the hot particle in slice 10–11 cm and the fourth and fifth peak are representing these combinations, i.e. the forth peak is if either of the 1.61 and 1.62 Bq particles are combined with the 2.37 Bq particle and the fifth peak is the combination of the 2.79 and 2.37 Bq particles.

Table 2: Inventory of ^{239,240}Pu determined by alpha spectroscopy.

Location	Total Pu [Bq/m^2]	Excess Pu [Bq/m^2]	Integrated Excess Pu [%]	^{137}Cs [Bq/m^2]	Location Latitude Longitude	Distance from impact [km]	Water depth [m]
V2	58938	58834	-	575	76°31.366'N 69°17.035'W	0	185
X2	24738	24560	0.9	768	76°31.505'N 69°15.841'W	0.58	181
Y	49072	49020	2.6	289	76°30.997'N 69°18.518'W	0.94	216
20	12973	12841	3.2	735	76°30.789'N 69°17.121'W	1.07	233
H'	11419	11332	3.9	482	76°31.962'N 69°15.176'W	1.36	183
22	3591	3518	5.6	406	76°30.137'N 69°16.167'W	2.21	196
25	23445	23294	6.2	839	76°30.424'N 69°13.876'W	2.33	237
s4	7481	7354	9.7	705	76°30.117'N 69°13.068'W	2.89	241
P	10321	10253	15	378	76°29.869'N 69°25.864'W	4.01	211
23	14397	14312	21	470	76°31.761'N 69°07.760'W	4.71	207
Hnø	11548	11414	40	747	76°34.688'N 69°12.855'W	6.40	199
G	2654	2579	48	415	76°35.032'N 69°05.014'W	8.60	195
D	277	223	55	302	76°39.115'N 68°59.652'W	16.3	89
C	1138	1099	56	215	76°39.993'N 69°30.179'W	17	120
1412	40	21.1	98	105	76°10.488'N 70°50.687'W	56.4	640
Ny-3	24	9.78	99	79	76°39.485'N 71°47.955'W	66.6	505

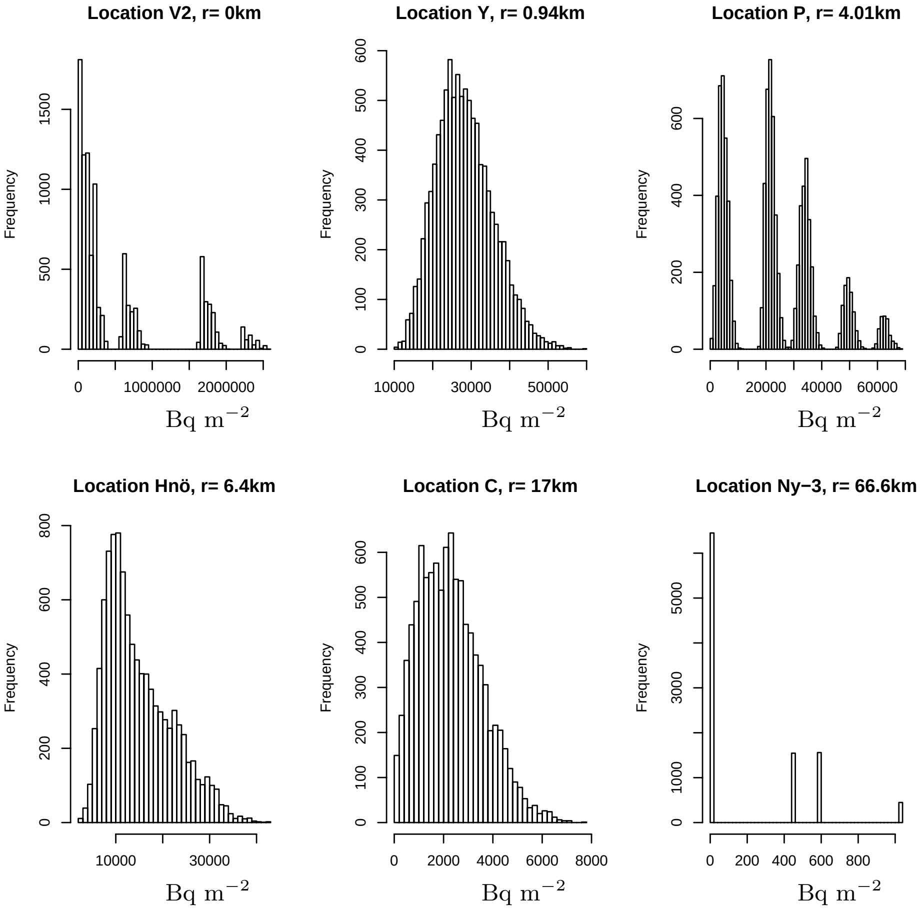

Figure 6: ^{239,240}Pu inventory distributions calculated from 10 000 sediment core combinations (permutations). It is clear that the distributions for locations V2 and P are highly influenced by hot particles. The statistics for each distribution can be seen in Table 3

At location Ny–3 only 2 of the 35 measured sub-samples were over a detectable level, however, these two measurements are considered as outliers. The activity at this location was too low to make any reasonable assessment of the local inventory and no hot particles appear to have been transported to this location. Therefore, the alpha spectrometric determined activity concentrations were used in the calculation procedure of the total inventory, see below.

The statistics for the local inventory distributions in Figure 6 can be seen in Table 3. As the distributions are not normal distributions, the standard deviations from the mean value have limited value. The results are instead represented with the minimum, maximum, mean and the median values. The first quadrant (1st Qu.) and the third quadrant (3rd Qu.) values are also included in the Table[2].

In Figure 7 the distributions obtained when a cutoff of 1.8 Bq/sample was

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[2] 50 % of the results, with the center median value, are included between the 1st and the 3rd quartile.

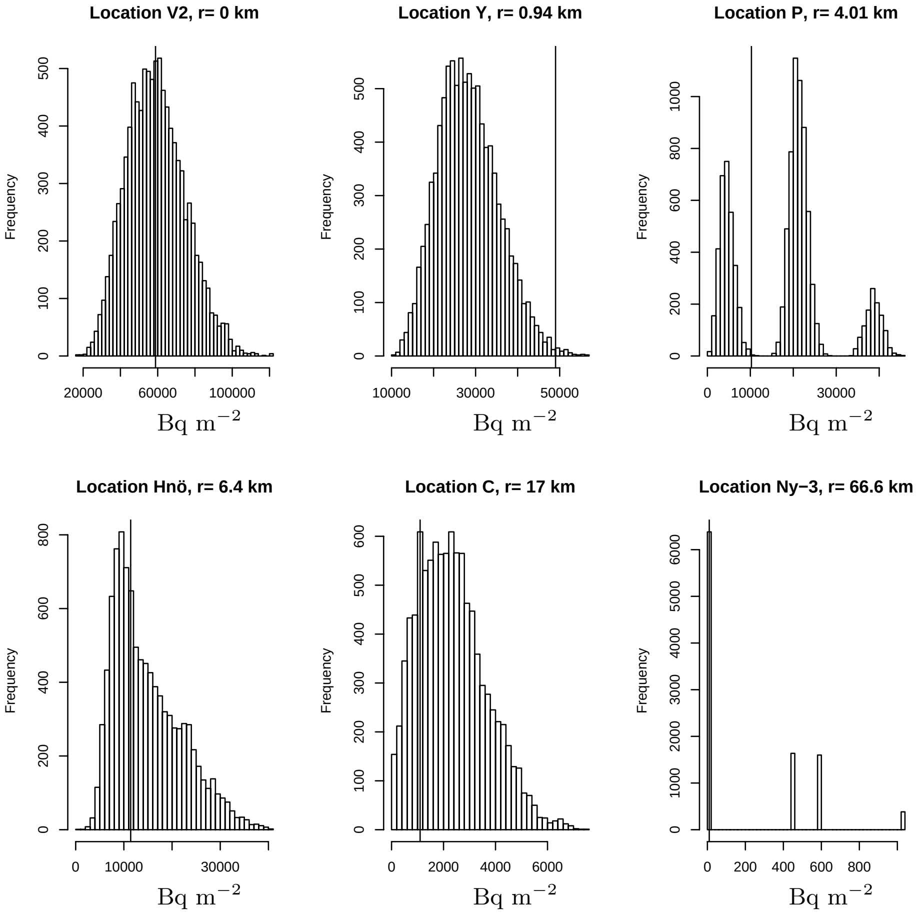

Figure 7: ^{239,240}Pu inventory distributions calculated as in Figure 6, but with a cutoff of 1.8 Bq/sample. The vertical lines indicate the inventory determined by alpha spectrometry. The statistics for each distribution can be seen in Table 4

applied. The vertical line in each distribution is the local inventory obtained from the alpha spectrometric measurements. The gamma screening results, when the cutoff is applied, is in accordance with the alpha spectrometric results, which support the hypotheses that the earlier estimates of local inventory have underestimated the amount of plutonium. It is also clear that the hot particles play an important role at the locations close to the point of impact. For that reason, when determinations of Pu inventory are to be done closed to the point of impact, the gamma screening technique should be used instead of the commonly used alpha spectrometric technique, whereas at locations Hnø and C either method of estimating the inventory can be used. At location Ny–3 the gamma screening technique of the sediment core is of no use and alpha spectrometric methods must be used to derive the activity concentrations.

A synthesis of the calculated total accidental inventories of ^{239,240}Pu is given in Figure 8. The different Pu inventory distributions are derived from 10 000 integrations of the 10 000 fitted curves for each of the different fitted functions.

Table 3: ^{239,240}Pu inventories [Bq m^{-2}] statistic summary of the distributions from Figure 6.

	Min	1st Qu.	Median	Mean	3rd Qu.	Max.
Location						
V2	15270	68930	212200	561100	722800	2561000
Y	10090	22920	27640	28250	32980	59940
P	356.1	5942	21820	23040	33860	68870
Hnø	2247	9456	13120	14940	19520	42600
C	0	1277	2167	2290	3110	7630
Ny-3	0	0	0	205.5	446.4	1028

Table 4: ^{239,240}Pu inventories [Bq m^{-2}] statistic summary of the distributions from the Figure 7, when a cutoff of 1.8 Bq is applyed. The figures are in Bq m^{-2}.

	Min	1st Qu.	Median	Mean	3rd Qu.	Max.
Location						
V2	17420.0	49860	61010	62170.0	73170.0	125500
Y	11190.0	22960	27240	28010.0	32360.0	53450
P	356.1	5490	20670	17940.0	23130.0	45940
Hnø	2826.0	9466	13000	14780.0	19220.0	39370
C	0.0	1292	2179	2313.0	3152.0	7593
Ny-3	0.0	0	0	202.9	446.4	1028

The histograms A (bi-exponential fit), B (exponential fit) and C (discrete function fit) are the real distributions when the data do not have any cutoff limit and D, E and F are the corresponding inventory distributions obtained when a cutoff of 1.8 Bq/sample is applied. In Tables 6 and 7 the statistics for each distribution can be seen. The tables also represent inventories out to different radiuses from the point of impact. The total estimated inventory statistics can be seen in the column with the header 0–99.6 km in each table. The median values for the total inventory is 9.5 TBq (1st Qu. = 6.7 TBq and 3rd Qu. = 13.2 TBq) for the bi-exponential fitted functions and 8.7 TBq (1st Qu. = 6.9 TBq and 3rd Qu. = 11.2 TBq) for the exponential fitted functions. In Table 6 it can be seen that the exponential fitted integration gives the lower value close to the point of impact and that the bi-exponential and the linear fitted integrations give equal amount of plutonium. The linear fitted integration probably overestimates the amount of plutonium at distances over 17 km as no real physical explanation for such dispersion can be given.

One criticism of these inventory estimations could be that only 6 sites are included. When a cutoff of 1.8 Bq/sample has been applied, the inventory agrees well with the data obtained from the alpha spectrometric measurements. However, the total inventory for the alpha spectrometric measurements is about 1.7 times higher when only the 6 sampling sites used in the gamma screening experiment are considered in the integration (”Exp-fit,6p” in Table 5), compared to if all sites are included (”Exp-fit” in Table 5). For that reason the total inventory calculated from the gamma screening experiment may be overestimated by a factor of 1.7. However, 2 of the 6 sites (V2 and Hnø) have underestimated

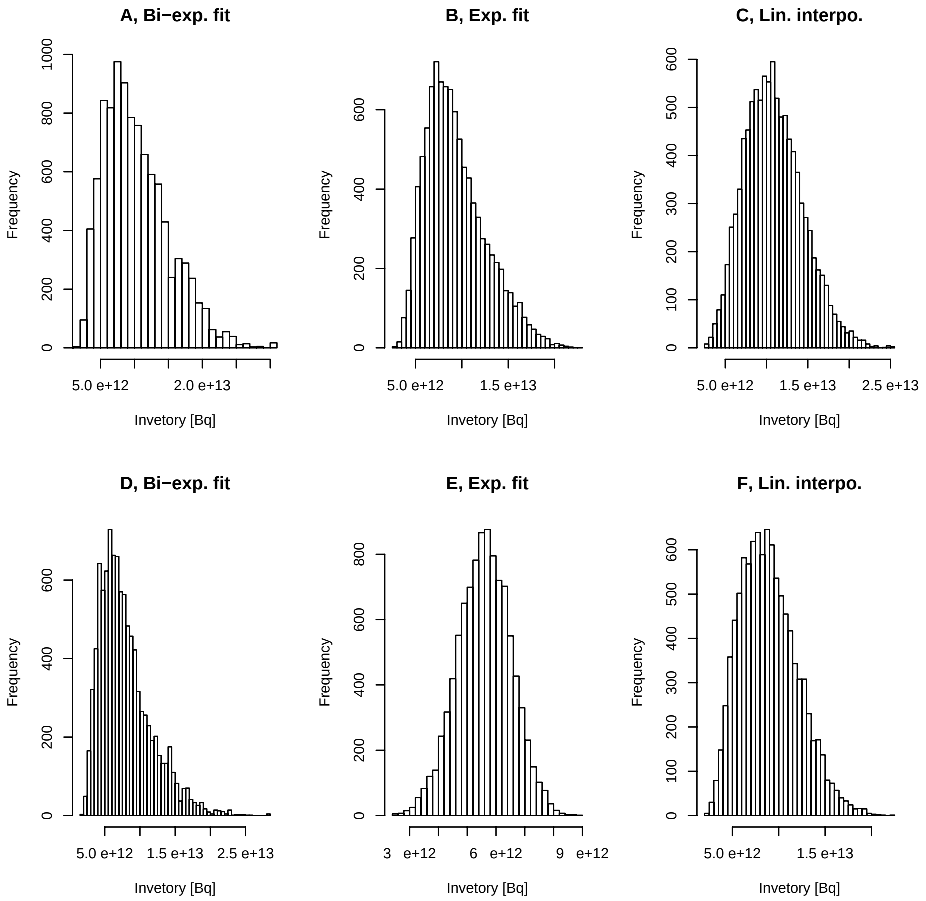

Figure 8: Histogram of the ^{239,240}Pu inventories [Bq] based on 10 000 integrations. Histogram A, B and C are derived with no cutoff of the activity in the sub-sample. For histogram D, E and F a cutoff of 1.8 Bq/sample is used. The statistics for the total inventory results are seen in Tables 6 and 7 in the column with the header, 0–99.3 km.

inventories as the sampled sediment cores have not reached background activity levels, see Figure 2. So the correction factor of 1.7 is overestimated.

4 Conclusions

This study illustrates the difficulties in determining activity concentrations and inventories in areas contaminated with hot particles. The key problem in these areas is deciding what should be considered a representative sample for the inventory calculation. Specific problems for the high arctic environment are the remote location and difficult sampling conditions with severe weather and drifting ice which sometimes make sampling impossible, and that the nuclides studied are mostly alpha emitters. In general, the problem of estimating the inventory in heterogeneously contaminated areas is more difficult for alpha emitting nuclides

Table 5: ^{239,240}Pu inventory [Bq] calculated from alpha measurements at different distances derived by three different fit methods. Exp-fit,6p is the Integrated function $A(r,\theta) = 28.028 \cdot 10^9 \cdot e^{-0.1243 \cdot r}$

From Alpha	0–0.94 km	0–4.01 km	0–6.4 km	0–7.5 km	0–17 km	0–66.6 km	0–99.3 km
Biexp-fit	8.966e+10	7.023e+11	1.365e+12	1.697e+12	2.748e+12	3.848e+12	3.856e+12
Exp-fit	4.030e+10	5.772e+11	1.227e+12	1.553e+12	2.583e+12	3.653e+12	3.661e+12
Linear-fit	1.029e+11	5.994e+11	1.590e+12	2.030e+12	2.463e+12	4.172e+12	4.203e+12
Exp-fit,6p	7.200e+10	1.023e+12	2.161e+12	2.728e+12	4.481e+12	6.185e+12	6.196e+12

Table 6: ^{239,240}Pu inventory [Bq] statistics at different distances derived by three different fit methods without cut of of the activity level.

	0–0.94 km	0–4.01 km	0–6.4 km	0–7.5 km	0–17 km	0–66.6 km	0–99.3 km
Biexp-fit							
Min.	3.677e+10	3.669e+11	6.510e+11	8.024e+11	1.346e+12	1.846e+12	1.847e+12
1st Qu.	1.243e+11	6.775e+11	1.220e+12	1.504e+12	2.716e+12	6.385e+12	6.729e+12
Median	1.837e+11	8.225e+11	1.489e+12	1.834e+12	3.385e+12	8.689e+12	9.553e+12
Mean	2.522e+11	8.965e+11	1.658e+12	2.066e+12	3.727e+12	9.273e+12	1.031e+13
3rd Qu.	3.428e+11	1.029e+12	1.859e+12	2.356e+12	4.511e+12	1.161e+13	1.318e+13
Max.	7.789e+11	2.084e+12	3.996e+12	5.015e+12	9.570e+12	2.612e+13	3.051e+13
Exp-fit							
Min.	2.601e+10	3.774e+11	8.097e+11	1.029e+12	1.745e+12	2.572e+12	2.580e+12
1st Qu.	8.042e+10	1.142e+12	2.412e+12	3.042e+12	4.998e+12	6.904e+12	6.914e+12
Median	1.089e+11	1.529e+12	3.205e+12	4.031e+12	6.505e+12	8.731e+12	8.741e+12
Mean	1.199e+11	1.673e+12	3.492e+12	4.384e+12	7.028e+12	9.312e+12	9.323e+12
3rd Qu.	1.496e+11	2.078e+12	4.318e+12	5.411e+12	8.594e+12	1.122e+13	1.123e+13
Max.	3.441e+11	4.671e+12	9.550e+12	1.188e+13	1.831e+13	2.274e+13	2.275e+13
Linear-fit							
Min.	4.283e+10	4.134e+11	8.034e+11	1.041e+12	1.791e+12	2.514e+12	2.545e+12
1st Qu.	1.198e+11	1.176e+12	2.302e+12	2.911e+12	4.599e+12	8.261e+12	8.292e+12
Median	2.436e+11	1.598e+12	3.137e+12	3.792e+12	5.864e+12	1.056e+13	1.059e+13
Mean	5.715e+11	1.770e+12	3.231e+12	3.916e+12	6.030e+12	1.085e+13	1.088e+13
3rd Qu.	7.251e+11	2.268e+12	4.053e+12	4.821e+12	7.253e+12	1.310e+13	1.313e+13
Max.	2.410e+12	4.788e+12	7.976e+12	9.149e+12	1.348e+13	2.540e+13	2.543e+13

Table 7: ^{239,240}Pu inventory [Bq] at different distances derived by three different fit methods with a cutoff of 1.8 Bq/sample.

	0–0.94 km	0–4.01 km	0–6.4 km	0–7.5 km	0–17 km	0–66.6 km	0–99.3 km
Biexp-fit							
Min.	3.958e+10	3.314e+11	6.288e+11	8.034e+11	1.331e+12	1.650e+12	1.650e+12
1st Qu.	7.363e+10	6.702e+11	1.298e+12	1.622e+12	2.794e+12	5.130e+12	5.253e+12
Median	8.254e+10	7.728e+11	1.524e+12	1.906e+12	3.314e+12	6.762e+12	7.126e+12
Mean	8.281e+10	7.792e+11	1.530e+12	1.914e+12	3.355e+12	7.278e+12	7.924e+12
3rd Qu.	9.158e+10	8.780e+11	1.738e+12	2.177e+12	3.846e+12	8.956e+12	9.710e+12
Max.	1.585e+11	1.511e+12	3.096e+12	3.876e+12	6.208e+12	2.156e+13	2.825e+13
Exp-fit							
Min.	2.287e+10	3.355e+11	7.257e+11	9.256e+11	1.592e+12	2.421e+12	2.432e+12
1st Qu.	5.287e+10	7.616e+11	1.625e+12	2.059e+12	3.448e+12	4.949e+12	4.961e+12
Median	6.080e+10	8.724e+11	1.855e+12	2.350e+12	3.926e+12	5.592e+12	5.605e+12
Mean	6.081e+10	8.725e+11	1.857e+12	2.352e+12	3.921e+12	5.579e+12	5.592e+12
3rd Qu.	6.873e+10	9.839e+11	2.091e+12	2.646e+12	4.402e+12	6.226e+12	6.239e+12
Max.	1.044e+11	1.479e+12	3.119e+12	3.935e+12	6.439e+12	8.828e+12	8.842e+12
Linear-fit							
Min.	4.553e+10	3.528e+11	6.791e+11	9.761e+11	1.725e+12	2.318e+12	2.349e+12
1st Qu.	7.836e+10	7.335e+11	1.467e+12	1.938e+12	3.413e+12	6.566e+12	6.598e+12
Median	8.662e+10	8.493e+11	1.706e+12	2.248e+12	3.980e+12	8.614e+12	8.645e+12
Mean	8.701e+10	8.575e+11	1.719e+12	2.270e+12	4.049e+12	8.913e+12	8.944e+12
3rd Qu.	9.535e+10	9.744e+11	1.953e+12	2.575e+12	4.619e+12	1.091e+13	1.094e+13
Max.	1.347e+11	1.595e+12	3.175e+12	4.120e+12	7.401e+12	2.205e+13	2.208e+13

than for other types of radiation. Another problem is that, in close vicinity to the point of impact, the activity distribution of the hot particles, which play an important role for the inventory, is unknown.

This study shows that earlier estimates have underestimated the total inventory in sediments in the Bylot Sound. The main reason for this is that the exponential curve fitted has been based on too few data points far away from the point of impact, resulting in that the slow component has not been considered. Earlier studies have also underestimated the importance of hot particles and treated the samples as if the activity distribution was homogeneous.

A general conclusion is that it is very important to know the amount and composition of hot particles in the sediment, i.e. number of particles, particle size distribution and chemical composition, in order to perform an adequate inventory estimation. Having a true log-normal activity distribution, by sampling from this distribution the calculated mean, used for such area, is most likely underestimated compared with the true mean, as the probability to sample the very few large hot particles is very low.

This study therefore concludes that the inventory is within the range of 5–15 TBq, probably close to 10 TBq, i.e. about 3.8 kg ^{239,240}Pu. This is close to the earlier estimated missed amount of 3 kg [1, 11]. Furthermore, in upcoming investigations in the Bylot Sound sediments, the activity determination should be based on a gamma screening technique out to a distance of 17 km from the point of impact and, at distances over 17 km, alpha spectroscopy should be used.

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Paper IV

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Plutonium hot particle separation techniques using real-time digital image systems
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NUCLEAR INSTRUMENTS & METHODS IN PHYSICS RESEARCH
Section A

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Plutonium hot particle separation techniques using real-time digital image systems

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Abstract

Two real-time digital imaging systems, able to replace conventional autoradiography for radioactive hot particle separation and identification, are presented in this paper.

The hot plutonium particles used for the study originate from the Thule nuclear weapon accident. Both of the real-time imaging techniques are initiated with sample splitting and measurements with a HPGe detector, in order to detect the gamma-emitting ^{241}Pu daughter ^{241}Am, which is an indicator of plutonium hot particle in the sample. The time required for the whole process of separation and identification of one single particle from a bulk sediment sample (150 g dry weight) is of the order of 1–2 days, and is highly dependent on its activity.

The real-time digital imaging systems presented in this paper are preferable, compared to conventional autoradiography and the CR-39 technique, when separation and identification of hot particles are needed as they are much faster and in addition give a real-time image of the particle. © 2002 Published by Elsevier Science B.V.

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Keywords: Hot particle; Thule accident; Real-time digital image system; Separation technique; Plutonium; Sediment

1. Introduction

Interest in detection of radioactive particles has increased during recent years. Thus, the IAEA has started a co-ordinated research project on radioactive particles, "Radiochemical, Chemical and Physical Characterization of Radioactive Particles in the Environment". This project is focused on radioactive particles released to the environment and part of the project is concerned with methods of localizing and separating these particles.

The study of these particles deals mainly with the physical–chemical form and solvability of the particles. The separation techniques most commonly used to date have been film autoradiography [1–3] and the so-called CR-39 detector [4–9] based on etching radioactive induced weakened areas away from a plastic sheet. These two methods are time consuming (exposure time up to 30 days) and both require analysis/visualization in a microscope. These two detectors are sensitive

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to ionizing radiation and, in addition, the film is sensitive to light.

In this paper two real-time digital imaging systems have been used to detect hot particles from sediment samples originating from the Thule accident. The accident and the area are described in detail elsewhere [3,10,11]. These two detector systems are mainly used in nuclear medicine to study the uptake of beta- and Auger-electron-radiating nuclides in tissues [12].

2. Materials and methods

Sediment samples from the Thule accident area (Bylot Sound), NW Greenland, were used in this study. The sediment samples were taken with a Finnish Gemini Twin Corer delivering two parallel 8 cm diameter cores. An earlier version of the Gemini Twin Corer, the Niemistö Corer, has been described in the literature [13]. The sediment in part of the Bylot Sound is highly contaminated with unfissioned plutonium from this accident. At the point of impact, the activity concentration of ^{239,240}Pu is about 60 kBq m^{-2} and the contamination is measurable up to 56 km from this site [10]. The activity concentration in the sediment is very heterogeneous due to the presence of hot particles. There are several reasons for the separation and study of hot particles. To improve the basis for modelling the long-term environmental fate of particulate removal and further, to improve inventory estimates, it is necessary to study the chemical composition as well as the activity distribution and physico-chemical form of the Pu particles. To be able to study these aspects, the particles must be identified as single particles and for that reason a separation method is needed.

2.1. Sample splitting

The sediment cores were divided into 1 cm sections at the sampling stations and stored frozen (−20°C) onboard the research ship Adolf Jensen. At Risø National Laboratory, Denmark, the sections were freeze dried. Each section contained about 150 g dry sediment. Measurements were performed using a high-purity germanium, HPGe, detector, using the 59.54 keV ($n_\gamma = 35.9\%$) gamma-line from the daughter of ^{241}Pu, i.e. ^{241}Am, as an indicator of hot plutonium particles. All sections ($N = 88$) from six different sampling stations were screened for radioactive particle content. If an ^{241}Am peak appeared, the sample was divided into two equal parts and analysed again. This halving process continued until a few μg were left, which is equivalent to halving the samples about 25 times. Depending on the activity and the amount of material, the acquisition time varied from 30 s up to a few minutes. Including the time required to divide the samples, the whole process could be performed in a maximum of 6 h (the lowest activity of the particles studied was ~ 1 Bq^{239,240}Pu). The residual part of the sample containing the particle was then spread homogeneous and attached on adhesive carbon tape, with a diameter of 25 mm. The carbon tape used, is of the same type as that used for sample fixing in a scanning electron microscope. A thin plastic or Mylar foil was then placed over the adhesive tape to cover the sample. These samples were analysed in the real-time digital imaging systems for determination of the particle position.

2.2. The IDE Bioscope

The real-time digital imaging system IDE Bioscope 3250 [14] is manufactured by the Integrated Detector & Electronics AS (IDE AS) in Norway. The detector is a 300 μm thick double-side silicon strip sensor. The strips are located on both the p- and n-sides and have a width of 50 μm. The sensitive area is 32×32 mm^2, and there are 640 strips on each side. The strips on one side are placed perpendicular to the strips on the other side. The energy deposited by an ionizing particle travelling through the detector is proportional to the kinetic energy of the particle (disintegrating energy). The advantage of this is that the detector system can measure the activity distribution, followed by calculation to obtain the absorbed dose rate. The signal is processed by a self-triggering read-out data chip, XA1.2 [15]. The detector system has 409,600 pixels and a system resolution better than 50 μm. In Fig. 1, a schematic illustration of the detector can be seen.

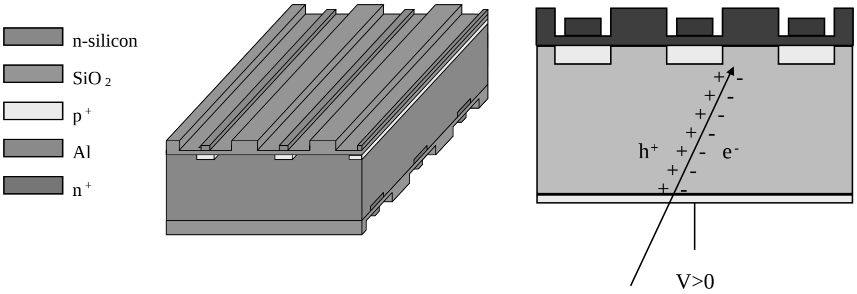

Fig. 1. A schematic illustration of the IDE Bioscope. The ionizing radiation produces electron–hole pairs. The applied electric field causes the electrons to drift down to the n-doped silicon and the holes up to the p-doped side. The energy deposited is proportional to the energy of the incident particle and to the path length inside the detector. The figure is redrawn from Reference [14].

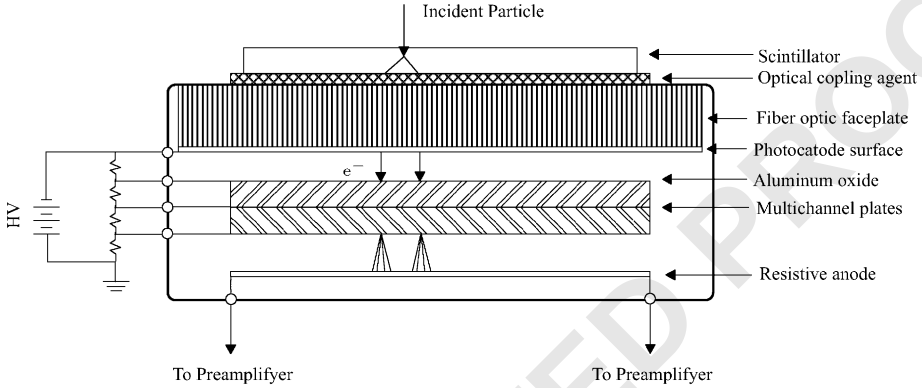

Fig. 2. The principle of the beta camera. The ionizing particle produces scintillation photons in the scintillator. The light is transported through the fibre-optic face-plate to a photocathode. The photocathode produces electrons which are multiplied by the microchannel plates. The signal is thereafter collected by the anode and the position of the event is determined in the same way as for an ordinary scintillation camera. The figure is redrawn from Reference [12].

2.3. *The beta camera*

This device was developed at the Department of Radiation Physics at Lund University, Sweden [12]. The beta camera is based on a 0.3 mm thick scintillator that emits light at a wavelength of 427 nm in the de-excitation process. This light travels through the fibre-optic face plate to the photocathode. The light interacts with the material in the cathode to produce electrons, which are accelerated to the multichannel plates. In the multichannel plate, these electrons produce a cascade of electrons, which are collected to form a detectable signal at the anode. The position of the event is determined as in an Anger camera. The signal is proportional to the energy of the ionizing particle interacting in the scintillator and this relation, as for the IDE Bioscope, can be used to estimate the absorbed dose rate [12,16]. In Fig. 2, a schematic illustration can be seen of the beta camera. The intrinsic resolution of the device is ~50 μm and the system resolution is of the order of 500 μm. The circular scintillation detector has a diameter of 40 mm.

3. Results and discussion

In Fig. 3 the results of the analysis of the same particle using the IDE Bioscope (left) and the beta camera (right) can be seen. The samples are assembled somewhat different for the two devices. For the IDE Bioscope the carbon tape, with the attached particle, is placed on a Mylar foil, which

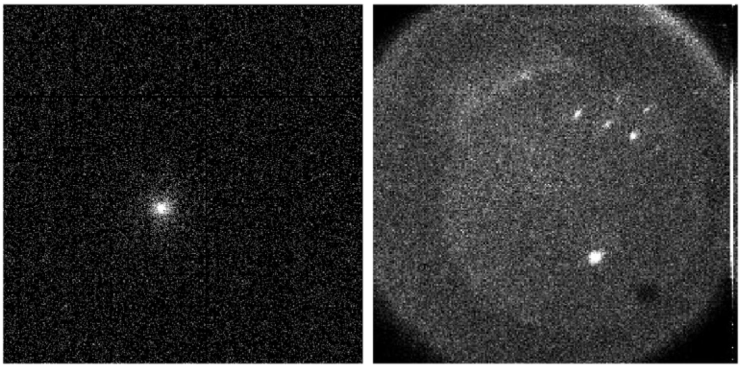

Fig. 3. Real-time images of the same particle using two different systems. On the left is the image obtained after 8 h in the IDE Bioscope, and on the right the image after 1 h of exposure to the beta camera. The five dots in the beta camera image are the superimposed position system. The distance between the dots is 3 mm.

is fasten in a frame with the dimensions 30 × 28 mm^2. The frame is then inserted into the device. The advantage of this is that it is easy to read out the position in the image and thus to localize the particle in the frame. The beta camera technique, on the other hand, has almost no limitations on sample size. It is possible to spread the sample over a large surface area and scan the surface until the particle or particles are found. However, the carbon tape used in our investigations of plutonium hot particles, had a diameter less than the diameter of the detector and for that reason, after placing the carbon tape on the detector, no scanning was needed. When using the beta camera, a position system must be employed. Since the beta camera is a light-sensitive device, it is convenient to use optical markers in the sample. This can be done after a particle has been found, for example, by punching small holes in the adhesive tape at known distances. The sample is then exposed to light and the holes will be visible, superimposed on the image obtained from the acquisition of the hot particle. An example of this method can be seen in the right-hand image in Fig. 3. In this image a circle can be seen, which originates from the protective plastic film over the sample. This film is luminous and the photons are detected in the beta camera. The beta camera has a higher sensitivity than the IDE Bioscope, and to collect the same number of counts from the same particle it is necessary to have a 4-times-longer collection time with the IDE Bioscope than with the beta camera. For the beta camera, a 3-min acquisition was required to produce a visible image on the screen from a particle with an activity of 120 Bq. The signal-to-noise ratio is higher for the IDE Bioscope. It is, however, possible to increase this ratio for the beta camera by applying an anti-coincidence device. By doing this, the noise level (i.e., the background count rate) can be lowered from 50 cps to about 0 cps [17].

In theory it would be possible to determine the total alpha activity of the particle, but this requires that the particles be naked and not coated by any material. The environmental particles in this study were coated with sediment material, as can be seen in Fig. 4. This image is produced by a 30 kV scanning electron microscope (Philips SEM 515) in backscatter mode.

There are four main advantages of a real-time digital imaging system when separating hot radioactive particles:

1. The technique is faster than conventional autoradiography.
2. It is easy to determine the position of the particle(s).
3. The signal is proportional to the incident particle energy and it can be used to estimate the activity (or at least the total alpha decay) of the particle.
4. The results are displayed in real time and do

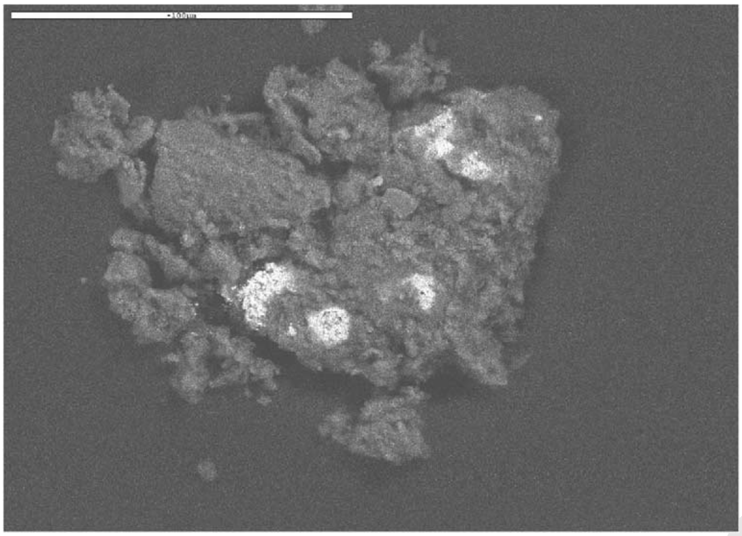

Fig. 4. An image produced by a 30 kV scanning electron microscope (Philips SEM 515) in backscatter mode. The light areas are the high-density plutonium and the dark areas are low-density sediment material. This is the particle that produced the real-time images shown in Fig. 3. The bar at the upper left indicates 100 μm.

not require processing after exposure, as the results from the CR-39 and film autoradiography.

Reports of electronic autoradiographs have been published by Zeissler [18]. In Zeisslers paper three different techniques are compared; semiconductor pixel array, phosphor plate and track-etch detectors. The semiconductor pixel array detector is similar to the IDE Bioscope described in this paper but has a smaller detector area, 7×9 mm^2 compared with 32×32 mm^2 for the IDE Bioscope. Zeissler pointed out the advantages of real-time display of the sample, but the small detector area is a disadvantage.

4. Conclusions

The use of real-time digital image systems is of great advantage for localizing plutonium-hot particles compared to film autoradiography and CR-39 techniques, as it is faster and it is easily processed. The beta camera was found to be the best device of the two detector systems we used, as it had a higher sensitivity, resulting in a shorter acquisition time, with good precision. However, the IDE Bioscope gives the position without the need for position markers and has a better resolution.

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Paper V

Eriksson M., Roos P., Dahlgaard H., Lindahl P. and Holm E.:
Isotopic ratios in Thule hot particles, source term of the Thule debris
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Isotopic ratios in Thule hot particles, source term of the Thule debris

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Abstract

This paper presents the first investigation of enriched uranium in the debris from the nuclear weapon accident in Thule, N.W. Greenland, using samples collected on several expeditions. Discussions over the past 34 years have focused on plutonium and, wrongly, it has been understood that the fusion weapons were of a plutonium type.

Our measurements on single, isolated hot particles from Thule sediments below the impact point, show that the weapons contained very significant quantities of ^{235}U. Furthermore, particles in the marine sediments have lost uranium to the sediment interstitial water and to the sea-water by leaching. There is a relationship between the amount of leached ^{235}U and the time spent in the sediments. Plutonium and americium on the other hand have not measurably left the particle lattice in the same rate. Moreover, we conclude that the Thule debris consists of more than one source, most probably two.

Key words: Hot-Particles, Plutonium, Uranium, Thule accident, alpha spectroscopy, ICP-MS, SEM, X-ray, source terms

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1 Introduction

In January 1968, a B52 aeroplane crashed on the sea ice about 12 km west of the Thule air base. The aircraft was carrying four hydrogen nuclear weapons. The impact triggered the conventional explosive material within the weapons

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and the explosion pulverized the fissile material in the bombs. The debris was scattered around and beneath the point of impact.

The source terms (isotopic ratios) of the debris have been investigated by others (1; 2; 3; 4; 5; 6). Some investigations suggest that the debris consists of different sources (1; 4). However, since the ratios were determined on bulk sediment samples, the ratios could represent a mixed ratio of different sources. Therefore single isolated particles, which most probably consist of nuclides from one single source, should be used to determine the different source terms.

In the first preliminary study of a hot particle from the Thule area (7), it was clear that the weapons consisted partly of uranium. This had never been reported before. Later, in 2001, another study of an isolated particle from the Thule sediment confirmed that the weapons consisted partly of uranium (8). However, in the official answers given by the U.S. Government to the Danish Government in 2000 on the question regarding the radionuclides involved in the debris (Question 4), uranium was not mentioned (9). Therefore, this subject requires more detailed investigation.

2 Material and Methods

The particles studied here were separated from bulk sediment samples, which had been collected during expeditions to Thule in 1979, 1984 and 1997, see Table 1. The separation technique has been described in detail elsewhere (10). Briefly, the technique is based on sample splitting, using the gamma emitting (59.54 keV, $n_\gamma = 35.9$ %) ^{241}Pu daughter ^{241}Am, as an indicator of hot particles. The particles were identified using real-time digital imaging systems. After separation, the single particles were measured on a High Purity Germanium (HPGe) detector in order to determine the activity of ^{241}Am (pulse-rate). Dissolution of hot particles is notoriously difficult and so by comparing the gamma activity with the alpha-activity of ^{241}Am after dissolution and chemical separation (described below) we were able to check that complete dissolution had occurred.

Different analytical methods were used to determine the elemental composition, activity and mass of U, Pu and Am in each particle. Some of the particles were analyzed on a 30 keV scanning electron microscope (SEM), Philips SEM 515, with an energy dispersive X-ray analyzer (EDX). The elemental compositions were derived from the X-ray spectra and the element ratios were derived from the M and L-shell X-ray lines of U and Pu. Inductively coupled plasma mass spectrometry (ICP-MS) and alpha spectroscopy were used to determine the isotopic and element ratios and the masses and activities of U, Pu and Am in the particles. Two different ICP-MS instruments were used. At the

Table 1
Sample data

Particle id.	Station	Sediment corer	Sediment slice	Sampling date
TPA	Thule-V	HAPS	0–3 cm	23–8–1979
TPB	Thule-V	HAPS	6–9 cm	11–8–1984
TPC	Thule-V	HAPS	3–6 cm	11–8–1984
TPD	Thule-V	HAPS	0–3 cm	23–8–1979
TPE	V2	Gemini	6–7 cm	25–8–1997

Agricultural University, NHL, Norway, an ELAN 6100 quadrupole instrument was used with the x-flow and an ultra-sonic nebulizer and at Risø National Laboratory, Denmark, a PlasmaTrace2 high resolution-ICP-MS was used with the x-flow nebulizer. Alpha measurements were made on passivated implanted planar silicon (PIPS) alpha-detectors.

The particles which would be analyzed by ICP-MS and alpha spectroscopy were dissolved in a mixture of hydrofluoric acid and nitric acid (ratio 1:3) in high pressure teflon bombs. The dissolution procedure began with 0.1 ml HF and 0.3 ml HNO_3 which was evaporated to dryness, and this was repeated 30 times. Finally, 1 ml HF and 3 ml HNO_3 were added to the closed teflon bomb and placed on a hot-plate so that the mixture was under pressure for 24 hours. The solution was then evaporated to dryness. In addition, one particle (later refered to as TPE) was dissolved in a microwave oven, MARS 5. A mixture of 7 ml HF, 7 ml HNO_3 and 1.5 ml HCl was added to the particle in a teflon bomb and heated for 20 min in the microwave oven at a maximum pressure of 250 PSI (17.2 Bar) and a maximum temperature of 200° C. 25 ml saturated boric acid was then added and the mixture was heated for another 20 minutes in the microwave oven. The last step was necessary to dissolve the Pu-fluoride complexes formed in the previous step. The solutions were evaporated to dryness and 3 times 0.3 ml HNO_3 were added and evaporated to dryness, this also to ensure that all the fluoride complexes were destroyed. The dissolved particles were thereafter diluted in 5 % HNO_3 (Ultra Pure Sea Star quality) to 50 ml with ultra pure H_2O ($>$18 MΩ cm). The analysis of Pu and U were done on un-separated aliquots of the sample solution as well as on radiochemically separated aliquots. The size of the aliquots were 0.2–1.5 ml, depending on the activity of the particle. The aliquots which were radiochemically separated, used ion exchange (AG 1×4, 100–200 mesh, BIO RAD). To minimize the use of acid, 1.5 ml columns with 0.7 ml resin were used. All acid used were of Ultra Pure Sea Star quality, except HF which was of pro analysis Merck quality. Unused teflon cells were acid washed in boiling 12 M HCl before use. These precautions were taken to reduce contamination by naturally occurring uranium isotopes.

The yield determinants used were ^{233}U, ^{242}Pu and ^{243}Am. Sub-samples of each dissolved particle solution were analysed with yield determinants as well as without. The sub-samples analysed without yield determinants were used to determine the isotopic ratios and the mass and activity of each nuclide in the particle were determined from the spiked solutions. In addition, procedural and machine blank samples were prepared to assess the background levels.

2.1 U, Pu and Am separation

The sub-samples were evaporated to dryness and thereafter dissolved in 8 M HNO_3. The solutions were absorbed onto the columns. The eluate was collected for Am and U, which were then separated using the method described by Holm (11). Thorium was then eluted with 9 M HCl, followed by the elution of Pu with NH_4I + 9 M HCl. The samples were then evaporated to dryness and the samples intended for ICP-MS analysis were diluted to 3 % HNO_3 solutions (10 ml). The samples measured by alpha particle spectrometry were electrodeposited onto stainless steel discs in accordance with the method described by Halstadius (12).

The sample preparation was performed in environmental laboratories which are also used for trace level uranium analysis. Therefore one set of samples was prepared in a clean lab at Risø National Laboratory to minimize uranium contamination.

In total, 5 hot particles were analyzed which were all collected in close vicinity to the point of impact. 5 sub-samples of each hot particle solution were analyzed by ICP-MS together with procedural blank samples.

2.2 Uncertainty estimation

The uncertainty limits reported in the present paper have been determined using the error propagation hypotheses where the standard deviation is calculated by Equation 1.

$$\sigma_y^2 = \left(\frac{\partial y}{\partial a}\right)^2 \sigma_a^2 + \left(\frac{\partial y}{\partial b}\right)^2 \sigma_b^2 + \left(\frac{\partial y}{\partial c}\right)^2 \sigma_c^2 + ... \tag{1}$$

where a, b and c are the variables of the determined quantity, y (mass, activity or ratio). Typical variables are: sub sample size, tracer concentration and counts in the peak. The uncertainties for the isotopic ratios are only dependent on the counting statistics when the ratio is determined from the same spectra, as in theses cases the isotopic ratios are independent of the tracer and the sample size. For mean values, the standard deviation (SD) and number of samples (n) are reported.

3 Results

3.1 Particle destruction

As mentioned before, PuO_2 is difficult to dissolve. Experiments performed at Risø National Laboratory (13) have shown that 8–40 % of the Pu remains undissolved in bulk Thule sediment samples when using the *Aqua Regia* leaching technique described by Talvitie (14). To ensure that the particles in the present study were dissolved, the gamma measurements of ^{241}Am on the undissolved particle and the determined alpha activity (determined from an aliquot of the dissolved particle solution) were compared. The results can be seen in Figure 1, with an almost perfect agreement (correlation coefficient, $R^2 = 0.9991$) between the two different methods. The gamma measurements are represented as the total count-rate (i.e. includes the background counts which however was insignificant in this context) of the ^{241}Am gamma line (59.54 keV) in counts per minute (CPM). The graph shows that, for this particular HPGe detector, the ^{241}Am activity of a particle can be calculated from the gamma measurements as:

$$A_{particle} = \frac{1}{4.956}(CPM - 1.6372) \qquad [Bq] \tag{2}$$

The good agreement between measurements indicates that the particles were totally dissolved. The alpha spectrometry results (Table 3) show an almost identical ^{241}Am/$^{239+240}$Pu ratio for all 5 particles. This means that the Pu activity could be determined in the Thule sediments, by indirect measurements on ^{241}Am.

3.2 Plutonium content

The results from ICP-MS can be seen in Table 2 and from alpha spectrometry in Table 3. Since the ICP-MS used in Norway was unstable at the time of the measurements combined with that a peak jumping mode (obvious risk to miss peaks) were used for evaluation, only the results from the PlasmaTrace2 machine at Risø are presented. However, the deviations between the Pu results from the two instruments were less than 2 % for the Pu measurements. The

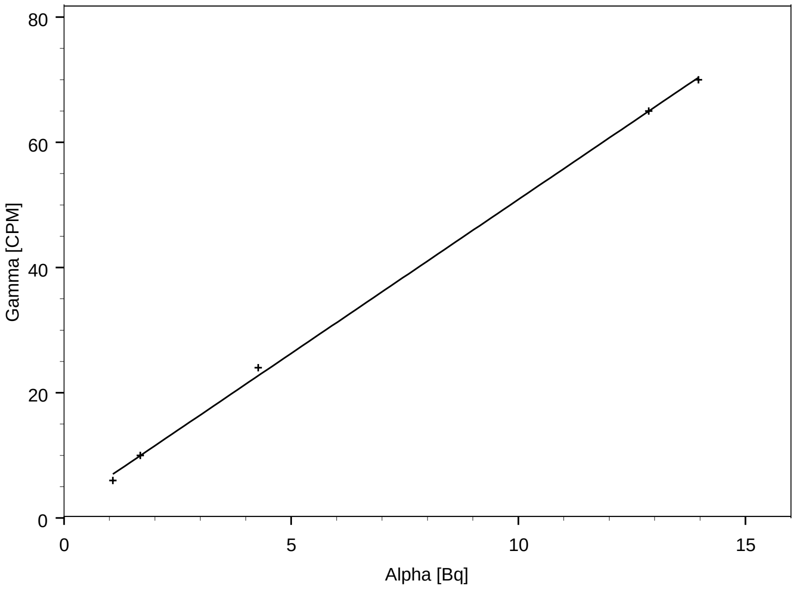

Fig. 1. Comparison of the ^{241}Am content in the particles, derived by two different methods. The count-rate, CPM, is derived from the measurements of the whole particles on an HPGe detector and the activity is derived by alpha spectrometric measurements of aliquots from the dissolved particle solution. The graph shows an almost perfect fit between the two different methods, which indicates that the particles are totally dissolved using the radiochemical method described in this article. The correlation coefficient, R^2, between the two data sets is 0.9991.

results from an UKAEA Pu reference material solution (sample number: UK Pu 5/92138) were in good agreement with the reported values (the mass ratios agreed within 0.01 %). The mean mass ratio, ^{240}Pu/^{239}Pu, for the 5 particles is 0.0551 ± 0.0008 (1 SD, n = 5) and the corresponding activity ratio is 0.2057 ± 0.0011 (1 SD, n = 5).

There is also a good agreement between the two different analytical techniques, i.e. the ICP-MS and alpha spectrometry for the ${}^{239+240}$Pu measurements. ^{238}Pu is difficult to measure by ICP-MS because it has a short half life and ^{238}U as an isobaric interference, and so it could only be measured by alpha spectrometry. The mean activity ratio of ^{238}Pu/${}^{239+240}$Pu is 0.0161 ± 0.0005 (1 SD, n = 5) and the mean activity ratio ^{241}Am/${}^{239+240}$Pu is 0.169 ± 0.005 (1 SD, n = 5), reference date: 2001–10–01.

Table 2
Pu isotope content and ratios in the particles on mass and activity basis as measured by ICP-MS

Particle	$^{239+240}$Pu	^{239}Pu	^{240}Pu	^{240}Pu/^{239}Pu
	ng	ng	ng	Mass ratio
TPA	2.51 ± 0.09	2.380 ± 0.088	0.133 ± 0.006	0.0544 ± 0.0017
TPB	4.37 ± 0.16	4.14 ± 0.15	0.232 ± 0.009	0.0558 ± 0.0013
TPC	10.66 ± 0.39	10.10 ± 0.37	0.559 ± 0.022	0.0559 ± 0.0011
TPD	28.9 ± 1.1	27.4 ± 1.0	1.521 ± 0.060	0.0554 ± 0.0012
TPE	32.2 ± 1.2	30.5 ± 1.1	1.709 ± 0.067	0.0541 ± 0.0011
	Bq	Bq	Bq	Activity ratio
TPA	6.52 ± 0.25	5.41 ± 0.20	1.111 ± 0.046	0.2056 ± 0.0065
TPB	11.35 ± 0.43	9.41 ± 0.35	1.943 ± 0.077	0.2065 ± 0.0049
TPC	27.6 ± 1.0	22.95 ± 0.84	4.69 ± 0.18	0.2042 ± 0.0041
TPD	74.9 ± 2.8	62.2 ± 2.3	12.75 ± 0.50	0.2050 ± 0.0044
TPE	83.5 ± 3.1	69.2 ± 2.5	14.32 ± 0.56	0.2071 ± 0.0041

Table 3
Pu isotope content and ratios in the particles on mass and activity basis as measured by alpha-spectroscopy

Particle	$^{239+240}$Pu	^{238}Pu	^{238}Pu/$^{239+240}$Pu	^{241}Am/$^{239+240}$Pu
	Bq	Bq	Activity ratio	Activity ratio
TPA	6.22 ± 0.23	0.100 ± 0.007	0.0167 ± 0.0010	0.173 ± 0.010
TPB	9.78 ± 0.35	0.156 ± 0.010	0.0165 ± 0.0009	0.172 ± 0.009
TPC	26.38 ± 0.94	0.413 ± 0.026	0.0158 ± 0.0008	0.162 ± 0.008
TPD	74.6 ± 2.8	1.152 ± 0.073	0.0156 ± 0.0008	0.172 ± 0.009
TPE	84.1 ± 3.0	1.325 ± 0.073	0.0158 ± 0.0007	0.166 ± 0.009

3.3 Uranium content

The uranium results from the ICP-MS measurements performed at Risø National Laboratory are shown in Table 4. As in all environmental laboratories were samples are prepared for uranium analysis by alpha spectrometry, typical procedural blanks may contain nano gram quantities of ^{238}U. These levels do not affect alpha spectrometric measurements but certainly affect the ICP-MS measurements. Typical concentrations of an aliquot in our ICP-MS

Table 4
Uranium in the particles measured by ICP-MS

Particle	^{235}U	^{238}U	^{235}U/$^{235+238}$U	^{235}U/^{239}Pu
	ng	ng	Mass ratio	Mass ratio
TPA	9.28 ± 0.63	8.34 ± 0.57	0.527 ± 0.002	3.90 ± 0.30
TPB	10.00 ± 0.68	12.02 ± 0.82	0.454 ± 0.002	2.41 ± 0.19
TPC	13.98 ± 0.95	16.29 ± 1.11	0.462 ± 0.002	1.38 ± 0.11
TPD	74.65 ± 5.06	65.34 ± 4.44	0.533 ± 0.002	2.73 ± 0.21
TPE	34.75 ± 2.36	30.27 ± 2.07	0.534 ± 0.003	1.14 ± 0.09

studies were 25 pg/ml of total uranium. The samples which were measured in Norway show a large variation in the ^{235}U/$^{235+238}$U mass ratio (3–23 %). All these samples were radiochemically separated and prepared in a standard environmental laboratory where high level (kBq) uranium samples were also occasionally analyzed, which could introduce a contamination with natural mass ratios to the samples. Laboratory contamination was indeed confirmed when the unseparated sub-samples were measured unseparated and more care about the laboratory contamination risk was taken, involving new and cleaned equipment. The mass ratios, ^{235}U/$^{235+238}$U, presented in Table 4 are from the samples that were prepared in a clean lab. These results show almost identical isotopic ratios for the 5 particles. Moreover, the ^{235}U measured in the particles on both ICP-MS machines were in reasonably agreement. Due to the relatively high ^{235}U concentration in the samples these measurements are less sensitive to contamination with respect to this nuclide. The mass ratio of the fissile material in the particles, ^{235}U/^{239}Pu is less affected by natural uranium contamination than the ^{Tot}U/$^{239+240}$Pu ratio. Therefore this ratio is presented in Table 4. It appears that the ratio decreases with the time that the particle has been exposed to the aquatic sediment. In Figure 2 the ratio as a function of time can be seen. We believe that the result reflects preferential leaching of the uranium from the particles.

3.4 SEM study of the particles

In Figure 3 a hot particle with a diameter of about 120 μm is shown. The SEM image was produced in back scatter mode. It is clear that the particle is coated with sediment material, which appears grey in the image. It is not verified if the particle has been coated in the sediment or if the coating occurred during the freeze drying of the sediment sample. The acceleration voltage of the electrons was 30 kV. These electrons do not have sufficient energy to penetrate the particle deeply. Some high density areas are however visible, represented

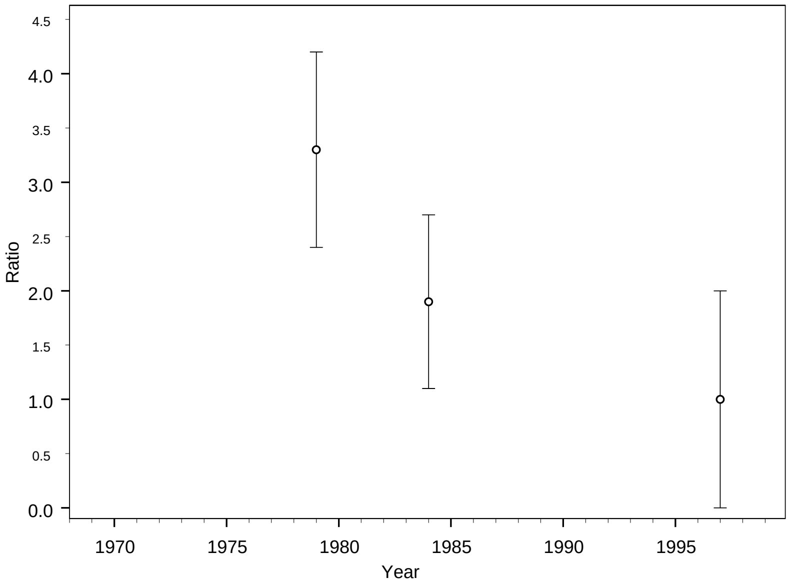

Fig. 2. The mean ratio, $^{235}U/^{239}Pu$ (± 1 SD), in particles collected during a specific year. There is a tendency that the uranium content is lower in the particles exposed to the sediment for a longer time, which would mean that there is preferential leaching of uranium from the particle in the sediment. The standard deviation for the ratio in 1997 is the square rote of the ratio, as only one particle have been analyzed from this year, the standard deviation from the ICP-MS measurement is much less than the shown, see Table 4.

by light areas in the image. When the acceleration voltage was lowered these areas decreased, meaning that the whole particle was coated with sediment material of different thicknesses.

Several spots on the particle were analyzed with the EDX analyzer. The two spots visible in Figure 3 are representive of the different density areas. Spot 1, is sediment material and spot 2 the high density material. The dominant peaks in the X-ray spectra (shown below the particle in Figure 3) at spot 1 are the K X-ray lines originating from Mg, Al, Si and Fe, which are major components of marine sediment. The X-ray spectra from spot 2 shows some large peaks around 3.3 keV which originate from the U and Pu M X-ray lines. The M_{β_1} peaks of uranium are however overlapped by the M_α peaks of plutonium and for that reason M-line profiles are required for the SEM to be able to determine the element ratio (U/Pu) of these two elements. These profiles were not available for the present SEM. Although the L X-ray lines are separated for the two elements, it is not possible to do quantitative measurements of these elements as their electron binding energies are close to the energy of the accelerated incident electrons. As a rule of thumb, about three times higher accelerating energy is required (accelerating voltage) to do quantitative estimates of elements in a sample when the EDX technique is used (15). To evaluate the ratio one must consider the inelastic cross section for electron interaction with the different electron shells. The cross section for L_3-shell interaction (30 keV incident electron sputters L_3-shell electron) is about 1.37 times higher for uranium compared to plutonium. Moreover, the L-shell binding energies for plutonium are higher than for uranium and as the incident electrons would lose energy in their passage through the coated sheet, there will be more electrons that could interact with uranium resulting in a biased elemental ratio. Perhaps it is also necessary to consider the particles as thick targets, the resulting emission of U and Pu X-rays would change with depth into the particle in a manner which would result in a U/Pu X-ray ratio that is dependent on target thickness and coating. A calibration with targets of the same size having a known U-Pu composition would probably be required.

4 Discussion

The determination of the source terms (characteristic isotopic ratios) of the Thule accidental debris have been reported elsewhere (1; 4). However, no unique values have been found and the isotopic ratios have been scattered, which suggests that there is more than one unique source term of the Thule accident debris. Therefore, we have studied single particles which, most probably, originate from one single source. The results from the particles studied here indicate only one single source with the unique isotopic ratios: ^{238}Pu/$^{239+240}$Pu activity ratio of 0.0161 ± 0.0005, n = 5 and the ^{240}Pu/^{239}Pu mass ratio of 0.0551 ± 0.0008, n = 5. These ratios are identical to the ratios observed by Mitchell et al. (4)(^{238}Pu/$^{239+240}$Pu = 0.0162[1] and ^{240}Pu/^{239}Pu = 0.055) in their most active sample (5.9 Bq). The other four samples Mitchell et al. (4) analyzed showed lower values which were shown statistically to originate from another source. Mitchell et al. (4) measured the Pu isotopic ratios on bulk sediment samples by high-resolution alpha spectrometry using a spectral deconvolution technique. For their most active sample, they confirmed the ratio with high-resolution X-ray spectrometry and later Stürup et al. (3) performed HR-ICP-MS measurements on the same samples. The results found were in good agreement for the three samples with highest activities while for the two low active samples statistical deviations were observed, see Table 5.

High-resolution X-ray spectrometry measurements on Thule sediment have also been reported by Komura et al. (5), showing a ^{240}Pu/^{239}Pu activity ratio of 0.22 ± 0.03, which is in good agreement with the ratios measured in the present study. Arnold and Kolb (6) report two activity ratios of ^{240}Pu/^{239}Pu

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[1] Decay corrected to year 2001

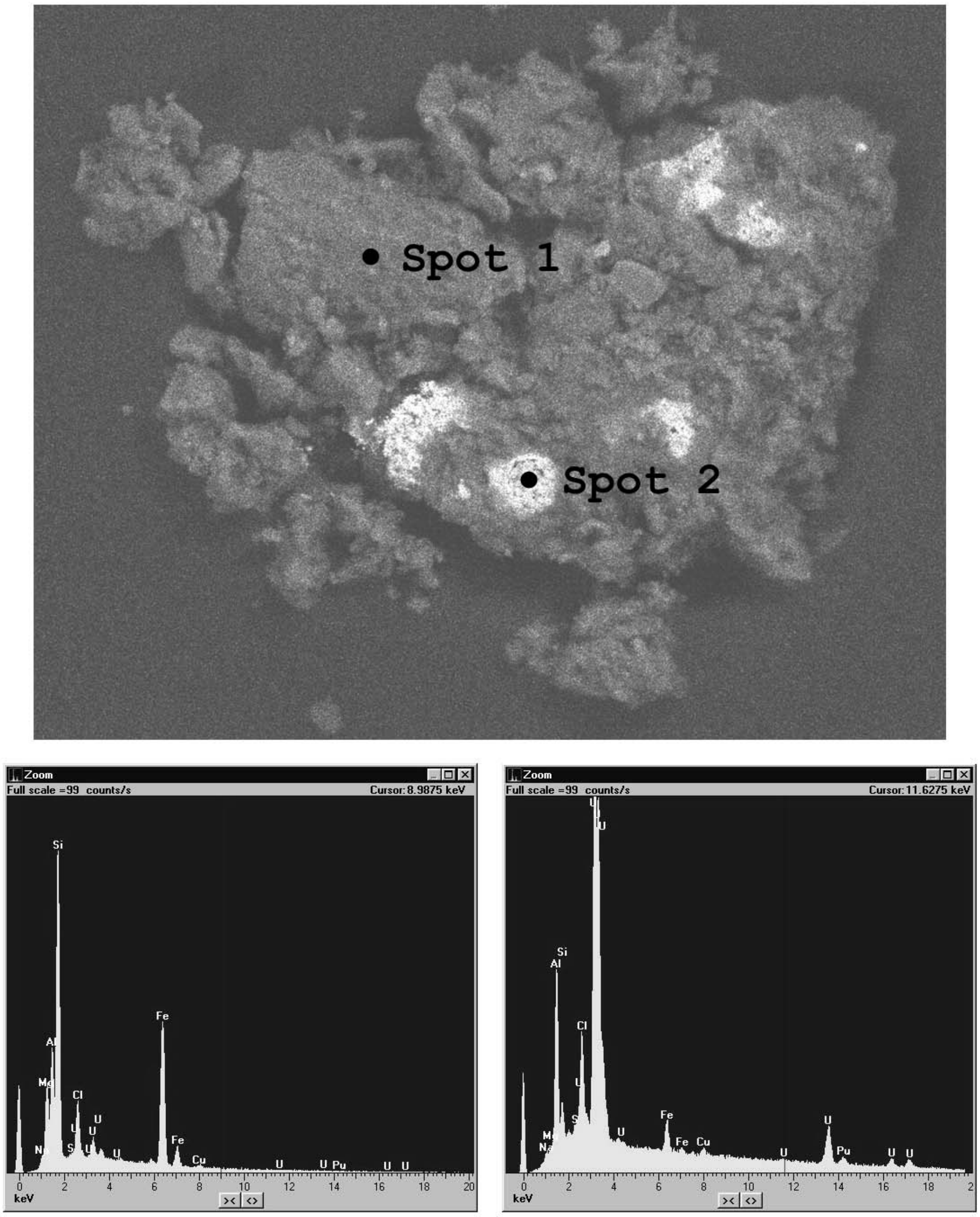

Fig. 3. A backscatter SEM image of a hot particle from the Thule sediments collected at the Thule-97 expedition. The particle is coated with sediment material (greyish area), but at some spots high density areas (light areas) can be seen. The elemental composition were analyzed by EDX at several spots on the particle. Two of the spot spectras can be seen. Spectra from spot 1 shows typical sediment material i.e. Al, Si, Mg and Fe. The spectra from spot 2 shows M and L X-ray from U and Pu.

for the Thule sediment, 0.10 ± 30% and 0.08 ± 110 %, which are in agreement with sample Thule-3 in Table 5.

If the sediment contains more than one unique source, the isotopic ratios

Table 5
Plutonium isotopic ratios, data from (a) Stürup et al (3) and (b) Mitchell et al (4)

Sample	^{240}Pu/^{239}Pu (a)	^{240}Pu/^{239}Pu (b)	^{238}Pu/$^{239+240}$Pu (b)	Sample activity (b)
	mass ratio	mass ratio	activity ratio	Bq
Thule-1	0.056 ± 0.001	0.055 ± 0.002	0.0162	5.9
Thule-2	0.043 ± 0.001	0.037 ± 0.003	0.0116	0.6
Thule-3	0.027 ± 0.001	0.029 ± 0.001	0.0092	2.4
Thule-4	0.030 ± 0.001	0.031 ± 0.002	0.0100	1.4
Thule-5	0.041 ± 0.001	0.034 ± 0.001	0.0108	0.8

determined on bulk sediment samples would show the mean ratio of these sources in low activity samples, provided the geographical distribution of the different isotopic sources is the same. The activity ratio of ^{238}Pu/$^{239+240}$Pu in Thule sediments has been determined in several hundreds of samples over the past 33 years (2; 16; 17; 18; 19; 20). These ratios have been measured by alpha spectrometry performed on bulk sediment samples (0.5–5g). The mean ^{238}Pu/$^{239+240}$Pu ratio from the sediments collected during the Thule 1984, 1991 and 1997 expeditions is 0.014 ± 0.004 (n = 328), decay corrected to 2001. This mean ratio is derived from the sediment close to the point of impact (within a radius of 8 km). In this area the contribution of global fallout Pu is less than 1 % of the Pu inventory. This ratio is lower than the ratios found in the five particles studied in the present paper, which indicates that more than one unique source is present. However, since the plutonium activity in the sediment is, to a great extent, associated with hot particles, and fairly high activity samples have been analyzed, it could be possible to investigate the unique ratios of the sources present in the sediment by applying some criteria to old data. One such criterion is to use the ratios in the sub-samples with the highest activities, which are likely to originate from one single hot particle. The counting statistics in the alpha spectra of these samples are also better and so the uncertainty on the ^{238}Pu measurements from interfering peaks originating from the short lived daughters from the thorium series is lessened. However, as the sediments at the point of impact have very high activity concentrations and numerus particles are present, a second criterion must be applied. That is, that the activity deviation between a particular sediment slice and the mean activity between the slice over and under this slice must be large, i.e. an abnormal activity concentration should be observed in the sediment depth profile. We have performed such a study on the samples collected at the Thule-97 expedition fulfilling these two criteria. It is clear from Figure 4 that almost none of the these samples have the calculated mean ^{238}Pu/$^{239+240}$Pu ratio of 0.014. The ^{238}Pu/$^{239+240}$Pu ratios are grouped more or less around two ratios of 0.016 and 0.010. In the plot to the left in Figure

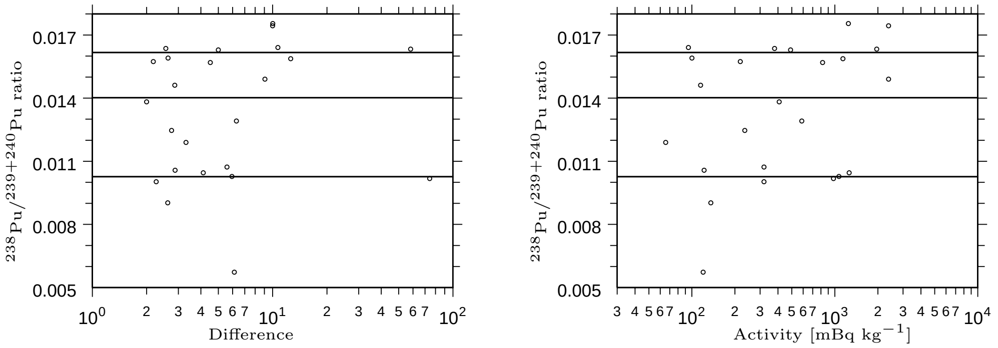

Fig. 4. The two plots show the ^{238}Pu/$^{239+240}$Pu activity ratios in bulk sediment samples. To the left are the ratios plotted against the deviation from the mean activity of the activity concentration above and under the slice and to the right are the ratios plotted against the activity concentration in the sub-sample. The ratios are grouped in two groups around 0.016 and 0.010, and it is very few observations close to the mean ratio of 0.014.

4, the ratios are plotted against the activity concentration deviation, i.e. the second criteria. The two samples with the largest deviation most probably originates from one single source (hot particle) and they have activity ratios of 0.0102 and 0.0163. In the right hand plot of Figure 4 the ratios are plotted against the activity concentration and it is clear that the samples with highest activity concentrations lie towards the 0.016 ratio group. Assuming that only these two unique ratios are present and the mean ratio observed is 0.014, this would mean that 2/3 of the debris originates from the source with the ^{238}Pu/$^{239+240}$Pu activity ratio of 0.016. The high ^{238}Pu/$^{239+240}$Pu ratio is in good agreement with the 5 hot particles studied in the present paper. These particles have all higher activity (6–84 Bq $^{239+240}$Pu) than the analyzed bulk sediment samples, where the highest activities of the samples were about 2.5 Bq $^{239+240}$Pu.

Dahlgaard et al. (1) have grouped the ^{240}Pu/^{239}Pu mass ratios data, determined by (HR)-ICP-MS measurement of 40 bulk sediment samples collected on the Thule-97 expedition, and plotted the ratio against the activity in the analyzed sample. It is clear from Figure 5 (redrawn from Dahlgaard et al. (2)) that the high activity samples are split into two groups, with mass ratios of 0.057 and 0.027. However, the data do not satisfy the second criterion described above. The mean ratio of these measurements is 0.0442 ± 0.0073. The most active sample has a ratio of 0.056 which is similar to the particles studied in this paper. This is an indication of a group around the mass ratio of 0.043, however these are samples from locations close to the point of impact, less than 1 km, and they are considered as low active for these locations. For that reason these bulk samples should be considered as a mix of all the sources and reflect the mean ratio between the sources.

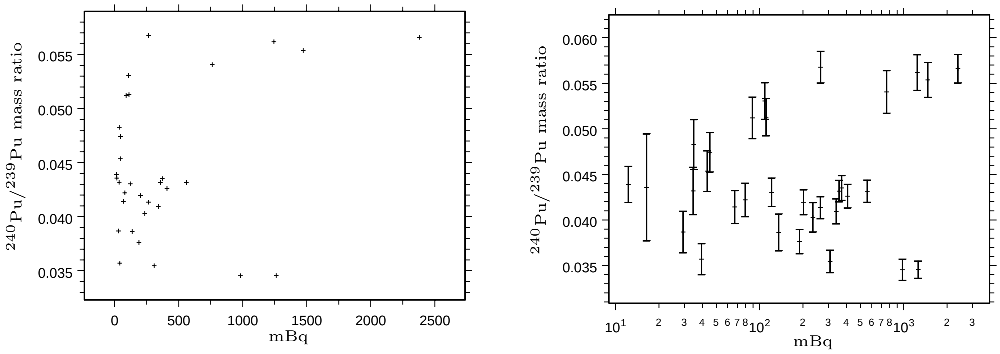

Fig. 5. The two plots show the ^{240}Pu/^{239}Pu mass ratio in bulk sediment samples. The two plots consists of the same data and the ratios are plotted against the activity in the sub sample. To the left is a linear scale and to the right a logarithmic scale for the sub sample activity. The mass ratios are grouped in two groups around 0.056 and 0.035. Data from Dahlgaard et al. (2).

This study concludes that the Thule debris has at least two different Pu sources, and most probably only two. It cannot be determined whether these two sources originate from different weapons or from different parts within the weapons. Most of the debris, about two thirds, originates from the source with a unique ^{240}Pu/^{239}Pu isotopic mass ratio of 0.056 and an activity ratio ^{238}Pu/$^{239+240}$Pu of 0.016, and about one third from the source with a mass ratio ^{240}Pu/^{239}Pu of 0.027 and an activity ratio ^{238}Pu/$^{239+240}$Pu of 0.010 (reference date, December 2001). One explanation, excluding the statistical chance that the present study only have sampled particles from the "high ratio group", could be that this source, during disintegration, produced larger particles. This is also indicated from the bulk sediment samples, where the samples with the highest activity originate from this source.

^{241}Am/$^{239+240}$Pu ratios have also been determined many times in Thule sediments. However, the ratios have in some cases been determined on different aliquots, which often is the case in the analysis of high activity samples. Therefore, the ratios determined are of no use in evaluating the unique source terms. The ratio is still increasing due to the decay of ^{241}Pu. To be able to compare data sets from different expeditions the amount of ^{241}Pu and the manufacture date of the different sources of the weapons must be known. It is probable that the ^{241}Pu content differs between the different sources in the Thule accident debris, as the ^{241}Am/$^{239+240}$Pu activity ratio reported shows large variations (1; 21). If the sources were made at different times it would be very complicated to determine the expected current ^{241}Am/$^{239+240}$Pu activity ratios. The mean ratio of the five particles is 0.169 ± 0.005 (reference date: December 2001).

Uranium analysis at trace levels (ppb, ng/g) is difficult as uranium is a naturally occurring element. It therefore imposes great demands on the purity of the reagents and equipment employed during the course of the analysis. In this study the ^{235}U/^{238}U ratio could easily have been biased by naturally occurring uranium contamination from the walls of the beakers, laboratory equipment used and from the reagents. A pure ^{235}U sample would be almost impossible to measure as the natural ratio of ^{235}U/^{238}U is 0.00727, thus only a slight contamination by natural U would seriously alter the ^{235}U/^{238}U ratio. For example, if ^{235}U should be analyzed in a one gram sediment sample from the Bylot Sound, containing one single Pu/U hot particle (example particle TPE in the present study), assuming that 100 % of the uranium was ^{235}U, the ^{235}U/^{238}U ratio would be about 0.0249 mass ratio (0.158, activity ratio) since in marine sediments a typical concentration is about 6.19 mg/g (77 Bq/g) of naturally occurring ^{238}U. The most robust ratio to use is therefore ^{235}U/^{239}Pu, as the total uranium to plutonium is easily biased by internal contamination of ^{238}U.

This study proves that the nuclear-weapons involved in the Thule accident were not, as has been said before, pure Pu-weapons, instead it is clear that the weapons are a mixture of Pu and U. As only particles originating from one unique source have been analyzed, this is at least true for these. The mass of ^{235}U was around 4 times the mass of ^{239}Pu in the fresh accidental debris.

As discussed earlier, the ^{235}U/^{239}Pu mass ratios in samples sampled at different years, indicate that uranium is leaving the particle lattice over time, see Figure 2. The variations are large, and for the the ratio at year 1997 only one particle have been analysed. The variations can be explained to some extent by that the leaching rate is probably a function of sediment depth.

The most probable sea water constituent responsible for potential disssolution of a uranium-plutonium oxide particle would be carbonate since it forms very stable complexes with actinides and lanthanides (22). It is well known that the strong uranium carbonate complex ($UO_2(CO_3)_2^{2-}$ / $UO_2(CO_3)_3^{4-}$) is the major reason for the long residence time in the oceans. In sea water the carbonate/bicarbonate concentrations depend on the partial pressure of CO_2 in the atmosphere. In normal sea water with a pH of around 8, bicarbonate dominates by about a factor of ten over carbonate, typical bicarbonate concentrations are in the mM range. In the sediment interstitial waters however the concentrations are often higher than in the overlying sea water due to the degradation of sediment organic matter.

There are several experiments conducted in laboratories where the leaching/corrosion of UO_2 from nuclear fuel has been studied in attempts to determine the breakdown of the initial barriers for the release of fission products. In these experiments (conducted in alkaline as well as acid salt solutions of different types) most data indicate a stronger release of uranium than plutonium. Röllin et al. (23) observed a ten-fold higher dissolution rate of uranium than plutonium from spent UO_2 fuel when exposed to bicarbonate solutions at millimolar concentrations. De Pablo et al. (24) proposed a model for uranium dissolution from UO_2 when exposed to bicarbonate solutions in oxic media. The model suggested an initial oxidation to U(VI) followed by binding of the bicarbonate to the U(VI) sites of the oxidised layer and later detachment of the U(VI)-carbonato surface complex. In their experiments they found dissolution rates in the order of 1.4 μmoles m^{-2} d^{-1} of uranium in 1 mM bicarbonate solutions at 10° C. This means only some 0.1-1 ng of uranium over a 29 year period for particles with sizes found in this investigation ($\sim$ 100 ng). The particles formed during the Thule accident are however likely to be rather different to the spent UO_2 fuel, which is of concern in nearly all the published reports on UO_2 dissolution. The specific surface area (porosity of particles) is probably different (fast cooling after fire at Thule) and also the $(U,Pu)O_2$ chemical structure. Certainly, the particles formed at Thule should be treated as site-specific particles and be regarded as a unit of their own. Knowledge on their dissolution and corrosion rates may only be derived from experiments conducted with the very same material.

When considering particle dissolution and potential release of weapons plutonium, it also has to be considered that over time most of the particles will reach sediment depths where oxic dissolution kinetics may not be applied (eg. the UO_2 model by De Pablo et.al. (24) described above), during oxygen deficient or anoxic conditions uranium may not become oxidised and thus the particle dissolution rates may be significantly reduced. Röllin et.al. (23) observed UO_2 dissolution rates which were a factor of 1000 less under reducing conditions than in oxic conditions with the same bicarbonate concentrations for both cases. On the other hand, dissolution rates of plutonium were only reduced by a factor of ten in the same experiment.

The leaching of the uranium should be investigated on future expeditions, using the uranium ratios as a water body tracer and try to determined the U/Pu ratio at bottom water at the point of impact to confirm the observation of uranium leaching. However, it could be difficult as sea water contains large amounts of natural uranium.

5 Conclusions

The source term for the Thule debris consists of more than one source, probably two. In at least one of the sources the main fissile material was ^{235}U (about 4 times more than ^{239}Pu). The study of the hot particles indicates a relationship between leached uranium and the time these particles have been present in the sediments.

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Abstract (Max. 2000 char.)

This thesis concerns a nuclear accident that occurred in the Thule (Pituffik) area, NW Greenland in 1968, called the Thule accident. Results are based on different analytical techniques, i.e. gamma spectrometry, alpha spectrometry, ICP-MS, SEM with EDX and different models, i.e. (CRS, CIC). The scope of the thesis is the study of hot particles. Studies on these have shown several interesting features, e.g. that they carry most of the activity dispersed from the accident, moreover, they have been very useful in the determination of the source term for the Thule accident debris.

Paper I, is an overview of the results from the Thule-97 expedition. This paper concerns the marine environment, i.e. water, sediment and benthic animals in the Bylot Sound. The main conclusions are; that plutonium is not transported from the contaminated sediments into the surface water in this shelf sea, the debris has been efficiently buried in the sediment to great depth as a result of biological activity and transfer of the plutonium to benthic biota is low.

Paper II, concludes that the resuspension of accident debris on land has been limited and indications were, that americium has a faster transport mechanism from the catchment area to lakes than plutonium and radio lead.

Paper III, is a method description of inventory calculation techniques in sediment with heterogeneous activity concentration, i.e. hot particles are present in the samples. It is concluded that earlier inventory estimates have been under estimated and that the new inventory is about 3.8 kg (10 TBq) of ^{239,240}Pu.

Paper IV, describes hot particle separation/identification techniques using real-time digital image systems. These techniques are much faster than conventionally used auto radiography and give the results in real time.

Paper V, is a study of single isolated hot particles. The most interesting result is that the fission material in the weapons involved in the accident mostly consisted of ^{235}U (about 4 times more in mass than ^{239}Pu). This paper concludes that there are at least two different source terms for the Thule accident debris. Another interesting feature is that it seems like uranium is leaching from the particles faster than plutonium and americium.

Descriptors

Environmental radioactivity, nuclear accident, Thule, Greenland, Bylot Sound, radionuclide, plutonium, uranium, americium, fallout, source term, inventory, isotopic ratio, separation technique, hot particle, heterogeneous activity concentration, gamma spectrometry, alpha spectrometry, ICP-MS, SEM, realtime digital image systems

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Mission

To promote an innovative and environmentally sustainable technological development within the areas of energy, industrial technology and bioproduction through research, innovation and advisory services.

Vision

Risø's research shall **extend the boundaries** for the understanding of nature's processes and interactions right down to the molecular nanoscale.
The results obtained shall **set new trends** for the development of sustainable technologies within the fields of energy, industrial technology and biotechnology.
The efforts made **shall benefit** Danish society and lead to the development of new multi-billion industries.

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