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# DETERMINATION OF TRANSURANIC ELEMENTS, THEIR BEHAVIOUR AND SOURCES IN THE AQUATIC ENVIRONMENT

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## **ACADEMIC DISSERTATION**

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**Keywords** transuranic elements, plutonium, aquatic environments, sources of transuranic elements, behaviour of transuranic elements, sediment, fish

## Summary

In this study, the distribution of transuranic elements, mainly plutonium, has been studied in order to clarify the possible sources and behaviour of these elements and the effect of the source on activity ratios in the aquatic environment. The research was conducted in the Arctic sea areas, including the nuclear accident area in Thule off the coast of Greenland, the Baltic Sea, and the Finnish freshwater environment. The study was carried out from 1986 to 2001, most of it after 1993. Altogether, 235 environmental samples, mainly sediments but also biota and lake water, were analysed, all of them for  $^{238}\text{Pu}$  and  $^{239,240}\text{Pu}$ , and a part for  $^{241}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{242}\text{Cm}$  and  $^{243,244}\text{Cm}$ . Because of the low-level concentrations of the nuclides, a great emphasis was placed on the quality of methods for determining concentrations and nuclide ratios. A new method for measuring  $^{241}\text{Pu}$  with a liquid scintillation was modified during the study.

The use of activity ratios of transuranic isotopes proved to be a good tool for the estimation of sources and their effects on activity concentrations in sediments. In the Barents, Petshora, and Kara Seas the activity concentrations of plutonium in sediments and biota were low; no other clear source of plutonium than the global fallout from nuclear weapons tests were observed. According to the activity ratios in sediments from the Kola Bay and the outlet of the Bay, it could be assumed that in addition to the global fallout, another source for plutonium existed. The concentrations of transuranic elements in the sediments off the Thule air base, in the area of a nuclear accident, were from one to three magnitudes higher than the fallout level in the Arctic sea areas. The presence of large and uneven quantities of hot, weapon-origin particles distorted the estimation of inventories. Significant variations in the isotope ratios in the accident area indicate that plutonium in Thule comes from more than one source of a quality.

An effect of Chernobyl-origin transuranic elements could be detected in the sediments of the Baltic Sea and in freshwater fish in Finland, which was

clearly seen from both the  $^{241}\text{Pu}$  concentrations and from the plutonium isotope ratios in vertical distributions of sediment samples in the Baltic Sea. The maximum concentrations of plutonium isotopes,  $^{241}\text{Am}$  and  $^{242}\text{Cm}$ , in Finnish freshwater fish were low, but the influence of the Chernobyl fallout could be best seen in the elevated  $^{241}\text{Pu}$  and  $^{242}\text{Cm}$  concentrations. The dose received from transuranic elements through consumption of freshwater fish after the Chernobyl accident was insignificant, 50 nSv per year when at maximum. Some results suggest different environmental mobilization between  $^{238}\text{Pu}$  and  $^{239,240}\text{Pu}$ , and between americium and curium. More study is needed in order to assure these assumptions and clarify their causes.

*IKÄHEIMONEN Tarja K. STUK-A194. Transuraanien määrittäminen, niiden lähteet ja käyttäytyminen vesiympäristössä. Helsinki 2003, 82 s + liitteet.*

**Avainsanat** transuraanialkuaineet, plutonium, vesiympäristö, transuraanialkuaineiden lähteet, transuraanialkuaineiden käyttäytyminen, sedimentti, kala

## Yhteenveto

Tässä työssä tutkittiin ensisijaisesti plutoniumin, mutta myös muiden transuraanialkuaineiden, esiintymistä vesiympäristöissä tarkoituksena selvittää niiden eri lähteitä ja käyttäytymistä sekä lähteiden vaikutusta nuklidisuhteisiin. Tutkimusalueina olivat Jäämeren eri alueet Thulen ydinonnettomuusalue Grönlannin rannikolla mukaan lukien, Itämeren alue sekä järviympäristö Suomessa. Tutkimus tehtiin vuosien 1986 ja 2001 välillä, pääpainon ollessa vuoden 1993 jälkeisessä ajassa. Työssä analysoitiin kaikkiaan 235 ympäristönäytettä, joista suurin osa oli sedimenttinäytteitä, mutta myös levä-, kala- ja järvivesinäytteitä kuului tutkimuksen piiriin. Kaikista näytteistä analysoitiin  $^{238}\text{Pu}$  ja  $^{239,240}\text{Pu}$ , osasta näytteitä myös  $^{241}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{242}\text{Cm}$  ja  $^{243,244}\text{Cm}$ . Tutkimuksen aikana kiinnitettiin erityistä huomiota aktiivisuuksien ja nuklidisuhteiden määritysmenetelmiin ja niiden laatuun, koska tutkittujen nuklidien pitoisuudet ympäristössä ovat erittäin pienet.  $^{241}\text{Pu}$ :n määrittämiseksi kehitettiin uusi, nestetuikelaskentaan perustuva menetelmä.

Aktiivisuussuhteiden käyttö päästölähteiden ja niiden vaikutusten arvioimiseksi sedimenttinäytteissä osoittautui hyväksi tutkimustyökaluksi. Barentsin, Petshoran ja Karan meren sedimenttien ja biotinäytteiden aktiivisuuskonsentraatiot olivat pieniä. Ydinkokeiden aiheuttama globaalin laskeuman havaittiin olevan ainoa selvästi tunnistettava plutoniumin päästölähde tällä alueella. Sen sijaan Kuolan vuonosta ja sen edustalta otettujen sedimenttinäytteiden isotooppisuhteiden perusteella arvioitiin, että siellä on globaalin laskeuman lisäksi jokin muu plutoniumin lähde. Thulen lentotutkikohdan läheltä, ydinonnettomuusalueelta otetuissa sedimenttinäytteissä transuraanien pitoisuudet olivat kymmenistä aina tuhatkertaisiin verrattuina Jäämeren alueen pitoisuuksiin yleensä. Transuraanien kokonaismäärän arviointi tällä alueella oli vaikeaa, koska sedimentit sisälsivät paljon epätasai-

sesti jakaantuneita ydinpommeista peräisin olevia korkea-aktiivisia hiukkasia. Thulen sedimenttien aktiivisuussuhteiden suuren vaihtelun perusteella arvioitiin, että alueella on ainakin kahdesta erilaisesta lähteestä peräisin olevaa plutoniumia.

Itämeren sedimenteissä ja Suomen järviympäristössä voitiin selvästi havaita Tshernobylin onnettomuudesta peräisin olevia transuraaneja. Parhaiten se voitiin havaita Itämeren sedimenttien syvyysjakaumien  $^{241}\text{Pu}$  pitoisuuksista sekä plutoniumin isotooppisuhteista jakaumissa. Suurimmat havaitut plutoniumin ja  $^{241}\text{Am}$ :n sekä  $^{242}\text{Cm}$ :n aktiivisuuspitoisuudet järvikaloissa olivat pieniä, kuitenkin Tshernobylin laskeuman vaikutus nähtiin selvästi kohonneissa  $^{241}\text{Pu}$  ja  $^{242}\text{Cm}$  pitoisuuksissa. Tshernobylin laskeuman transuraanien aiheuttama annos sisävesikaloista suomalaisille oli erittäin pieni, suurimmillaan vain 50 nSv vuodessa. Joidenkin järvivesikalatulosten perusteella näytti siltä, että  $^{238}\text{Pu}$  ja  $^{239,240}\text{Pu}$  käyttäytyisivät ympäristössä erilailla, samoin erilaista käyttäytymistä havaittiin americiumin ja curiumin välillä. Tämän havainnon varmistaminen ja mahdollisten käyttämiserojen syyn selvittäminen vaatisi lisätutkimuksia asiasta.

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## List of publications

This thesis consists of the scientific review (Chapters 1 - 5) and the study based on the following original research publications referred to in the text by their Roman numerals:

- I Ikäheimonen TK, Rissanen K, Matishov D, Matishov G. Plutonium in fish, algae and sediments in the Barents, Petshora and Kara Seas. *The Science of Total Environment* 1997; 202: 79-87. Reprinted with the kind permission of Elsevier Science.
- II Rissanen K, Ikäheimonen TK, Matishov D, Matishov G. Radioactivity levels in Kola Bay. *Radiation Protection Dosimetry* 1998; 75: 223-228. Reprinted with the kind permission of Nuclear Technology Publishing.
- III Ikäheimonen TK, Ilus E, Klemola S, Dahlgaard H, Ryan T, Eriksson M. Plutonium and americium in the sediments off the Thule air base, Greenland. *Journal of Radioanalytical and Nuclear Chemistry* 2002; 252: 339-344. Reprinted with the kind permission of Kluwer Academic Publishers B.V.
- IV Moring M, Ikäheimonen TK, Pöllänen R, Ilus E, Klemola S, Juhanoja J, Eriksson M. Uranium and plutonium containing particles in a sea sediment sample from Thule, Greenland. *Journal of Radioanalytical and Nuclear Chemistry* 2001; 248: 623-627. Reprinted with the kind permission of Kluwer Academic Publishers B.V.
- V Ikäheimonen TK. Measurement of  $^{241}\text{Pu}$  in environmental samples. *Journal of Radioanalytical and Nuclear Chemistry* 2000; 243: 535-541. Reprinted with the kind permission of Kluwer Academic Publisher B.V.
- VI Ikäheimonen TK, Saxén R. Transuranic elements in fish compared with  $^{137}\text{Cs}$  in certain lakes in Finland. *Boreal Environment Research* 2002; 7: 99-104. Reprinted with the kind permission of The Board of the Boreal Environment Research.



# 1 Introduction

Man-made transuranic elements have been released into the environment since the use of nuclear weapons and nuclear tests. Other releases into the environment have been associated with nuclear fuel cycles and some accidents but also through the active dumping of wastes into oceans. Most of the isotopes of these elements are alpha-active with long physical and biological half-lives, which make them highly radiotoxic. Due to this fact, monitoring of their spreading from sources and studying their behaviour in the environment are important.

The aim of the study was to investigate the influence of possible different sources of transuranic elements, the distribution of these nuclides in aquatic environments as well as the exposure of Finnish people due to fish. The Arctic sea areas, the Baltic Sea and the Finnish freshwater environment were selected for the research areas. In the Arctic areas, the area of the accident off Thule and many detailed unknown sources in other areas affected distributions of transuranic elements. The fallout from the Chernobyl accident, including transuranic elements, extended over Finland. Considering its effect on the freshwater environment in Finland and the Baltic Sea area, these were chosen as the objects of this study. Altogether, 235 environmental samples from these areas were sampled and analysed.

Due to usually very low concentrations of transuranic elements in the environment, their analysis is demanding. Therefore, the methodology and quality of results are evaluated.

The main emphasis is on plutonium (Pu), and its isotopes  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$  together with  $^{240}\text{Pu}$ , and  $^{241}\text{Pu}$ , but also americium (Am), its isotope  $^{241}\text{Am}$  and curium, its isotope  $^{242}\text{Cm}$  (and  $^{243,244}\text{Cm}$ ), which were all studied in this work. Pu isotopes are measured without different oxidation states. The results obtained are reported in publications I to VI, and some additional information especially concerning the methods, are also presented here.

## 2 Chemical and nuclear properties of transuranic elements

Transuranic elements (later referred to as TRU) are elements with an atomic number greater than 92.

Pu, Am and Cm are included in the actinide group with atomic numbers of 94, 95, and 96 respectively. These elements were discovered by the group during the “Manhattan Project”, plutonium in 1941, curium in 1944 and americium in 1945. (IAEA 1966, Seaborg 1993). In the actinide elements, the 5f electron shell is filled analogous to the 4f shell in lanthanides (atomic numbers 58 - 71). The 5f electrons are less effectively shielded than those of 4f. Due to the unstable 5f electrons, actinide elements have more complex chemical properties than the lanthanides do. In particular, due to multiple oxidation states, their environmental behaviour is difficult to predict. Plutonium has five different oxidation states from III to VII and most of them can occur simultaneously in solution. However, americium and curium seem to behave more likely as the rare earths and probably prefer to exist in the trivalent state in the environment. Nevertheless, it is possible for them also to be in tetravalent states, for example in strongly oxidizing natural waters (Edgington 1981, Seaborg 1993). Their chemical compound, oxidation state, redox conditions, complexation, colloid formation and sorption or desorption characteristics affect the environmental behaviour of these elements (Allard et al. 1984, Silva and Nitsche 1995, Watters et al. 1980).

Most transuranic isotopes are alpha emitters with long half-lives, but there is also a beta-emitter,  $^{241}\text{Pu}$ . Studied TRUs are mainly man-made elements. Nominal amounts of  $^{239}\text{Pu}$  are continuously produced from  $^{238}\text{U}$  by spontaneous fission. Both  $^{244}\text{Pu}$  and  $^{239}\text{Pu}$  were assumed to be produced by supernova explosions during the creation of the universe. Since  $^{244}\text{Pu}$  has a half-life of  $8.3 \times 10^7$  years, no or very little of it could have survived to the present time. Natural  $^{239}\text{Pu}$  is likely to be associated with uranium deposits, and is assumed to have had a concentration about  $1 \mu\text{Bq/kg}$  in the earth’s crust and in the oceans during the evolution of life (Taylor 2001).

The radiological properties of studied nuclides are given in Table I.

**Table I.** Transuranium nuclides studied with their radiological properties (in italics, if not alpha decay) (Firestone and Shirley 1996). (Specific activities ( $A_s$ ) have been calculated according to equation:  $A_s = \lambda_i N_A / M_i$ , where  $\lambda_i$  is the decay constant of the radionuclide,  $N_A$  is the Avogadro number and  $M_i$  is the mass number of the radionuclide; unit  $s^{-1}/g$ .)

Nuclide	Half-live	Main intensities %	Energy MeV	Specific activity TBq/kg
<b>Pu-238</b>	87.74 a	28.6 71.4	5.456 5.499	633
<b>Pu-239</b>	24110 a	11.5 15.1 73.3	5.106 5.144 5.157	2.29
<b>Pu-240</b>	6563 a	26.4 73.5	5.123 5.168	8.38
<b>Pu-241</b>	14.4 a	<i>&gt;99 (beta)</i>	<i>max. 0.0208</i>	3820
<b>Am-241</b>	432 a	13.3 85.1 <i>36.0 (gamma)</i>	5.443 5.486 <i>0.0595</i>	127
<b>Cm-242</b>	163 d	25.9 74.1	6.069 6.113	122 000
<b>Cm-243</b>	29.1 a	11.5 73.2	5.742 5.785	1870
<b>Cm-244</b>	18.1 a	23.6 76.4	5.762 5.805	3000

## 3 Sources and their effects on TRUs in environment

### 3.1 Atmospheric sources

The main sources of the TRUs released into the atmosphere are the nuclear weapons tests in 50s and early 60s, the Chernobyl accident in 1986, and the SNAP-9A satellite accident in 1964 for  $^{238}\text{Pu}$ . The estimates of the amounts released into the atmosphere varied according to references. These variations are shown in Table II.

**Table II.** Sources of TRUs released into the atmosphere.

Nuclide	Weapons tests PBq	SNAP-9A PBq	Chernobyl accident PBq	References
<b>Pu-238</b>	0.28 - 0.36	0.5 - 0.63	0.025 - 0.035	1,2,3,4,5,6
<b>Pu-239,240</b>	11 - 15	-	0.055 - 0.072	1,2,4,5,6, 10
<b>Pu-241</b>	140 - 360	-	5 - 6.2	2,4,5,6,7
<b>Am-241</b>	12*	-	0.006	7
<b>Cm-242</b>	minor	-	0.6 - 0.78	5,6,8
<b>Cm-243,244</b>	minor - 0.33	-	0.006	4,5,9

(\* when Pu-241 has totally decayed)

(References: 1. Hardy et al. 1973, 2. UNSCEAR 1982, 3. Perkins and Thomas 1980, 4. UNSCEAR 2000, 5. WHO 1989, 6. USSR 1986, 7. Allard et al. 1984, 8. Holm and Persson 1978, 9. Beasley and Ball 1980, 10. Harley 1980)

### 3.2 Other sources

Other sources can exist concerning aquatic and especially the marine environment. Weapons tests sites, nuclear reprocessing plants, and radioactive waste dumping and accident sites have contributed to the radionuclide contamination of the aquatic environment. The most important are: 1) The Marshall Islands (including the Enewetok and Bikini Atolls) 2) Novaya Zemlya, 3) Christmas Island, 4) French Polynesia (including the Mururoa and Fangataufa Atolls), and 5) Lop Nor. Discharge data is available from the reprocessing plants in 1) Sellafield, situated on west coast of England, 2) La Hague, on northwest coast of France, and 3) the Indian reprocessing plants in Trombay and Tarapur on east coast of India. Reprocessing plants situated on rivers are the Savannah River Laboratory in South Carolina, USA and Krasnoyarsk, Tomsk and Mayak on the Siberian rivers and Marcoule on the

Rhone, France. Mostly low-level wastes have been dumped into the Atlantic and Pacific Oceans and more active wastes into the Arctic seas (Livingstone and Povinec 2000).

In this study, the areas for research are the Arctic seas, the Baltic Sea and the freshwaters in Finland. Sources which can, in addition to atmospheric sources, increase the amount of radionuclides in these environments are the reprocessing plants of Sellafield and La Hague, the Thule aircraft accident near Greenland in 1968, nuclear tests, dumped nuclear wastes in the environment of Novaya Zemlya, the Barents and Kara seas, arctic river runoff from the contaminated areas of the former Soviet Union, and radioactive wastes on the Kola Peninsula.

### **3.2.1 Discharges from European reprocessing plants**

The discharges from Western European reprocessing plants have been estimated and measured over recent years. TRUs from Sellafield dominate these discharges. A peak in discharges occurred from 1970 - 1980, whereas the total discharge amounts were, until 1991, 100 TBq for  $^{238}\text{Pu}$ , 610 TBq for  $^{239,240}\text{Pu}$  and 945 TBq for  $^{241}\text{Am}$ . The activities of  $^{241}\text{Pu}$  have been about two orders of magnitude greater than those of alpha emitting Pu-isotopes. After 1991, the amounts per year have been one TBq or less. The discharges of  $^{242}\text{Cm}$  and  $^{243,244}\text{Cm}$  have been 0.1 - 0.5 TBq per year and 0.05 - 0.25 TBq per year respectively, with a reducing effect between the years 1978 - 1990 (Cook et al. 1997, Kershaw et al. 1992). The most contaminated area is the Irish Sea, but traces of discharges have been observed as far as the Arctic seas (Holm et al. 1986, Baskaran et al. 1995).

The discharges from La Hague have not been estimated in such detail. From 1971 to 1995, the estimate for alpha emitting Pu-isotopes is 2.4 TBq. Amounts of  $^{241}\text{Pu}$  in discharges have been more than a hundred fold (EC 1995, EC 1996, EC 1997). Overall, liquid releases of Pu-isotopes from La Hague have been 0.4% of that of Sellafield (Guegueniat et al. 1995).

### **3.2.2 Nuclear tests, dumped wastes and leakages from other sources**

In Novaya Zemlya, 132 nuclear test explosions were performed. The local fallout from these tests can affect TRU concentrations in the Arctic sea area (Bradley et al. 1995).

There are several dumping sites for six nuclear submarine reactors and an icebreaker, including their fuels, and ten other reactors without fuel near

Novaya Zemlya (Sjöblom and Linsley 1995). In addition, a major part of the nuclear fuel and core barrel from a PWR reactor was also dumped there (Lynn et al. 1995). The total amount of these dumped wastes has been calculated as 4.7 PBq in 1995, of which about 0.1 PBq come from actinides (IAEA 1997). Most of activity of the actinides was from  $^{241}\text{Pu}$ , 0.08 PBq (Baxter et al. 1998). In addition, a sunken nuclear submarine (Komsomolets), sunk in 1989, lays in the Norwegian Sea with its reactor and weapons. The total amount of  $^{239,240}\text{Pu}$  was estimated to be about 25 TBq in the submarine (Hoibrøten et al. 1995). The most contaminated areas are the local coastal areas of Novaya Zemlya, such as the Chernaya, Stepovoy, and Abrosimov Bays (Livingstone and Povinec 2000, Smith et al. 2000).

Liquid and solid wastes were released and dumped into the Barents and Kara Seas until 1991. The estimated amount of liquid wastes was 890 TBq of total activity, of which the amounts of dumped  $^{239,240}\text{Pu}$  and  $^{241}\text{Pu}$  are 9 and 78 TBq respectively (IAEA 1997, Livingstone and Povinec 2000, Namjatov 1995). Most of the solid wastes were dumped into the Kara Sea, where the total activity was 590 TBq.

The Ob and Yenisey river systems can transport radioactive contamination to the Kara Sea from the reprocessing spent fuel from the Mayak, Tomsk-7 and Krasnoyarsk-26 installations and the Semipalatinsk weapon tests site located on riversides inland (Kenna and Sayles 2002, Paluszkiewicz 1995).

Several military installations and the civilian “Atomflot” icebreaker fleet base exist on coast of the Kola and Motovsky Bays. Leakages from these sites as well as from ships in bad condition containing spent nuclear fuels in the Kola Bay can be possible local sources for TRUs in the sea area (Gusgard 1995, Matishov et al. 1999). The total amount of these possible contaminants is unknown.

### **3.2.3 The nuclear accident at Thule**

In 1968, a US aircraft carrying four thermonuclear weapons crashed onto the sea ice near the shore of Thule Airbase, Greenland. According to several investigations in the area from 1968 – 1991, the total estimated amounts of Pu isotopes left in Thule area was: 1.4 TBq of  $^{239,240}\text{Pu}$ , 4.6 TBq of  $^{241}\text{Pu}$ , 0.025 TBq of  $^{238}\text{Pu}$  and 0.07 TBq of  $^{241}\text{Am}$  (Aarkrog 1971, Aarkrog 1977, Aarkrog et al. 1980, Aarkrog et al. 1984, Aarkrog et al. 1987, Aarkrog et al. 1988, Aarkrog et al. 1997). The IAEA has come to an estimation of a smaller total amount of Pu isotopes: 3.1 TBq (IAEA 2001). In his thesis, Eriksson (2002) made a new



estimation of the amounts, and reached a much higher value for the amount of  $^{239}\text{Pu}$ : 10 TBq.

### 3.3 Activity ratios and chemical forms of TRUs of different sources

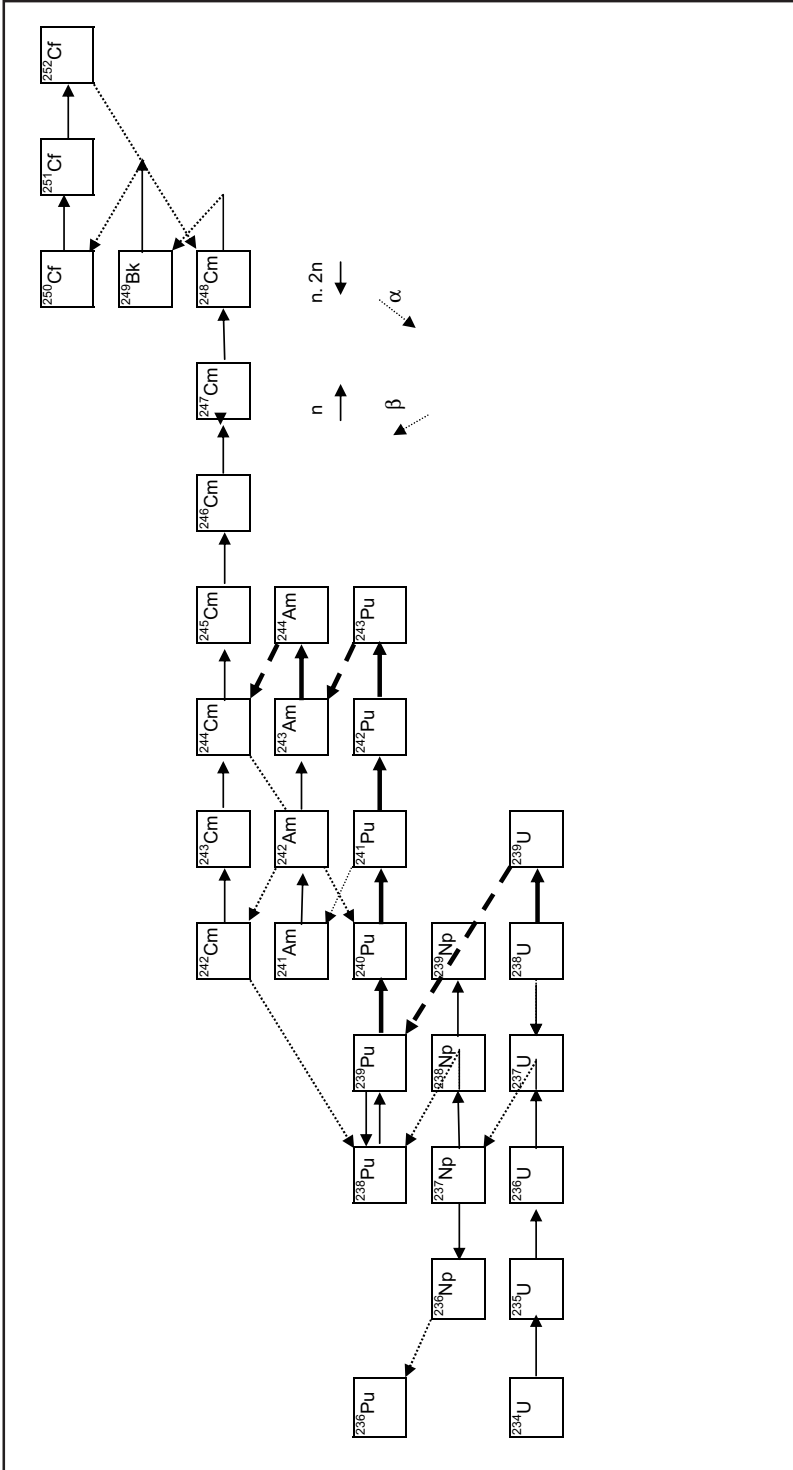
#### 3.3.1 Effect of origin mechanisms on activity ratios and amounts of isotopes

The isotopic composition of TRUs varies considerably depending on whether they originate from nuclear explosions or reactor operations. In a reactor, the neutrons are captured at slower rate than they are in explosions. The resulting isotopes may decay before additional neutron capture. In a nuclear explosion, neutron capture occurs in an extremely rapid session. There is no opportunity for the decay of the various isotopes that could break the chain of successive neutron capture. This leads to different mixtures of TRU isotopes (Perkins and Thomas 1980).

The amounts of TRU isotopes of reactor origin are much higher relative to  $^{239}\text{Pu}$ , particularly in the region just below and above the mass number 239 than those from nuclear weapons testing. The relative amounts of other isotopes to that of  $^{239}\text{Pu}$  depend on the reactor type and the burnup-time with increasing effect (Friberg 1998). The most abundant Pu nuclide resulting from tests was  $^{241}\text{Pu}$ . According to Perkins and Thomas (1980), the ratio  $^{241}\text{Pu}/^{239,240}\text{Pu}$  was 15 in the atmosphere in 1963. Most of the  $^{241}\text{Am}$  in weapon tests was formed *in situ* from the decay of  $^{241}\text{Pu}$ . In nuclear reactors,  $^{241}\text{Am}$  is particularly important because it is a relatively large contributor to the total alpha of high-burnup fuel. In addition to  $^{239}\text{Pu}$ ,  $^{238}\text{Pu}$  and  $^{242}\text{Cm}$  isotopes will also be principal alpha activities from nuclear reactors (Friberg 1998). The build-up chain of TRUs in nuclear fuels is shown in Figure 1.

#### 3.3.2 Activity ratios of TRUs from different sources

Different isotopic composition can be used to estimate or clarify the source of TRUs detected in the environment. The activity ratios of  $^{238}\text{Pu}/^{239,240}\text{Pu}$  and  $^{241}\text{Pu}/^{239,240}\text{Pu}$  are highest in the fuel of reactors and it is found there depending on the burn-up time. The next higher ratios are in the releases of nuclear reprocessing facilities, smaller than that in the fallout of nuclear tests and the smallest in weapons-grade plutonium (Friberg 1998, Holm et al. 1986).



**Figure 1.** Build-up chain of actinides in nuclear fuels with major (bold arrows) and minor (thin arrows) pathways (dashed lines) symbolise short-lived radioactive decay) (Koch 1995).

In 1986, the  $^{238}\text{Pu}/^{239,240}\text{Pu}$  ratio in the releases from the Chernobyl accident, where reactor fuel acts as a source, was typically about 0.5 and that of  $^{241}\text{Pu}/^{239,240}\text{Pu}$  was 83 (Aarkrog 1988, USSR 1986). Due to the rather short half-life of  $^{241}\text{Pu}$  (14.4 y), most of that originating from weapons tests has already decayed to  $^{241}\text{Am}$ , and the Chernobyl-origin  $^{241}\text{Pu}$  will lead to excess amounts of  $^{241}\text{Am}$  in contaminated areas during this century (Paatero 2000).

The activity ratios of discharges of reprocessing facilities depend on irradiated fuel and conditioning, and the storage of nuclear materials and radioactive wastes. For instance in the Sellafield plant, the burn-up time of fuel and nature of waste treatment have changed during the lifetime of the plant operation. Nuclide ratios have not been constant, and the estimated value has varied, as explained in the literature. During the 90s, the ratio of  $^{238}\text{Pu}/^{239,240}\text{Pu}$  was 0.21 (Kershaw et al. 1995), 0.28 according to Holm et al. (1986), and 0.19 as calculated by Cooper et al. (2000). The  $^{241}\text{Pu}/^{239,240}\text{Pu}$  ratio in discharges in the middle of the 90s was estimated to be 11 (Mitchell et al. 1999).

In atmospheric weapon testing, these ratios depend on the yield of the device; being somewhat higher in the high yield device,  $^{238}\text{Pu}/^{239,240}\text{Pu}$  was on average about 0.028 (Cooper et al. 2000). In the fallout in the northern hemisphere, the SNAP-9A satellite accident in 1964 increased the ratio to about 0.03 – 0.04 (calculated in 1995; Hardy et al. 1973, Perkins and Thomas 1980). In the near field tropospheric fallout of weapon tests such as on the Enewetok and Bikini Atolls, the  $^{238}\text{Pu}/^{239,240}\text{Pu}$  activity ratios varied from 0.006 to 0.0009 respectively (Cooper et al. 2000). In weapons-grade Pu, the  $^{238}\text{Pu}/^{239,240}\text{Pu}$  ratios have been small, such as 0.008 in the Kyshtym accident, and 0.014, which is found in the environment of the Thule accident (Cooper et al. 2000, Eriksson 2002). The activity ratios of different transuranic isotopes from different sources have been put together and presented in Table III.

### 3.3.3 Chemical forms of TRUs

The chemical form of nuclides depends greatly on the mode of formation of the nuclides. In the fallout from weapons tests, a noticeable fraction (about 67 %) of the total plutonium later deposited on the earth and oceans was produced by a reaction (n, $\gamma$ ) with  $^{238}\text{U}$  and the subsequent decay of  $^{239}\text{U}$  through  $^{239}\text{Np}$  to  $^{239}\text{Pu}$ . This portion of Pu was formed as single atoms after the explosion and thus, it was not involved in a reaction to form a high-fired oxide, as was the other part of Pu in the explosion (NCRP 2001, Watters et al. 1980). However,  $^{239}\text{Pu}$  exists mostly as  $\text{PuO}_2$  in near-field-fallout. It could be formed through reactions involving atomic particles and device component, or from the residual

**Table III.** Summary of the activity ratios of TRU isotopes from different sources (calculated to 1995 except for the Chernobyl accident in 1986. All references in brackets).

Source and means of release	Activity ratio			
	<u>Pu-238</u> Pu-239,240	<u>Pu-241</u> Pu-239,240	<u>Am-241</u> Pu-239,240	<u>Cm-242</u> Pu-239,240
Fallout from high yield weapon tests (northern hemisphere) + SNAP 9A	0.026 - 0.029* (1,2,3)  0.03 - 0.04 (4,5)	2.64 * - 4.9 (1,5)	0.25 – 0.40 (5,6,7)	-
Semipalatinsk+Novaya Zemlya, low-yield weapon tests	0.027* (1)	0.71* - 1.8 (1,8)	0.05 (6)	-
Mike test (Enewetok) near field fallout	0.0064* (1)	3.40 - 3.63* (1,8)	-	-
Bravo test (Bikini) near field fallout	0.001* (1)	2.90* - 3.4(1,8)	-	-
Weapons-grade Pu (Kyshtym accident)	0.0082* (1)	0.35* (1)	-	-
Weapons-grade Pu (Thule accident)	0.014 (9)	-	0.1 (10)	-
Waste from Sellafield	0.19* - 0.29 (1,2, 3,11,12)	11* - 19 (1,2,13)	-	-
Chernobyl accident in 1986	0.47 - 0.54 (3,14,15)	82 - 95 (3,14,15)	0.061 - 0.13 (14,15)	8 - 14 (14,15)
Reactor fuel (depending on reactor type and burnup-time) 50 % of final burnup = bold numbers #	0.1 – 9  <b>0.49 - 1.3</b> (16)	0.01 –120  <b>63 - 100</b> (16)	0.007 – 0.54  <b>0.06 - 0.16</b> (16)	0.8 – 185  <b>7.2 - 21</b> (16)

(\*Extracted data from 1., # extracted data from 16. References: 1. Cooper et al. 2000, 2.

Holm et al. 1986, 3. Holm et al. 1992, 4. Hardy et al. 1973, 5. Perkins and Thomas 1980,

6. Smith et al. 2000, 7. Yamato 1982, 8. Koide and Goldberg 1981, 9. Eriksson 2002,

10. Aarkrog et al. 1987, 11. Kershaw et al. 1995, 12. Baskaran et al. 2000, 13. Mitchell et al. 1999,

14. USSR 1986, 15. Aarkrog 1998, 16. Friberg 1998.)

unfissioned or unreacted weapons-grade fissile fuel associated with particles.  $^{238}\text{Pu}$  is born by the reaction of fast neutrons with  $^{239}\text{Pu}$ , by unreacted atoms originally associated with a particular device, by the decay of  $^{242}\text{Cm}$ , or it was used as a tracer in some tests (NCRP 2001, Schell et al. 1978, Schell et al. 1980).

In nuclear reactor accidents, the relative activities of radionuclides depend both on the chemical and physical properties of released elements and on the fuel composition. TRUs are low-volatility elements that do not easily form any inorganic volatile compounds (Friberg 1998). In the Chernobyl accident, different kinds of particles from the reactor core have been detected. Some of them were fuel particles consisting primarily of U oxides, but also condensed particles from molten and vaporized fuel could be found. These particles could be depleted or enriched for Pu, depending on the time of release (Cuddihy et al. 1989, Krivokhatsky et. al 1991, Perkins et al. 1989, Salby et al. 1994). Pavlotskaya et al. (1994) have found different forms of Pu in condensed particles, some of sparingly soluble and some in mobile form. The fuel composition in a core can consist of a mixture of fuel with different burnup times. This can lead to complicated estimates of the relative activities of TRUs, which is due to the different ratios of isotopes (see Table III).

The chemical form of Pu released during nuclear fuel reprocessing and fabrication can vary greatly. The form can range from relatively insoluble oxide particles, which are of different compositions than fallout, to relatively soluble inorganic salts and organic complexes, which may be present in solid and liquid wastes (Watters et al. 1980). Thus, the different source of TRU isotopes affects the chemical form of different nuclides, which in turn can affect the behaviour of the nuclides in the environment (Buessler 1997, NCRP 2001).

## 4 Behaviour of TRUs in the aquatic environment

### 4.1 Distribution between water and sediment

After introduction into aquatic systems, a number of factors and processes control the transport and fate of the TRUs over time. The distribution of Pu between water and sediment greatly depends on the oxidation state (Choppin and Morgernstern 1999, Pilviö 1998, Watters et al. 1980). Because the pH of oceans is well buffered, being quite equal, Pu is typically in the Pu(V) or Pu(VI) state in waters under oxidising conditions and as Pu(IV) in sediments. Experimental studies in, for instance, the area of Buzzards Bay, the Irish Sea, Thrombay Harbour, and the Baltic Sea show that in comparatively shallow water bodies, usually more than 90 % of total Pu is rapidly transferred to sediments associated with particulate materials. In deep oceans, as well as in the Mediterranean Sea, the situation is different: most Pu remains in the water phase for a long time due to a slow mixing of water masses and slow sedimentation rates (Emery et al 1980, Fucai et al. 1981, Molero et al. 1995). In the water phase, TRUs can be either soluble or fixed in particulate fraction, the chemical properties of water decide which. For instance, in the Baltic Sea, the proportion of soluble Pu varied from 25 to 70 % of total Pu in the water on different sampling dates (Ikäheimonen et al. 1997).

The solubility of Pu in natural waters is complex. The pH, amounts of humic and fulvic acids and many complex formation agents affect the solubility of Pu in freshwaters. pH can vary greatly, and it can be relatively low (about 4). In such conditions, Pu can also be as strong complexes (Allard et al. 1984, Sholkovitz 1983).

Several equilibrium reactions affect the distribution of Pu between water and sediment fractions. The main equilibria are the:

- 1) redox equilibrium between oxidation states in the water column,
- 2) formation of inorganic and organic complexes (as hydroxides, bicarbonates, carbonates, sulphates etc.),
- 3) reactions of these complexes with iron-aluminium-manganese compounds in sediments.

The pH-value, the amounts of dissolved carbon, and changes in water chemistry both in fresh and marine waters can strongly affect the position of these reactions (Edgington 1981). The relationship between radionuclide concentrations in sediment and water is described by the distribution coefficient  $K_d$ , where

$K_d$  = concentration in sediment (Bq/kg d.w.) / concentration in water (Bq/kg) (IAEA 1985).

The typical sediment – water distribution coefficient for Pu in a freshwater environment, as well as in coastal and brackish waters, is  $2 \times 10^5$ , ranging from  $10^4$  to  $10^6$  (IAEA 1985, NCRP 2001). In the marine environment, the differences between the soluble and particulate phases were noted but the average values of  $K_d$  in equilibrium between seawater and sediment was  $1 - 2 \times 10^5$  (IAEA 1985, NCRP 2001, Noshkin 1980). Am is preferentially taken up by any remaining particles in the aquatic environment (Aargrok 1984, McDonald 2001, Ryan 2002). Generally the  $K_d$  values both for Am and Cm in ocean and coastal waters were one decade bigger than that of Pu, being  $1 - 2 \times 10^6$  (Harley 1980, Molero et al. 1995).

## 4.2 TRU concentrations in water

### 4.2.1 Seawater

Generally, the concentrations of  $^{239,240}\text{Pu}$  in marine waters originating from global weapons test fallout varied according to whether the water was filtered and were typically from a few to a few tens mBq per  $\text{m}^3$ . Those of  $^{238}\text{Pu}$ ,  $^{241}\text{Pu}$  and  $^{241}\text{Am}$  were less than 1, between 20 - 40 (at present), and about 1-2 mBq/ $\text{m}^3$ , respectively (Halstadius et al. 1986, Holm et al. 1986, Ilus et al. 1993, Yamato 1992, Taylor 2001). However, there are some sites or areas where elevated concentrations in water columns have been observed. The most investigated area is the vicinity of the Sellafield reprocessing plant in the Irish Sea, where  $^{239,240}\text{Pu}$  concentrations have been over a thousand times higher than the global fallout levels. The effect of the Sellafield discharges can be observed in the southern Norwegian Sea, where the concentration levels are still elevated (Cook et al. 1997, Halstadius et al. 1986, Kershaw et al. 2001, Leonard et al. 1999, León Vintro et al. 2002, McKay et al. 1993). The influence of Sellafield can be seen from the Pu nuclide ratios in the Arctic waters. The local concentrations of TRUs near weapons test sites and some dumping sites are higher than generally in seawater. In the vicinity of the Enewetok Atoll nuclear test area, the seawater concentrations of  $^{239,240}\text{Pu}$  were still about 3 Bq/ $\text{m}^3$  in 1997 (Bourlat et al. 1995, Livingstone and Povinec 2000, Noshkin et al. 1998). Other sites where locally higher TRU concentrations have been observed are Chernaya Bay in the Arctic sea, as well as near the nuclear weapon test areas in Novaya Zemlya and the Thule accident area (there, mainly the near-bottom water) (Aarkrog 1984, Dahlggaard et al. 2001, Smith et al. 2000). In addition, in the Baltic and the North Sea, especially the  $^{242}\text{Cm}$  concentrations were elevated after the Chernobyl accident (Ikäheimonen et al. 1988, Nies 1990).

### 4.2.2 Freshwater

The  $^{239,240}\text{Pu}$  concentrations in freshwaters were generally at the same level as in seawaters, when Pu originated from global fallout (Taylor 2001). However, some exceptional circumstances can increase the normal fallout level of Pu in freshwater. This phenomenon has been observed in organic-rich freshwaters, highly alkaline waters, and also anoxic near-bottom waters where a great portion of Pu is in the water phase (Sholkovitz 1983). Elevated concentrations of TRUs have been observed in the freshwaters by nuclear industry areas, e.g. in the Savannah River, and Hanford and Oak Ridge in the USA ( Emery et al. 1976, Trabalka et al. 1987). In the freshwater system near Chernobyl, the concentrations of  $^{238}\text{Pu}$ ,  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  varied within one decade in rivers and small lakes and were still in 1996 at their highest of 10 mBq/m<sup>3</sup>, 200 mBq/m<sup>3</sup> and 200 mBq/m<sup>3</sup> respectively. About 70 % of these nuclides were in particulate fraction of water (Matsunaga et al. 1998).

### 4.3 Sedimentation and concentrations in sediments

The association of transuranic elements with sediment is dependent on particle size: the association favours fine clay or clay-silt particles (Edgington 1980, Leonard et al. 1999, McKay 1993, McKenzie 1999). The size of particles can affect 5 - 10 fold on the  $K_d$ -factor (Assinder et al. 1997, Edgington 1980, Ilus et al. 1995). Pu and Am are mainly associated with sesquioxides and undissolved organic complexes such as celates, Am can also be associated with carbonates (Cook et al. 1984, McDonald et al. 2001, Loyland et al. 2000).

The place of final sedimentation depends on several things in an aquatic system: on local current patterns, wave actions, erosion by bottom currents and on bottom configuration. The finest particles can be easily transported long distances into the accumulation basins in deeper parts of the water basin (Baskaran et al. 1995, Davies and Gorsline 1976, Grasshoff and Voipio 1981, Kankaanpää 1997, Kuenen 1965, Leivuori 200, Vallius 1999).

The concentrations of TRUs in sediments can thus vary according to both the source and the type of bottom, including the sedimentation rate in the area. For instance, in the Baltic Sea, in soft bottom areas, where the sedimentation rate can be more than 20 mm/y,  $^{239,240}\text{Pu}$  concentrations were at the highest, about 15 Bq/kg (Ilus et al. 2001). However in the Kara Sea area, where the sedimentation rate is usually less than 2 mm/y, the concentration was typically about 1- 2 Bq/kg (Baskaran et al. 1995, Livingstone and Povinec 2000 ). The source in both areas was global fallout, which is slightly smaller in the pole areas, but not one decade.



High concentrations of TRUs in sediments have been observed in nuclear tests and dumping areas or in vicinity of reprocessing plants. Perhaps the most studied area is the Irish Sea, where surface sediments consisted, in 1995, of up to 500 Bq/kg and 1000 Bq/kg of  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  respectively (Kershaw et al. 1999a). In the Chernaya Bay, a local concentration of 15 000 Bq/kg of  $^{239,240}\text{Pu}$  was detected in the middle of 90s (Smith et al. 2000). In the Enewetok and Thule sediments, the concentrations of  $^{239,240}\text{Pu}$  were several thousands of Bq per kg (Aarkrog et al. 1987, Noshkin et al. 1998).

The sediment layers can be dated using vertical distributions of TRUs in the undisturbed sediment core. The period of maximum fallout from nuclear weapon tests in the mid 60s can be observed in sediment samples of  $^{239,240}\text{Pu}$ . This has been used to determine the sedimentation rates or events seen in the sedimenting process (Ilus et al. 1998, Ilus et al. 2001). The total amounts of radionuclides per area ( $\text{Bq}/\text{m}^2$ ) in the sedimenting basin can be calculated, when the area of sample is known. This number, however, represents only the area where sedimenting has been even. In order to calculate the total amounts for the whole sea area, the configuration and type of bottom as well as the different total amounts in different areas have to be known. For instance, in the Baltic Sea, the total amounts of  $^{239,240}\text{Pu}$  varied from 22 to 123  $\text{Bq}/\text{m}^2$  in different areas depending on bottom type and erosion (Simola et al. 1979).

#### 4.4 Redistribution from sediments

When TRUs are finally fixed in fine sediment particles, they are available to bottom organisms and can be removed back to water (Beasley and Cross 1980, Wahlgren et al. 1980, Watters et al. 1980). The redistribution of Pu from sediments back to the water phase has been observed in the investigations of nuclear weapons tests areas at the Enewetok and Bikini Atolls (Noshkin 1980, Noshkin et al. 1983, Noshkin et al. 1998, Schell et al. 1980). The release of TRUs has also been found in later studies in marine and freshwater environments (Cook et al. 1997, Halstadius et al. 1986, Hamilton-Taylor et al. 1987, Hinton et al. 2001, Pinder 1992, Smith et al. 2000, Wahlgren et al. 1980). However, the amounts of redissolved Pu have been low, as in the Irish Sea, which was below 1% for Pu from the total amount and much lower for Am (Leonard et al. 1994). Some observations of the preferential remobilization and dissolution of  $^{238}\text{Pu}$  over  $^{239}\text{Pu}$  have also been reported (NCRP 2001, Noshkin et al. 1988, Schell et al. 1980, Volchok et al. 1975).

## 4.5 Accumulation in biota

In general, the accumulation of TRUs in aquatic plants, invertebrates and fish appears to be higher than in terrestrial plants, vertebrates and mammals. Aquatic organisms may accumulate TRUs from a complex interaction of water, diet and sediment exposure. Usually, both in freshwater and the marine environment, the accumulation of Pu and other TRUs were observed to decrease relative to water at higher trophic level. The highest levels of activities were found in coastal flora representing primary producers, and the lowest levels were in fish representing tertiary consumers (Guary and Fraizier 1977, NCRP 2001, Ryan 2002, Watters 1983). The uptake of TRUs can occur by assimilation or by adsorption. For instance, in brown algae (*Ascophyllum nodosum*), TRUs are assimilated rather than absorbed by the plant. For other algae, adsorption is more likely. For phytoplankton and free-floating and haptophytic algae, accumulation happens rapidly. Mussels, shrimp and marine worms uptake TRUs directly from seawater: mussels and shrimps also uptake from contaminated food (Beasley and Cross 1980, NCRP 2001). Generally, Am and Cm have observed to be more bioavailable than Pu, but opposite results also exist (Aarkrog et al. 1987, Livingstone and Bowen 1977, Noshkin et al. 1987, Pentreath and Lovett 1978, Ryan 2002, Watters 1983). It is usually assumed that the behaviour of Am and Cm are similar, but differences between the accumulations of Am and Cm have also been discussed (Beasley and Cross 1980, Eicke 1981, Miramend et al. 1987, Pentreath 1987).

In fish, the different habits of fish species affect the accumulation of TRUs; bottom-feeding fish accumulate these elements more than fish living in surface waters do (Bowen 1974, Eyman and Trabalka 1980, Noshkin 1988). The activity of TRUs is lowest in the flesh of fish, less than 10 % of the activity in the whole fish. TRUs accumulate mostly in the digestive tract, liver and bone (Bourlat et al. 1997, Noshkin et al. 1988, Pentreath 1978).

## 4.6 Concentrations in biota

Elevated concentrations of TRUs in biota have been observed in contaminated aquatic areas. Molluscs and algae are good bioindicators for TRUs, and they can be used “as markers” of contamination in the area. Very high local concentrations of  $^{239,240}\text{Pu}$  in *Macoma* (mussel) and *Fucus* (alga) were detected in the Chernaya Bay near nuclear test area, 104 Bq/kg and 15 Bq/kg respectively, in the mid 90s (Smith et al. 2000). In studies during 1988 – 1997, concentrations above the normal level were also observed in the Irish coastal biota where up to 2.8 Bq/kg of  $^{239,240}\text{Pu}$  was measured in *Fucus* (Ryan et al. 1999). However,

concentrations in *Fucus* have been less than 0.5 Bq/kg in the Swedish and Finnish coastal areas, where the origin of Pu was global fallout (Ilus et al. 2002, Kanish et al. 1995).

Normally, without other than global fallout contamination, fish concentrations are less than 1 mBq/kg (Kanish et al. 1995, Ryan et al. 1999, Skwarzec et al. 2001). In the investigation at the Enewetok and Bikini Atolls (1998), concentrations of  $^{239,240}\text{Pu}$ ,  $^{241}\text{Pu}$ ,  $^{241}\text{Am}$  and  $^{244}\text{Cm}$  were measured in flesh of reef and pelagic fish species. The concentrations in reef fish were 3 – 20 times higher than in pelagic fish. At their highest, the amounts of those nuclides were 179 mBq/kg of  $^{239,240}\text{Pu}$ , 36 mBq/kg of  $^{241}\text{Pu}$ , 39 mBq/kg of  $^{241}\text{Am}$  and 0.5 mBq/kg of  $^{244}\text{Cm}$  (Robinson and Noshkin 1999). The concentrations in fish in the Irish coastal waters were at the highest from about 10 mBq/kg of  $^{239,240}\text{Pu}$  and  $^{238}\text{Pu}$ , to 140 mBq/kg of  $^{241}\text{Am}$  (Ryan et al. 1999). In the Thule accident area, concentrations two orders of magnitude higher for  $^{239,240}\text{Pu}$ , when compared with the fallout level, were measured in fish soon after the accident in 1968. Elevated levels in fish were not found two years later or after that (Aarkrog 1971, Aarkrog 1977). Perhaps the most discussed results of fish concentrations are those of Suchanek et al. (1996) concerning the radioactive dumping site on the Farallon Islands near the Californian coast. They have measured several hundreds of mBq of  $^{239,240}\text{Pu}$  and  $^{238}\text{Pu}$ , and about 1500 mBq/kg of  $^{241}\text{Am}$  in fish flesh. Suchanek also found a considerably high environmental mobilization of  $^{238}\text{Pu}$  over  $^{239,240}\text{Pu}$ .

## 4.7 Concentration factors for biota

The transfer of radionuclides from water into biota is generally described by the concentration factors (CF). The CF is the ratio of the activity concentration in the organism (Bq/kg) to the activity concentration in water (Bq/kg). For fish, wet weights are normally used, whilst for plants, dry weights are used. When considering aquatic organisms, nuclides both in the water phase and in sediments can affect the concentrations in organisms depending on the habits or living sites of the organisms (Beasley and Cross 1980, Eyman and Trabalka 1980, NCRP 2001, Ryan 2002).

In addition, concentration ratios (CR) are used to describe the relationship between radionuclides in biota and sediment (Ryan 2002). If the deposition is known, the transfer factors (TF) can be used to calculate the amount of radionuclides from deposition to biota (unit  $\text{m}^2/\text{kg}$ ) (IAEA 1994, Saxén and Koskelainen 1992). The typical CFs for aquatic organisms are presented from different literature sources in the Table IV.

**Table IV.** Typical concentration factors for Pu, Am and Cm in freshwater and marine environments.

Species	CF for Pu		CF for Am		CF for Cm		References
	Fresh w.	Ma-rine	Fresh w.	Ma-rine	Fresh w.	Ma-rine	
Phytoplankton	$10^4$	$10^5$	$1.5 \times 10^4$	$2 \times 10^5$	Ab. $10^4$	$3 \times 10^5$	1,2,3
Zooplankton	$2 \times 10^3$	$10^3$	-	$2 \times 10^3$	Ab. $10^4$	$2 \times 10^3$	1,2,3,4
Crustacean	$10^3$	$3 \times 10^2$	$2 \times 10^3$	$5 \times 10^2$	Ab. $10^5$	$5 \times 10^2$	1,2,4,5
Molluscs	$10^3$	$3 \times 10^3$	$10^4$	$2 \times 10^4$	$10^4$	$3 \times 10^4$	1,6
Macro algae	$5 \times 10^3$	$2 \times 10^3$	$5 \times 10^4$	$8 \times 10^3$	$5 \times 10^4$	$8 \times 10^3$	1,6
Fish (edible p.) Benthic feeders	$3 \times 10^2$	$6 \times 10^1$	$3 \times 10^3$	$2 \times 10^2$	$3 \times 10^3$	$3 \times 10^3$	1,4,6
Fish (edible p.) Piscivores	$5 \times 10^0$	$8 \times 10^0$	$5 \times 10^1$	$5 \times 10^1$	$5 \times 10^1$	$5 \times 10^1$	4,6,7

(References: 1. IAEA 1985, 2. Wahlgren et al. 1976, 3. Kuzo et al. 1987, 4. NCRP 2001, 5. Beasley and Cross 1980, 6. Eyman and Trabalka 1980, 7. Guary and Fraizier 1977.)

## 5 General analytical methods

The concentrations of TRUs in environmental samples are normally very low. Large amounts of stable elements, and natural radionuclide concentrations, which are of many orders of magnitudes higher than those of TRUs present several requirements for determination methods (Ibrahim et al. 1995). It is usually necessary to preconcentrate and purify TRUs from a large amount of material. A number of radiochemical procedures have been published over the past few years. Generally, these procedures consist of several steps: 1) sampling and pretreatment, 2) addition of tracers, 3) preconcentration and/or decomposition of the sample, 4) the radiochemical separations of Pu, Am and Cm using several steps and 5) measurements of activities and data handling.

Sampling is always crucial when studying different environmental phenomena. Therefore, the sampling methods should be carefully considered when planning the overall research. The representativeness of the samples has to be ensured. Over recent years, attention has been drawn to the uncertainties of the results due to sampling. These uncertainties are estimated to be even bigger than those that result from analytical methods and measurements (Barwick and Ellison 2000, Byrnes 2000, Fettweis and Schwenn 1998). Large water samples, usually one or several hundreds of litres, are taken by pumps or big vessels, typically into plastic canisters. Acidifying samples in order to prevent the adsorption of radionuclides to the canister walls is done immediately. Several samplers exist for sediment sampling, some for hard and some for soft bottoms. In order to determine vertical distributions, a corer with equipment for slicing is used. Biota samples are gathered from examination areas with samplers or by hand, depending on samples. Freezing sediment and biota samples is a common pretreatment method before their decomposition (Byrnes 2000, IAEA 1970, Ilus et al. 2000).

Internal tracers are added into samples, usually before preconcentration or decomposition.  $^{236}\text{Pu}$  and  $^{242}\text{Pu}$  are used for Pu measurements and  $^{243}\text{Am}$  and/or  $^{244}\text{Cm}$  for Am/Cm measurements (Harvey and Lovett 1984). Preconcentration by co-precipitation with hydroxides or oxalates has been commonly used for water samples. Dry or wet ashing, acid leaching and total composition with leaching in a microwave oven, alone or with a combination of oven and another of these methods, are used for sediment and biota samples (Livingstone et al. 1975, Martin and Pope 1982, Solatie et al. 2002, Toribio et al. 2001, Yu-Fu et al. 1991). The total leachability of TRUs, especially if in oxide forms, has been discussed. Some of insoluble oxides can stay in the residue if

only leaching with *aqua regia* or nitric or hydrochloric acids is used. In these cases, leaching with hydrofluoric acid or fusion has to be used (Dulaiova et al. 2001, Eriksson 2002, Friberg 1998).

Many chemical methods can be used for purifying TRUs. Of these, solvent extraction, ion exchange chromatography, extraction chromatography, co-precipitations or various combinations of the above are most often used (Yu-Fu et al. 1991). In solvent extractions, trioctylamine (TOA), tridodecylamine (TLA), Alamine-336, trioctylphosphine (TOPO), di(2-ethylhexyl)phosphoric acid (HDEHP) and tenoyltrifluoroacetone (TTA) have been used (Bernabee et al. 1980, Lee and Lee 1999, Martin and Pope 1982, Murray and Statham 1976, Myasoedov 1987). Anion exchange chromatography is frequently used. Adjusting the oxidation states of Pu is used for this technique. Both anion and cation exchanges and extractions were used to purify Am and Cm (Livingstone et al. 1975, Yamato 1982, Yu-Fu et al. 1991).

Over the past few years, extraction chromatographic methods based on commercially available, highly specific resins, (*UTEVA*, *TRU* and *TEVA* by Eichrom's Industries) have become popular separation methods. Analytical procedure can be shortened remarkably with this new technique (Boll et al. 1997, Cadieux and Reboul 1996, Horowitz et al. 1995, Maxell 1997, Outola 2002). This method has proved to be especially good for small sample sizes and high activities such as active waste measurements (Pilviö 1998, Spry et al. 2000).

The most common method to assay the contents of alpha-emitting TRUs is alphaspectrometry. To achieve the best accuracy in measurements, a thin, almost massless and uniform deposit of activity is necessary and the measurement has to be carried out in a vacuum. Preparates can be produced by electrodeposition, coprecipitation, evaporation, electrospraying or vacuum sublimation. Semi-conductor detectors or ionization chambers are usually used to measure alpha spectra (Fettweis and Schwenn 1998, Paatero 2000). Normal alpha spectrometry does not separate the energies of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ , nor  $^{243}\text{Cm}$  and  $^{244}\text{Cm}$ . Usually, the sum of their activities is reported. E.g., if an inductive-coupled plasma mass spectrometry (ICP-MS) or a thermal ionization mass spectrometry (TIMS) is used to measure the mass amounts of TRUs, those nuclides can be separated (Kenna and Sayles 2002, Maxell 1997, McMahon 2000). The determination of alpha-emitting TRUs by liquid scintillation counting has also become common practice. However, the backgrounds of these instruments are much higher than those backgrounds of alpha spectrometers and the resolution is quite poor (Yu-Fu et al. 1991). By using a spectral deconvolution technique, it is possible to separate  $^{238}\text{Pu}$  and  $^{239,240}\text{Pu}$  (Kaiholo 2000).

The beta-emitting  $^{241}\text{Pu}$  can be measured by direct beta counting with a liquid scintillation counter from a shared sample or from a disc, or after dissolving Pu from the disc (Cook et al. 1998, Condren et al. 1996, Lee and Lee 1999, Paatero 1994). An indirect method has also been used. It is based on measuring the alpha-activity of the daughter,  $^{241}\text{Am}$  of  $^{241}\text{Pu}$ , after a delay time of years (Livingstone et al. 1975b).

With elevated  $^{241}\text{Am}$  concentrations, it can be measured gamma-spectrometrically from its 59.5 keV peak with a low-background, high-resolution HPGe detector without chemical separation. However, the low energy of gamma peak can complicate a measurement, especially for density correction (Beks 2000).

## 6 Research areas

In this study, samples for the determination of TRUs were collected in various kinds of aquatic environments: marine (Arctic sea areas), brackish water (the Baltic Sea), and freshwater (Finnish lakes) environments.

### 6.1 Sediment studies

Concentrations and distributions of Pu in sediments were studied in wide areas of the Arctic sea, including the Barents, Petshora, and Kara Seas, coastal areas of the Kola Peninsula and outlet areas of the Ob and Yenisey rivers. However, the sampling locations represent only areas of free access; the prohibited military areas of north-west Russia were not included (Paper I). More detailed examinations were carried out in the Kola Bay, e.g., near the base Atomflot, the naval shipyards of Severemorsk, and the inner and outer parts of the Bay (Paper II). Another arctic area studied in detail was the accident area near the Thule Airbase in the coastal area of Greenland (Paper III). An isolated hot particle from a sample of this area was also analysed for Pu and Am (Paper IV). Pu analyses were carried out from the sediment samples of three sedimentation basins in the Baltic Sea: one in the Gulf of Finland (station XV-1), one in the Gulf of Bothnia (station EB-1) and one in the Baltic Proper (station Teili-1) (Paper V).

### 6.2 Biota and freshwater studies

Pu studies were carried out in alga samples gathered in coastal areas of the Barents, Petshora, and White Seas including a site on the southern coast of Novaya Zemlya (Paper I). Fish were sampled from the large, common fishery areas of the Barents Sea for Pu analyses (Paper I). TRUs were determined from fish samples from 17 freshwater lakes situated mostly in south and central Finland. Fish in Lake Päijänne were studied in more detail, water samples from this lake were also analysed (VI).

The research areas are roughly shown in Figure 2. More detailed figures are given in papers for Arctic and freshwater areas.



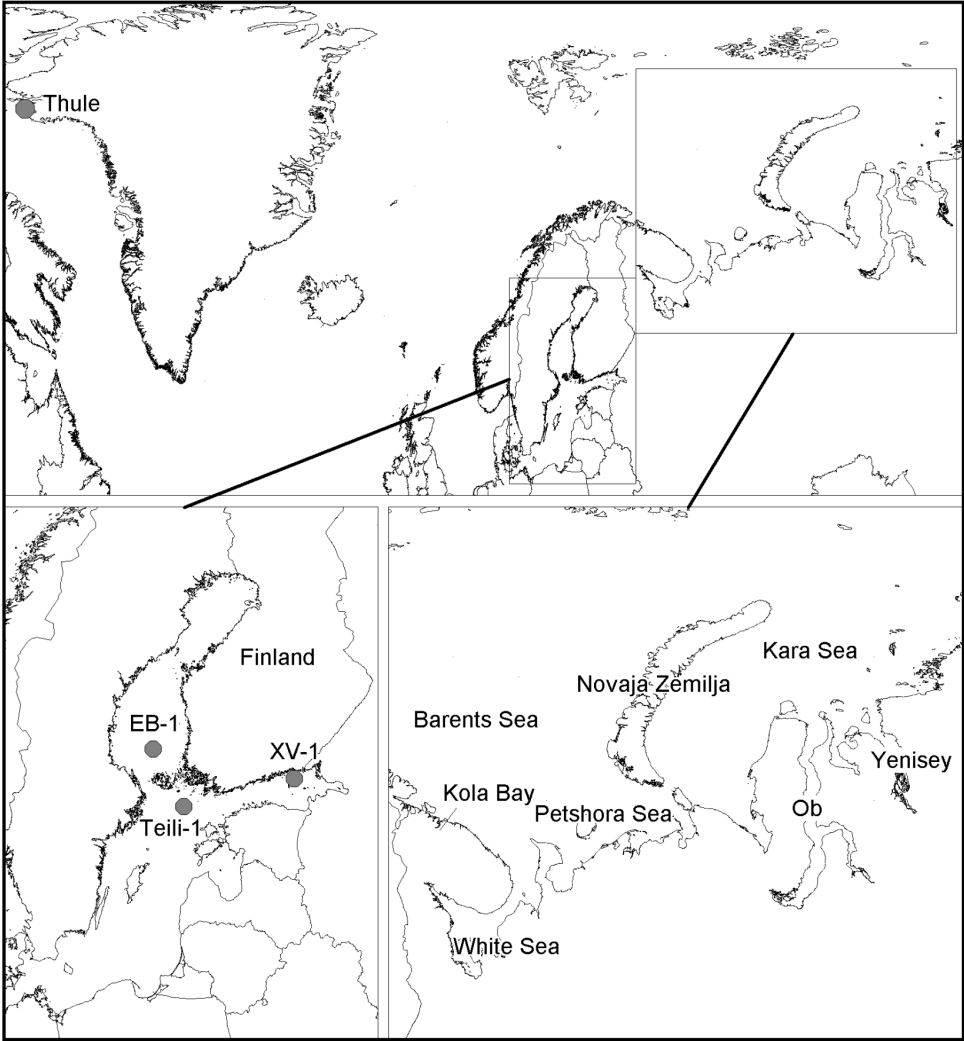


Figure 2. Research areas.

## 7 Methods used in this study

### 7.1 Sampling and pretreatment

#### 7.1.1 Sediment

Several factors affected the choice of sediment samplers: which samplers were available during the cruise, which of those were suitable for the bottom under study and other circumstances such as the water depth. Rough grabs were used for sampling sediment from coarse bottoms and in difficult circumstances (Papers I, II). No slicing of sediment could be performed for these samples. Only the uppermost layer of sediment, which could also be mixed, was analysed. Box corers, with diameters about 20 x 20 cm, could be used for softer bottoms without big stones, and these were used when possible (Papers I, II, V). Box corers allowed more quantitative sampling; the samples could be sliced into different layers either by hand or with special equipment. The gravity corers were suitable for soft bottoms. Quantitative sectioning of sediment core could be carried out without disturbing the sediment (Papers II, III, V). Since corers covered only small areas at a time (diameters from 6 to 8 cm), more than one core was usually needed to get enough material (Ilus et al. 2000).

The fresh weights of samples varied from some tens of grams to kilograms according to the sampler areas. Sediment samples were stored in a frozen state. The samples were dried (105°C) or freeze-dried and homogenised before their analysis. Usually about 10 grams of dried sediment was used for the analysis, but much less amounts (less than 1 g at minimum) were needed for some Thule sediments (Papers I, II, III, V).

The isolation of a hot particle based on autoradiography is described in detail in Paper III.

#### 7.1.2 Biota

Algae samples were gathered by hand from the coast or by diving in the deeper waters. Only living algae were used (paper I). The fresh weights of algae were usually 1- 2 kg. The samples were stored frozen before handling. The algae were dried (105°C), milled and homogenised before analysis. 20 grams of the dried sample was used for analysing.

The fish were sampled by trawling open sea areas of the Barents Sea (Paper I). The freshwater fish were caught with nets or other smaller fishing

equipment by local fishermen in Finland (Paper VI). The amounts of fresh fish samples varied from one to several kilograms. The samples were stored frozen before handling. The fish were cleaned and gutted, only the edible parts were taken to represent the fish flesh samples. The fish liver, spawn, and bones were pooled generally for several individuals in each sample. About 200 – 300 grams of fresh flesh, 20- 60 grams of liver and spawn, and 40 grams of bone were taken for analysis. The samples were dried (105°C) and homogenised before analysis, and some liver samples were used as fresh.

### **7.1.3 Lake water**

Lake water samples were sampled direct into 30-litre vessels from surface water (VI). The subsamples in vessels were acidified (pH 1 – 2), mixed and allowed to stand in the laboratory before being combined in a large container of 100 – 200 litres. Unfiltered water was used for the analysis.

## **7.2 Analytical methods**

Two different methods were used to determine the alpha-activities of  $^{238}\text{Pu}$  and  $^{239,240}\text{Pu}$ . The method used most was based on anion exchange. An extraction chromatography with special resins *UTEVA* and *TRU* (Eichrom), was tested for analysing a batch of the Thule sediment and the hot particle.

### **7.2.1 Anion exchange for Pu separation and preparation of measuring disc**

The anion exchange method was described in detail in a STUK report published earlier (Taipale and Tuomainen 1985). The method was modified and combined from the methods of HASL (1973), Wong (1974) and Hakanen and Jaakkola (1976). This method was also discussed in Papers I, II, III, V, and VI. The separation scheme is presented in Figure 3.

Tracers of  $^{242}\text{Pu}$ , and of  $^{243}\text{Am}$  in case Am and Cm had to be analysed, were added to the sample before preconcentration (water) or acid leaching (sediment and biota). TRUs were coprecipitated with ferric hydroxide from large water samples. Acid leaching with strong nitric acid and a mixture of nitric and hydrochloric acids at 200 – 300 °C, was performed for sediment and biota samples. Leaching with hydrofluoric acid together with nitric acid was also carried out for some Thule sediment samples. The leaching was completed with hydrogen peroxide.

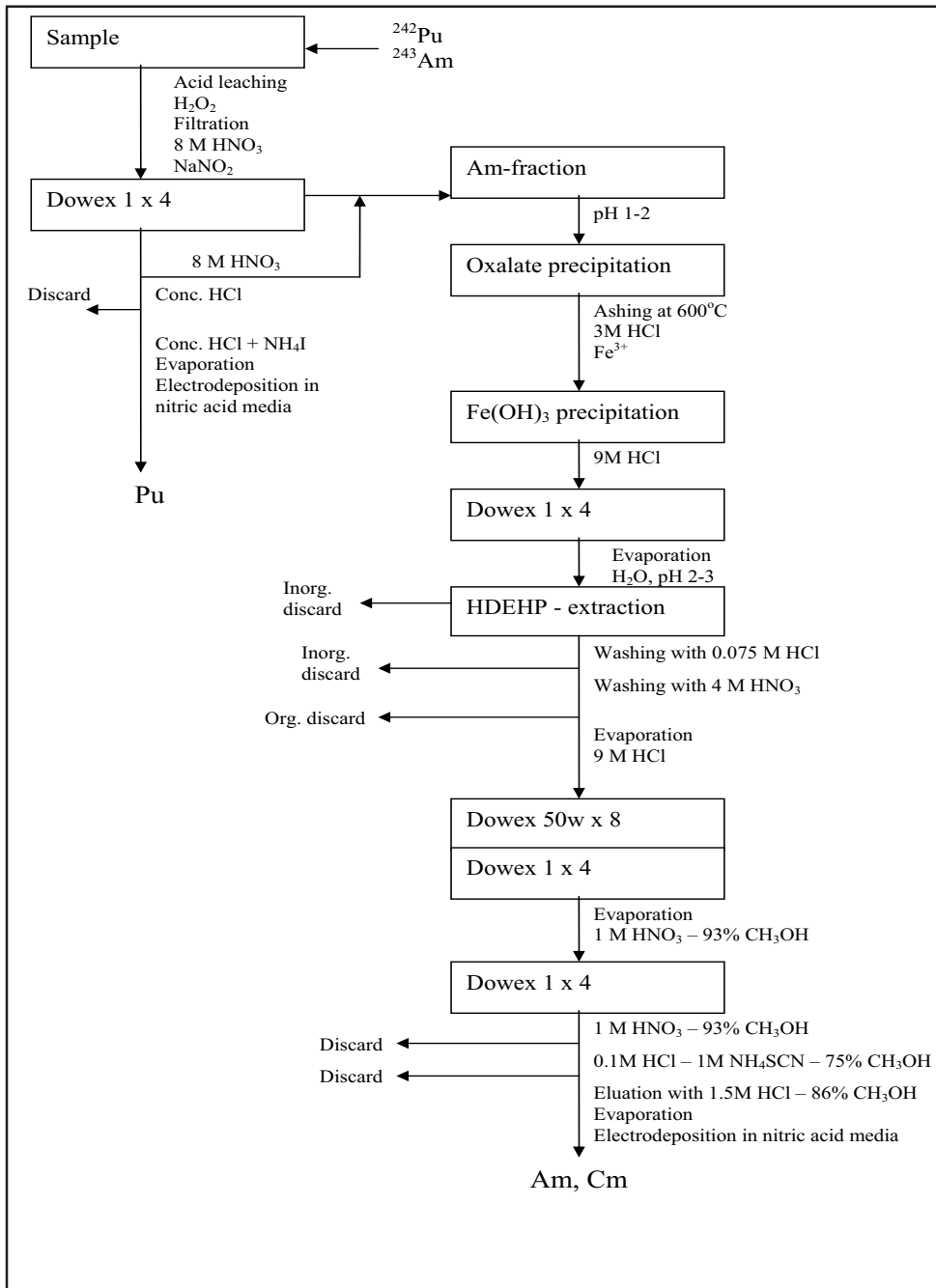


Figure 3. Separation scheme for Pu and Am from environmental samples.

An anion exchange with Dowex 1 x 4 (50 – 100 mesh) resin was performed from 8 M nitric acid media after stabilizing Pu to the IV oxidation state with hydrogen peroxide and sodium nitrite. Am and Cm were not fixed onto the resin but the effluent containing these nuclides was stored for Am+Cm analysis. Nitric acid washing was carried out for eluting all iron. Other disturbing elements, especially thorium, were given strong hydrochloric acid washing. Pu was eluted from the resin by reducing it to the III oxidation state with the mixture of ammonium iodide and hydrochloric acid. If  $^{241}\text{Pu}$  was measured, the sample was divided into two aliquots before electrodeposition, one for alpha measurement and the other for liquid scintillation measurement. Pu was electrodeposited from nitric acid – ammonia media (pH 2) with Pt-spiral as an anode and usually stainless steel disc as a cathode. The recovery of Pu was usually 60 – 100 %.

### 7.2.2 Extraction chromatography for TRU separation

The separation procedure is based on the method published by Pilviö and Bickel (1998). The method was also discussed in Papers III and IV.

Highly specific resins *UTEVA* and *TRU* (Eichrom) have been developed by Horwitz et. al. (1990, 1992). They consist of diamyl amylphosphonate sorbed onto inert polymer and octyl(phenyl)-N,N-di-isobutyl-carbamoyl-methylphosphine oxide (CMPO) dissolved in tributyl phosphate and sorbed onto inert substrate, respectively. The packed-ready columns of resins (2 ml) were used. The *UTEVA* resin was used to separate the III oxidation states of Pu, Am and Cm from U in 3 M nitric acid – aluminum nitrate media, where Pu was reduced with ferro sulfamate and ascorbic acid. U could be eluted from the resin afterwards with weak hydrochloric acid if needed. After this, the separation of Pu from Am and Cm was performed with a *TRU* resin in 2 M nitric acid – sodium nitrite media, which oxidize Pu to the IV state. Trivalent Am and Cm were extracted from the resin with hydrochloric acid and then Pu was extracted with 0.1 M ammonium oxalate. In this study, the Pu fractions of separation were analysed from the Thule sediments (Paper III) and the Pu and Am fraction from the hot particle (Paper IV), while other fractions were saved for later studies. After separation, sample division and electrodeposition were performed as described above. The recovery of Pu and Am varied between 40 – 80 %.

### 7.2.3 Treatments for $^{241}\text{Pu}$ measurement

A liquid scintillation measurement was applied to another Pu fraction with the method described in the Paper IV. The sample, diluted into weak hydrochloric acid was measured in scintillation cocktail *Optiphase HiSafe II* after cooling and keeping in the dark. These measurements of  $^{241}\text{Pu}$  were performed for the Thule sediments, the hot particle and the Baltic Sea sediments (Papers III, IV and V).

The in-growth method of  $^{241}\text{Am}$  from the Pu preparate was described in Paper IV. The electrodeposited and alpha-measured Pu preparates were stored for several years and re-measurements were performed. This method was used for freshwater biota and lake water samples (Paper VI).

### 7.2.4 Separation of Am and Cm with ion exchanges and liquid extractions

This method was described in detail in the STUK report published earlier (Talpale and Tuomainen 1985, see also Figure 3). It was developed and modified by combining several methods suitable for low-level environmental analysis (Bojanowski et al. 1975, Fukai et al. 1976, Holm et al. 1979, Lebedev et al. 1974, Murray and Statham 1976). The Am/Cm fraction was evaporated, dissolved into water, and calcium oxalate coprecipitation was performed. After ignition oxalates, the calcium was removed by the coprecipitation of Am/Cm with ferric hydroxide. The iron was separated with anion exchange. Liquid extraction with HDEHP-TBP-toluene mixture (HDEHP= 2(diethyl-hexyl) phosphoric acid; TBP= tributyl phosphate) was performed to remove lanthanides and thorium. Double cation-anion exchange in 9 M hydrochloric acid was performed to remove the remaining thorium and iron, polonium and uranium. The final purification was carried out with anion exchange in nitric acid – methanol media ( 1M  $\text{HNO}_3$ - 93%  $\text{CH}_3\text{OH}$ ) by washing the resin with thiocyanate – methanol in hydrochloric acid ( 0.1 M  $\text{HCl}$ - 75%  $\text{CH}_3\text{OH}$ - 1M  $\text{NH}_4\text{SCN}$ ). The elution of Am and Cm was carried out with a hydrochloric acid – methanol solution (1.5 M  $\text{HCl}$ - 85%  $\text{CH}_3\text{OH}$ ). All remaining impurities of lanthanides, lead and polonium, as well as other stable elements could be separated with this method. The similar behaviour of Am and Cm during separation was tested during the validation of the method with tracers of  $^{243}\text{Am}$  and  $^{244}\text{Cm}$ . Am/Cm was electrodeposited, as described earlier - only the electrodeposition time was longer to ensure good yields. The recovery of Am and Cm was usually 50 – 80 %. The method was used for analysing Am and Cm from a freshwater environment (Paper VI).

### 7.2.5 Treatment of sediment samples for gamma spectrometric $^{241}\text{Am}$ measurements

Dried, homogenized sediments were put tightly and evenly into plastic beakers with a diameter of 21 cm. The heights of the samples ranged from 1 to 12 millimetres and their densities were from 0.6 to 0.8 g cm<sup>-3</sup>. Carefully cleaned beakers were measured gamma spectrometrically. The gamma measurements of the hot particle and subsamples of the “mother” sediment were also performed in plastic beakers and were described in Paper IV in detail. Gamma spectrometric measurements for  $^{241}\text{Am}$  were used in the study of the Thule sediments and the hot particle (Papers III and IV).

### 7.2.6 Measurements

The alpha activities were measured using three different kinds of alphaspectrometer consisting of low-background silicon semi-conductor detectors or passivated ion implanted (PIPS) detectors in vacuum chambers, and compact systems with high-voltage supplies, pre-amplifiers, linear amplifiers, pulse-height analyzers and computers. The measurements were carried out in a vacuum of less than 1 mmHg. The resolution of alpha peaks was typically 50 – 60 keV for samples, whereas for a standard source, it was less than 30 keV. The counting efficiencies varied between 25 – 38 % depending on the detector, the distances between the detector and the sample discs, and the purity of the sample. The channels for spectra varied between 256 and 1024 depending on the system. The measuring times depended on the samples; for sediments it was typically 4000 minutes whilst for biota and water, it varied between 6000 – 10000 minutes (Papers I, II, V, VI). For the more active Thule sediments, the measuring times varied, according to activities, from some hundreds of minutes to 4000 min (Paper III). Automatic computer programmes were used to calculate alpha activities, but data checking by hand was also necessary. The activities of the hot particle were measured in a separate alphaspectrometry system and the results were calculated by hand (Paper IV). The minimum detectable activity (MDA) calculating by the Currie method varied according to the measuring time; it was usually between 0.1 – 0.3 mBq per sample, except for the Pu of the Thule sediments, when shorter measuring times increased the MDAs (see Paper III) (Canberra 1997, OASIS 1996).

The indirect measurement of  $^{241}\text{Pu}$  activities was also performed with alphaspectrometers. The method was described fully in Paper V. After a waiting time of 12 – 13 years, the discs were remeasured and the activities of ingrown  $^{241}\text{Am}$  were calculated. Finally, the amounts of  $^{241}\text{Pu}$  could be calculated from

these and earlier results. This measuring system was used in the study of the freshwater environment (Paper VI). The MDA depended on the waiting time, the  $^{238}\text{Pu}$  activity and the measuring time, and it was usually more than 10 mBq per sample.

The author was not responsible for the gamma-spectrometric measurements and they are not discussed in detail in this study (see Papers III and IV: Seppo Klemola). The measurements were performed with low-background n-type HPGe detectors. The method is based on a system modified at STUK (Sinkko and Aaltonen 1985, Aaltonen et al. 1994). The relative efficiencies of the detectors varied between 20 – 28%. Varying height and density were taken into account in the calculation of the results. The full-energy peak efficiencies for  $^{241}\text{Am}$  varied between 7 - 20 %. The MDA varied from 2 to 50 Bq/kg. The variation was due to the different amounts of sediment measured.  $^{241}\text{Am}$  activities were measured using gamma-spectrometers in the study of the Thule environment (Paper III, partly IV).

The beta activities of  $^{241}\text{Pu}$  were measured with a low-background scintillation spectrometer (Wallac, Quantulus 1220). The method is described in greater detail in Paper V. The equipment has an anticoincidence detector and a pulse shape analyser (PSA) that allows discrimination between alpha and beta pulses. The efficiency calibration was based on using tritium standards for quenching measurements. The beta activities were calculated from both alpha measurements and liquid scintillation measurements (see Paper V). The MDA was 7 mBq per sample. The method was used for the study in the Thule area and in the Baltic Sea (Papers III, IV and V).

### **7.3 Quality assurance**

Quality management was created in order to ensure the high quality of the results in our laboratory. Quality assurance was maintained during the research by a regular, systematic assurance programme. It consisted of certified standards with high purities used for energy and efficiency calibrations and checking up on the stability of equipment and it was also used for internal tracers. Parallel and blank samples were analysed and measured regularly, and background measurements were regularly taken. Certified reference material was also analysed and measured with all appropriate methods according to the assurance programme. Suitable intercomparisons or proficiency tests were taken advantage of, if available (see Table V).

Uncertainty estimations comprise total uncertainties, consisting also of uncertainties, e.g. due to analysis, calibrations and weightings, but not those



due to sampling (Canberra 1997, OASIS 1996). Uncertainties varied greatly according to activities and measuring times; for  $^{239,240}\text{Pu}$  they were generally less than 10 % and for other nuclides, they were 10 –30 % (2 sigma). All other methods of analysis used, including the gamma spectrometric measurement but not the chromatographic method for separation of Pu and Am by Eichroms resins, were accredited in 1999.

## 8 Results and discussion

Most of the results are presented and discussed in Papers I – VI. The summary of the results, as well as certain additional results and discussion, especially for methods, is presented here.

### 8.1 Applicability of methods

#### 8.1.1 Separation methods for Pu and Am/Cm

This study favoured wet ashing and acid leaching for solid samples. It is commonly known that acid leaching is good for dissolving TRUs from almost all kinds of environmental samples. However, if Pu is present in an oxide form, as could be in hot particles, more leaching with HF or total dissolution, with e.g. in microwave ovens, is necessary to complete the dissolution (Cooper et al. 2000, Friberg 1998, Solatie et al. 2002, Yamato 1992). No additional leaching was used for the Thule hot particle, which could lead to incomplete dissolution (Paper IV).

Anion exchange for separation of Pu, and separation of Am/Cm with anion exchanges and liquid extraction worked excellently for all kinds of environmental samples. This method was competent and reliable for very low-level activities that needed large sample amounts and they therefore contain large amounts of interfering substances. This has been examined over the years with numerous intercomparison and proficiency tests with different kinds of material, e.g. seawater, sediment, soil, fish, alga. The combined results of tests are presented in Table V. All the results have been in good agreement with the confidence intervals or real values and thus showed these methods to be accurate and valid.

The disadvantages of the method mentioned above are that it is time-consuming and produces large amounts of waste (organic waste, large amounts of strong acids, used resins). All these could be avoided with the chromatographic method tested for the Thule sediments. No difficulties existed when testing the method with normal IAEA reference materials. However, the interference of uncommonly large amounts of U was observed in this study when using *UTEVA* and *TRU* for separation of Pu from the Thule sediments. Some  $^{238}\text{Pu}$  results were lost because of unclean spectra during incomplete separation (Papers III).

In addition, other authors have observed difficulties in the chromatographic extraction method with low-level activities and large samples or with the abnormal environmental activities of other nuclides. With large amounts of stable elements, e.g. iron and aluminium, a so-called matrix effect can occur; higher activities of U and Th may disturb extractions by obstructing columns or hindering total separation and thus lowering recovery, or they may lead to unclean spectra. In order to prevent these, additional steps, more amounts of resins, double extraction and pumping with extractions might be needed (Boll et al. 1997, Cadieux and Reboul 1996, Dulaiova et al. 2001, Goutelard et al. 1998, Toribio et al. 2001). It is not clearly known whether Am and Cm behave similarly during chromatographic extractions (Boll et al. 1997, Pilviö and Bickel 2000). Other disadvantages are that the resins are also quite expensive and their regeneration efficiency is not quite clear (Martin and Pope 1982).

### **8.1.2 Spectrometric measurements**

All the measured alpha spectra were good, except those few Thule samples where the Pu separations were incomplete. It is commonly known that using alphaspectrometric measurements of Pu and Am/Cm preparates is a competent and accurate method if the separation of nuclides has been successful, the detectors are clean and have good resolutions, and the amount of internal tracer and measuring nuclides are suitable (Harvey 1984, Glover 1984). Estimating the tracer amount is quite easy for samples with normal environmental levels of TRUs, where the level of activities can also be estimated. For samples with unknown levels of activity, some premeasurement is necessary to fix the sample and tracer amounts. With the Thule sediments, this was carried out by gammaspectrometric measurements of  $^{241}\text{Am}$  and by estimating of amounts of Pu according to  $^{241}\text{Am}$  (Paper III).

In a case where the tracer and measuring nuclide amounts are not in balance, the overlapping of spectra is possible and this may complicate the result calculations (Harvey 1984, Ibrahim et al. 1995). When the isotope ratio of  $^{238}\text{Pu}$  to  $^{239,240}\text{Pu}$  is considerably less than in the environment, it is usually difficult to measure  $^{238}\text{Pu}$  activities although they are at a normal environmental level. Even though the amount of tracer was suitable for the measuring time suitable for  $^{239,240}\text{Pu}$ , the time may be too short for  $^{238}\text{Pu}$ . Increasing the times should cause overlapping of the peaks of other nuclides. This was the case when measuring certain Thule sediment samples and was discussed in Paper III.

The unavailability of separation energies of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ , and also those of  $^{243}\text{Cm}$  and  $^{244}\text{Cm}$ , if present, is drawback in alphaspectrometric measurements. Mass spectrometry is necessary when measuring  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  separately.

The  $^{241}\text{Pu}$  measurements were discussed in Paper IV. Since then, a new  $^{241}\text{Pu}$  method has been developed. The method, which uses efficiency calibration by tritium, proved to be an adaptable and precise method (see Table V). The method was also tested in comparison to the ICP-MS method, and has been later used by other authors (Solatie 2002, Povinec et al. 2002).

An ingrowth method is practicable for environmental research but it can be used only for old samples. The waiting times depend on the activity level to be measured. For measuring the Chernobyl fallout level of  $^{241}\text{Pu}$ , which was much higher than the global fallout level in those days, two years was the minimum time for samples with the highest activities and 10-12 years was used for the biota samples (Papers V and VI).

Overall, it is very important to choose carefully the method of sampling and analysis according to the aim and based on all previous knowledge. Quality assurance has to be kept at a high level all the time to ensure the good quality of results. This procedure was also followed in this study. The results of the intercomparison and proficiency tests are shown in Table V.

**Table V.** Results of the intercomparisons and proficiency tests for  $^{238}\text{Pu}$ ,  $^{239,240}\text{Pu}$ ,  $^{241}\text{Pu}$  and  $^{241}\text{Am}$  determinations during 1993 - 2001. The anion exchange method for alpha-emitting Pu isotopes, liquid scintillation method for  $^{241}\text{Pu}$  and anion exchanges + liquid extraction method for  $^{241}\text{Am}$  were used. (MORS = The Group of Experts on Monitoring of Radioactive Substances in the Baltic Sea).

Code and type of inter-comparison or prof. test	Pu-238 Studied ( $\pm 2\sigma$ )	Pu-238 Confidence interval	Pu-239,240 Studied ( $\pm 2\sigma$ )	Pu-239,240 Confidence interval	Pu-241 Studied ( $\pm 2\sigma$ )	Pu-241 Confidence interval	Am-241 Studied ( $\pm 2\sigma$ )	Am-241 Confidence interval
IAEA-300 sediment Bq/kg	0.15 (0.08)	0.14 – 0.15	3.5 (0.70)	3.09 - 3.90	-	-	1.20 (0.4)	1.14 - 1.40
IAEA-315 sediment Bq/kg	9.0 (1.8)	8.9 - 10.3	65.0 (10.4)	67.3 - 72.0	-	-	17.2 (3.4)	18.8 - 21.0
IAEA-379 sediment Bq/kg	0.15 (0.08)	0.10 - 0.15	3.7 (0.72)	3.1 - 4.1	-	-	-	-
NKS-KAT sediment Bq/kg	0.07 (0.04)	0.05 - 0.10	1.01 (0.12)	0.05 - 0.10	-	-	-	-
NKS-Balt sediment Bq/kg	0.09 (0.04)	0.04 - 0.15	1.68 (0.2)	1.1 - 2.1	-	-	-	-
IAEA-381 Seawater mBq/kg	3.5 (0.8)	3.1 - 3.5	14.0 (2.0)	13.0 - 14.0	263 (80)	180 - 300	13.0 (2.0)	13.3- 17.6
IAEA-382 fish flesh Bq/kg	0.11 (0.034)	0.11 -0.20 (range of MORS)	0.66 (0.10)	0.66 - 1.0 (range of MORS)	-	-	-	-
IAEA prof. test, <u>soil</u> Bq	0.034 (0.006)	0.036 (real val.)	0.076 (0.012)	0.07 (real val.)	0.466 (0.098)	0.50 (real val.)	-	-
<u>standard</u> Bq/g	0.115 (0.018)	0.114 (real val.)	0.248 (0.034)	0.244 (real val.)	1.39 (0.25)	1.59 (real val.)	-	-
IAEA prof. test, <u>min.</u> Bq	-	-	-	-	0.183 (0.026)	0.139 (real val.)	0.0191 (0.002)	0.0171 (real val.)
<u>standard</u> Bq/g	-	-	-	-	0.66 (0.078)	0.73 (real val.)	0.070 (0.007)	0.091 (real val.)
	-	-	-	-	1.45 (0.06)	1.37 (real val.)	0.166 (0.016)	0.170 (real val.)

## 8.2 Concentration levels of Pu, Am and Cm

### 8.2.1 Sediments

$^{238}\text{Pu}$  and  $^{239,240}\text{Pu}$  concentrations and activities per unit area ( $\text{Bq}/\text{m}^2$ ) of  $^{239,240}\text{Pu}$  in the Barents, Petshora, and Kara Seas as well as in the Kola Bay and outlets of the Ob and Yenisey rivers were slightly lower than in the Baltic Sea. In these Arctic seas, the  $^{239,240}\text{Pu}$  concentration was  $4.3 \text{ Bq}/\text{kg}$  and that of  $^{238}\text{Pu}$  was  $0.17 \text{ Bq}/\text{kg}$  at the highest. In the Baltic Sea sedimentation basins, the highest concentrations were  $8$  and  $0.36 \text{ Bq}/\text{kg}$  respectively. However, if one only looks at these activity concentrations, no other source than global fallout can be seen. The global fallout was slightly higher in the latitudes of the Baltic Sea than it was in the Arctic areas (Hardy et al. 1973). The variation in concentrations depends greatly on the sedimentation rates and the type of sediment, such as dry matter contents, and the contents of organic matter in the sediment. In addition, the topography of the bottom affects the concentrations in such a way that in the outlets of Arctic rivers, where the organic matter content is high but the fine sediment is constantly washed to open seas, the concentrations are low. However, the finest sediment is accumulated from large areas into the known sedimentation basins in the Baltic Sea. In the vertical distribution of  $^{241}\text{Pu}$ , the peak originating from the Chernobyl fallout could be seen in the Baltic Proper. The Pu concentrations measured are in good agreement with other studies of the Arctic areas (Baskaran et al. 2003, Heldal et al. 2002, Strand et al. 1996). Similar results concerning  $^{239,240}\text{Pu}$  in the Baltic Sea area have also been reported by other authors (Holm 1995, Ilus et al. 2003, Suplinska 2002).

In the Thule accident area, the concentrations of  $^{238}\text{Pu}$ ,  $^{239,240}\text{Pu}$ ,  $^{241}\text{Pu}$  and  $^{241}\text{Am}$  were generally one to three orders of magnitude higher than the fallout level in the Arctic areas. The highest  $^{239,240}\text{Pu}$  concentration was as high as  $7\,600 \text{ Bq}/\text{kg}$ , and that of  $^{241}\text{Pu}$   $5\,900 \text{ Bq}/\text{kg}$ . In the separated  $10\text{-}\mu\text{m}$  particle, the  $^{239,240}\text{Pu}$  amount was  $1.4 \text{ Bq}$  and that of  $^{241}\text{Pu}$  was  $1.6 \text{ Bq}$ . A large and uneven amount of similar hot particles found in the area made estimating the total inventory and areal amounts very difficult. Much more data would be needed for proper estimations. Eriksson (2002) has developed a non-destructive method for total inventory estimations based on large data and the evaluation of hot particles in the area. He achieved a total value of  $10 \text{ TBq}$  of  $^{239,240}\text{Pu}$ . This is much higher than in earlier estimations, where the value was  $3.1 \text{ TBq}$ , which was based on similar results in this study (IAEA 2001, Smith et al. 1994).

The vertical distribution of nuclides in the Thule area showed the mixing

and contamination of sediments down to at least the depths studied (20 cm). This was somewhat deeper than the depths in an earlier study in 1984, when the biggest concentrations were 3 – 6 cm deep and the contamination reached up to 15 cm (Smith et al. 1994). Elevated levels were observed in all sampling sites in a 4-km radius from the accident site. Eriksson (2002) has detected the contamination spreading from the Bylot Sound area to a distance of 100 km. Generally, no contamination could be seen in the surface seawater taken during the same cruise in 1997 (McMahon et al. 2000). However, the amount of the radioactivities of TRUs in the Thule area is high and it is one possible source for marine contamination of the near areas, if remobilization of TRUs from sediments occurs.

### 8.2.2 Biota and lake water

The concentrations of  $^{239,240}\text{Pu}$  in alga samples were low in the Barents, Petshora, and White Seas, ranging from 0.022 to 0.28 Bq/kg. All the  $^{238}\text{Pu}$  concentrations were below the detection limit. Differences were observed only between different species; no traces of local contamination could be seen.

The  $^{239,240}\text{Pu}$  concentrations in fish in the Barents Sea were also very low, most of them not detectable. It was detectable in a few samples of liver and bones, the parts of fish where Pu best accumulates. The only detected amount of  $^{239,240}\text{Pu}$  in fish flesh was observed in the bottom feeding species *Raja radiata*. No effect of any local contamination source could be seen. The results are in good agreement with the knowledge of the behaviour of Pu in biota.

The effect of the Chernobyl fallout could be seen in TRU concentrations of Finnish freshwater fish. Since TRU fallout in Finland is well studied, an excess of TRUs in fish was detected in the area of high fallout, whereas in the lakes in the south-east part of Finland, no TRUs could be found (Paatero 2000, Paatero et al. 2002). However, the  $^{238}\text{Pu}$ ,  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  concentrations were still low, those of  $^{239,240}\text{Pu}$  only few mBq per kilo. The exceptionally high  $^{241}\text{Pu}$  concentrations, 110 mBq/kg at highest in fish flesh, were quite clear signs of fresh fallout. Another sign was detection of short-lived  $^{242}\text{Cm}$ , 340 mBq/kg at the maximum. In addition, a small amount of  $^{243,244}\text{Cm}$  was detected in one liver sample (20 mBq/kg), which was not presented in Paper VI.

The concentration of 0.6 mBq/kg of  $^{239,240}\text{Pu}$  in fish flesh was chosen as detection value for the fresh fallout. Because of the lack of exact data, this selection was based on the best knowledge of concentrations in fish generally. According to Table IV, the CF for both marine and freshwater fish is the same (the only exception is bottom feeding fish). When the concentrations of water

both in marine and freshwater environments are at same level in the areas where only global fallout exists, the concentrations of marine fish can be used as reference values for the study. Ryan et al. (1999) considered the normal fallout level of  $^{239,240}\text{Pu}$  concentration to be less than 1 mBq/kg in fish flesh. In the Southern Baltic Sea, Pu concentrations of cod flesh have been less than 0.034 mBq/kg (Kanish et al. 1995). Yamada (1997) reported a maximum concentration of 0.14 mBq/kg of  $^{239,240}\text{Pu}$  in salmon flesh in the Japan coastal waters during 1991. In the study by Robinson and Noshkin (1999), in 1998, near the Enewetok and Bikini Atolls, representing the lowest concentrations of  $^{239,240}\text{Pu}$  in pelagic fish, the background values were 0.03 and 0.5 mBq/kg, respectively. Skwarzec et al. (2001) have measured concentrations of  $^{238}\text{Pu}$  and  $^{239,240}\text{Pu}$  up to 0.3 mBq/kg in the Gdansk Bay of the Baltic Sea.

The effect of Chernobyl fallout could be seen in the Pu, Am and Cm concentrations in the water of Lake Päijänne. In addition, a small amount of  $^{243,244}\text{Cm}$  was found (3mBq/m<sup>3</sup>), which was not presented in Paper VI. Similar results from the same area have been reported by Pilviö (1998).

## 8.3 Activity ratios and accumulations

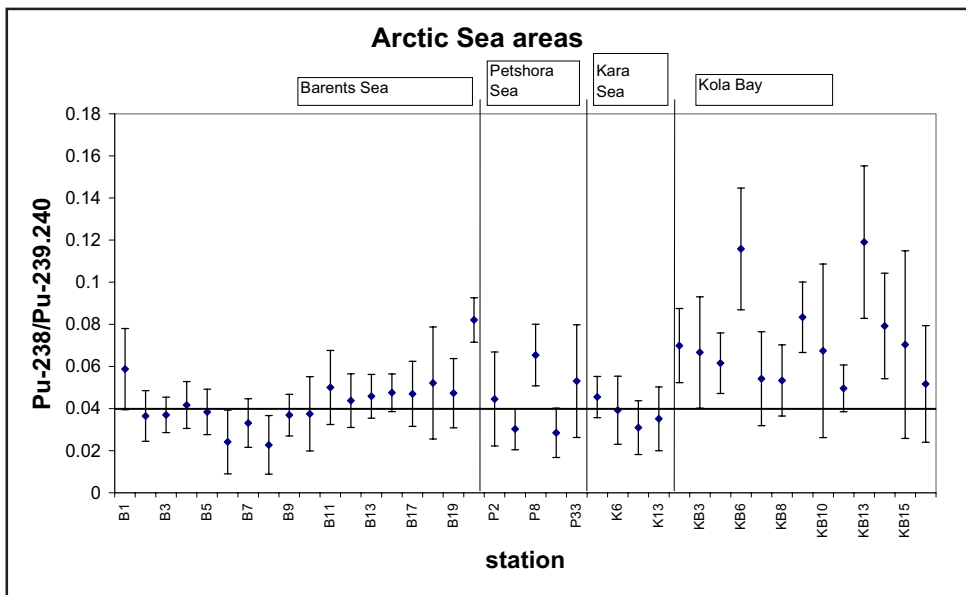
### 8.3.1 Sediments

The use of activity ratios of isotopes is a better tool for determining the source, or effect of different sources, than simple comparison of concentrations in sediments. The  $^{238}\text{Pu}/^{239,240}\text{Pu}$  ratio from global fallout only was estimated to be about 0.03 – 0.04 (see Table III). The ratios for surface sediments in the Barents, Kara, and Petshora Seas as well as those in the Kola Bay are presented in Figure 4. It can be seen that in the Barents and Petshora Seas, the ratios agree quite well with the value for global fallout within uncertainties (2 sigma) and no clear underlying values exist, except an increased value at one site in both areas. These two higher ratios can be due to the minor influence of the Sellafield discharges with a portion of about 20 % of the total Pu. However, the ratios in the Kola Bay are generally higher than the maximum global value. As a conclusion, it is obvious that in the Kola Bay, there are one or more local sources of Pu with a higher Pu ratio. The effect of Sellafield Pu is not probable, because water currents are from Bay to the outlet and open sea. The Chernobyl fallout plume of TRUs did not probably reach the Arctic areas. It is most likely that the origin of the Pu is leakage from one or more local reactors or from reprocessing waste.

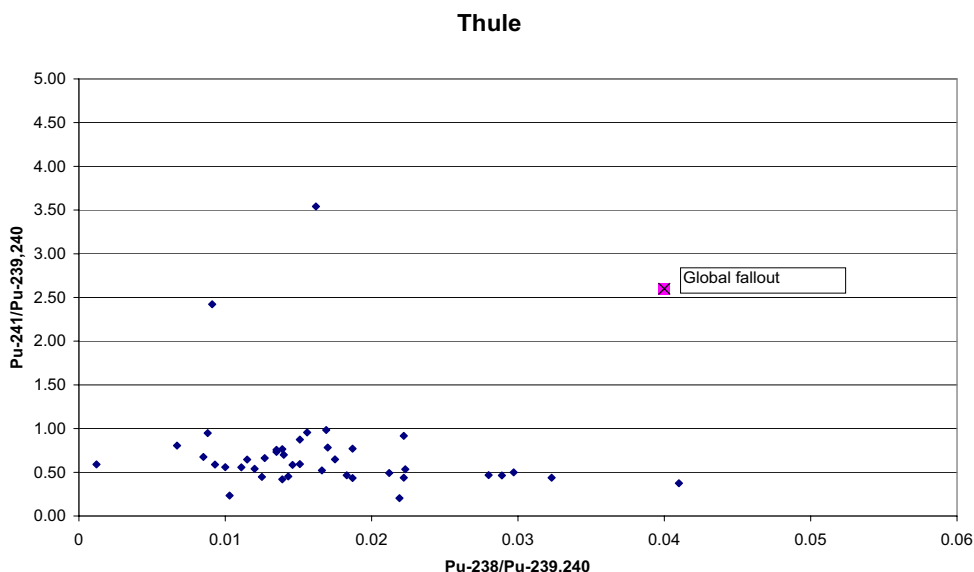


Similar results from the Barents and Kara Seas areas concerning the ratios of  $^{238}\text{Pu}/^{239,240}\text{Pu}$  have been reported by Hamilton et al. (1994) and Baskara et al. (2000). Their conclusion was that only global fallout could be seen. However, in the Barents Sea, the effect of Sellafield discharges has been observed by several authors. Baskaran et al. (1995) have estimated that the portion of Pu originating from Sellafield is 26 – 46 % of Pu in the Barents and Greenland Sea whilst in the Kara Sea, including the outlets of the Ob and Yenisey rivers, only global fallout could be detected. In other studies, where the use of the ratio of  $^{239}\text{Pu}/^{240}\text{Pu}$  is also possible, discharges from Tomsk, Mayak and Semipalatinsk could be seen in the river delta and outlet area of the River Ob (Cochran et al. 2000, Cooper et al. 2000, Kenna and Sayles 2002). This was not possible to detect from the  $^{238}\text{Pu}/^{239,240}\text{Pu}$  ratios.

As expected, the isotope ratios of TRUs were quite different in the Thule accident area. The mean values of  $^{238}\text{Pu}/^{239,240}\text{Pu}$ ,  $^{241}\text{Pu}/^{239,240}\text{Pu}$  and  $^{241}\text{Pu}/^{241}\text{Am}$  were 0.018, 0.72 and 4.0 respectively. The ratios of  $^{238}\text{Pu}/^{239,240}\text{Pu}$  to those of  $^{241}\text{Pu}/^{239,240}\text{Pu}$  are presented in Figure 5. Both ratios, in general, are lower than in global fallout because of the origin of nuclear weapon Pu.



**Figure 4.** The variation in ratios of  $^{238}\text{Pu}/^{239,240}\text{Pu}$  with 2 sigma uncertainties in surface sediments of the Barents, Petshora, and Kara Seas and the Kola Bay. (The maximum of the global fallout value 0.04 is also marked).



**Figure 5.** Activity ratios of the Thule sediments.

However, the variation of especially the ratios of  $^{238}\text{Pu}/^{239,240}\text{Pu}$  is quite large. For one type of weapons-grade Pu bomb, the ratio can be expected to be quite equal. This kind of large ratio may indicate that the Pu in Thule accident could originate from at least two sources of different quality. This assumption also confirms the results of the separated particle compared with the analyses of bulk samples. Eriksson (2002) came up with the same result in his thesis by also using the mass ratios of  $^{239}\text{Pu}/^{240}\text{Pu}$ .

The Chernobyl fallout of TRUs as well as the old global fallout can be seen in the Baltic Sea area. Figure 6 presents both  $^{238}\text{Pu}/^{239,240}\text{Pu}$  and  $^{241}\text{Pu}/^{239,240}\text{Pu}$  ratios in addition to Figure 5 in Paper V (measured at the same time as the results presented in Paper V). These vertical distributions show that in 1 cm slices in Teili-1, the maximum of ratios exist between 7- 9 cm. This is a clear influence of the Chernobyl accident, where the ratio is considerable higher than that of global fallout. The maximum of  $^{137}\text{Cs}$  concentrations, representing the Chernobyl fallout, were also in those slices. Moreover, some fresh fallout could be seen in the upper layers, e.g. in the uppermost layer; the ratios are clearly higher than those for global fallout. This is probably due to erosion and the accumulation of sediments from harder or lower areas into this basin. At other sites, where only 5 cm slices were analysed, the effect is not so obvious. Slightly higher ratios can be seen for both  $^{238}\text{Pu}/^{239,240}\text{Pu}$  and  $^{241}\text{Pu}/^{239,240}\text{Pu}$  in uppermost

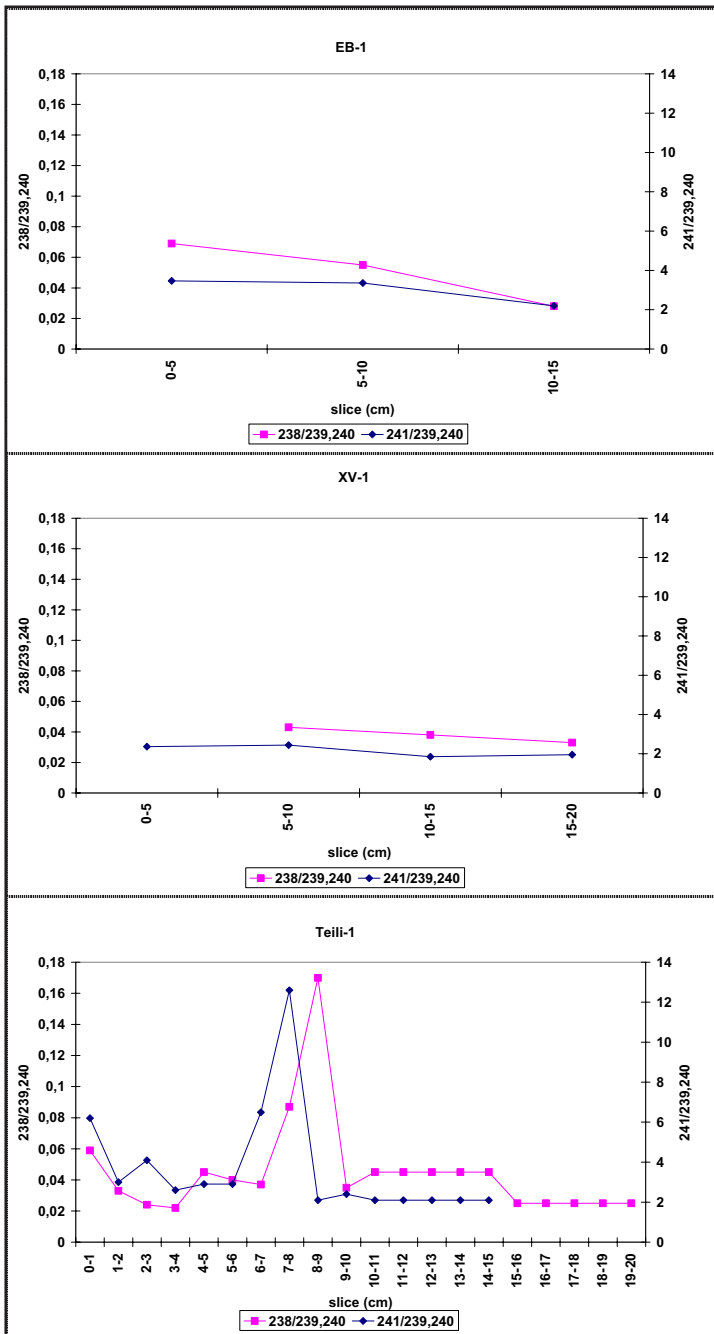
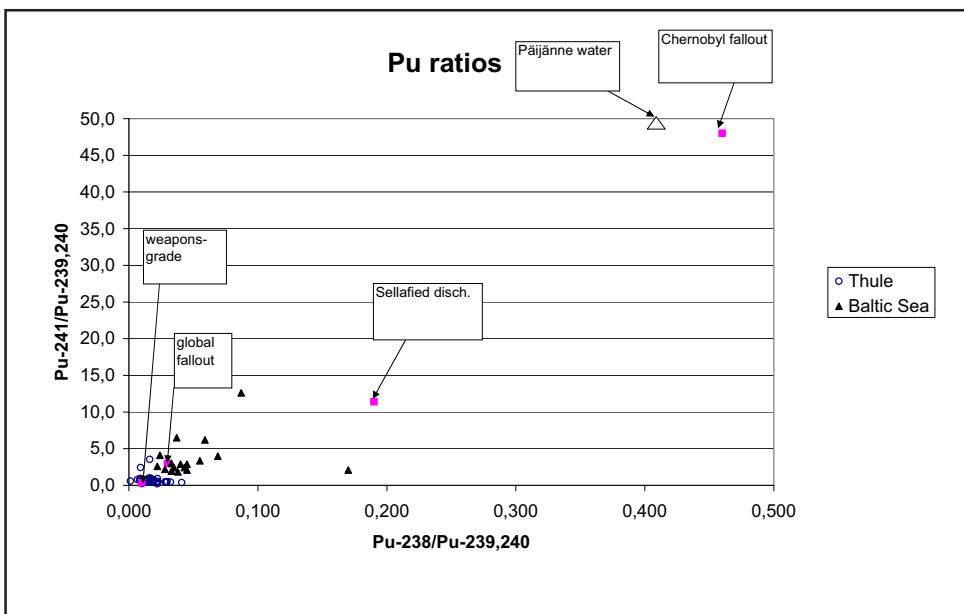


Figure 6. Vertical distribution of activity ratios in the Baltic Sea sediments.

layer, especially in EB-1 site. Ilus et al. (1995) have also recognised that Pu from Chernobyl could be seen in the Baltic Sea sediments from the Pu ratios, while the addition of Pu was minor compared with the global fallout. According to Holm (1995),  $^{238}\text{Pu}$  and  $^{241}\text{Pu}$  affect the level of these isotopes in the Baltic Sea, but not  $^{239,240}\text{Pu}$ . No clear signs of Chernobyl derived Pu could be seen in the southern part of the Baltic (Suplinska 2002). Similar Pu results can also be seen in sediments from the Black Sea, which, due to the Chernobyl fallout, is another very contaminated sea (Strezov et al. 1996).

The portion of Chernobyl origin  $^{241}\text{Pu}$  to global fallout can be calculated according to the equation presented by Paatero et al. (1994). For the  $^{239,240}\text{Pu}/^{241}\text{Pu}$  ratio, a value of 0.405 is used for global fallout and a value of 0.0197 for the Chernobyl fallout. According to this, at Teili-1 in the Baltic Proper, at its maximum (8-9 cm), the portion of Chernobyl originating  $^{241}\text{Pu}$  was 5.5 times higher than that of global fallout.  $^{241}\text{Pu}$  from Chernobyl, which was about twice that of the global fallout, still existed in the uppermost layer.



**Figure 7.** Activity ratios of the Thule and the Baltic Sea sediments (decay-corrected to 1996).

The activity ratios for  $^{238}\text{Pu}/^{239,240}\text{Pu}$  compared with those of  $^{241}\text{Pu}/^{239,240}\text{Pu}$  in Thule and Baltic Sea sediments and Lake Päijänne water are presented in Figure 7. In addition, the ratios of different sources are fixed in the Figure. It can be clearly seen that most of the Thule ratios were close to the weapons-grade Pu ratio. Most of the Baltic Sea ratios are near to the global fallout ratio but, however, they are somewhat higher, more in the direction of the Chernobyl fallout ratio. The ratio for the water in Lake Päijänne is quite near to that of the Chernobyl fallout.

The concentrations of  $^{239,240}\text{Pu}$  in the Baltic Sea water have been quite equal, only few  $\text{mBq}/\text{m}^3$  (Mulsov et al. 2003). A value of  $5 \text{ mBq}/\text{m}^3$  can be used for the  $K_d$ -calculation. According to this, the distribution factor for surface sediment in the Baltic Sea is  $2 - 5 \times 10^5$ . This is in good agreement with the values given by the IAEA for coastal marine areas (IAEA 1985).

### 8.3.2 Freshwater fish

Some activity ratios of  $^{238}\text{Pu}/^{239,240}\text{Pu}$  in freshwater fish were anomalous. In those samples where the ratios could be calculated, it was between 1.0 and 7.2 with the uncertainty of about 50 % (2 sigma). Statistical tests of data are not possible because of the low number of results. If all the Pu in the fish had been of Chernobyl origin, the ratio could be 0.5 at maximum. The proportion of Pu from the decayed  $^{242}\text{Cm}$ , calculated from the maximum  $^{242}\text{Cm}$  concentration, is very small due to the short time between the accident and the measurement and it cannot explain the high ratios. There can be explanations for this: 1) the deposition from the accident was so uneven that it could still be seen in fish samples or 2) the bigger availability of  $^{238}\text{Pu}$  compared with that of  $^{239,240}\text{Pu}$  for fish. Analytical errors are not probable because of the good quality of the method and very clean spectra. The isotope ratios were uneven both in the air and deposition samples during the first days after the accident (Saxén and Taipale 1987, Sinkko et al. 1987). This could be due to different kinds of fuel or condensed particles with different burnup-times. However, in general, the ratio was about 0.5 in all samples, representing the deposition studied by Paatero (2000). The differences in the bioavailabilities of  $^{238}\text{Pu}$  and  $^{239,240}\text{Pu}$  could be a reason. NCRP (2001) has also discussed a suggestion that Pu isotopes could behave differently in biological systems when compared with the environmental system. Due to the limited amount of samples, only few observations are available. Therefore, the correctness of this kind of conclusion is questionable but the results do show a clear trend to high ratios. Repeating the study is not possible because it was performed in fresh fallout situation soon after the accident.

Other authors have also observed this kind of behaviour of Pu isotopes in biological samples: Booher et al. (1998), Emery et al. (1976), Fresquez et al. (1999), Noshkin et al. (1988), Schell et al. (1978) and Suchanec et al. (1996) have reported of observations or results of the enhancement of  $^{238}\text{Pu}$  in aquatic environments and Gilbert et al. (1988) have reported such observations in the terrestrial environment. Kuzo et al. (1987) have come up with an opposite conclusion for the bigger accumulation of  $^{239,240}\text{Pu}$  to that of  $^{238}\text{Pu}$ , and Bourlet et al. (1995) reported that no differences exist. The NCRP (2001) has concluded that  $^{238}\text{Pu}$  is more soluble as oxides than  $^{239,240}\text{Pu}$  is. The reason for this could be due to differences in their specific activities, inasmuch as  $^{238}\text{Pu}$  clusters would have a higher probability of being released from particle because of its shorter half-life (see Table I). This explanation, however, assumes that the  $^{238}\text{Pu}$  and  $^{239,240}\text{Pu}$  are in separate particles originally (NCRP 2001, Schell et al. 1980).

Different in concentration factors were found for Am and Cm, suggesting the Cm was more bioavailable over Am. However, also in this case, the amount of data was very limited, but the difference was about one decade. Trabalka et al. (1987) observed that Cm is more soluble than Am in the test reactor leaching pond in Idaho, USA. In the Savannah River environment, a bigger CF for Cm over Am has been found (Whicker et al. 1999). Ryan (2002) has reported similar and opposite behaviour for Am and Cm. The results of Matsunaga et al. (1998) in the vicinity of Chernobyl and Eicke (1981) indicate higher solubility for Cm. However, Pentreath (1981) concluded that there are no differences in bioavailability between Am and Cm, or if Am is more available. The possible reasons for the different behaviour of Am and Cm could be the fact that they are, however, different elements, and  $^{242}\text{Cm}$  also has much higher specific activity (see Table I) (Beasley and Cross 1980, Eicke 1981, Trabalka and Garten 1983).

## 8.4 Transfer of TRUs from deposition to fish

The deposition of TRUs from the Chernobyl accident has been studied in Lake Päijänne area (Paatero et al. 2002). According to these results, the transfer factors (TF) could be calculated. The TFs from deposition to fish flesh were  $3 \times 10^{-3}$  and  $18 \times 10^{-3} \text{ m}^2/\text{kg}$  for  $^{239,240}\text{Pu}$  and  $^{241}\text{Am}$  respectively. These values are 10 – 20 times higher than those values calculated for reindeer meat,  $1.7 \times 10^{-4} \text{ m}^2/\text{kg}$  for  $^{239,240}\text{Pu}$ ; and thousands of times bigger than the TFs calculated for plant production,  $7 - 15 \times 10^{-7} \text{ m}^2/\text{kg}$  (Friberg 1998). In her thesis, Outola (2002) reported the highest TF of Pu for mushrooms to be about  $5 \times 10^{-5} \text{ m}^2/\text{kg}$ . This is two orders of magnitude less than for freshwater fish. This means that in a

possible serious fallout situation in the future, the limit set by the EU for Pu and transplutonium elements in food, other than milk or liquid foods, is exceeded in freshwater fish first and only after that in reindeer meat, mushrooms, or plant production (EURATOM 1987). However, to exceed the EU limits, the deposition should be 3000 times higher for Pu and 1500 times higher for Am than the highest transuranic elements fallout recorded in Finland following the Chernobyl accident (Paatero et al. 2002).

## **8.5 Doses from TRUs due to consumption of freshwater fish**

The dose received through consuming of Finnish freshwater fish has been calculated from the highest measured concentrations. Using a consumption of 7.9 kg/y of fish, according to Markkula and Rantavaara (1997) and dose factors recommended by the IAEA (1996), a dose of about 50 nSv/y is received (dose factors for  $^{238}\text{Pu}$ ,  $^{239,240}\text{Pu}$ ,  $^{241}\text{Am}$  and  $^{242}\text{Cm}$  are  $2.3 \times 10^{-7}$ ,  $2.5 \times 10^{-7}$ ,  $2.0 \times 10^{-7}$ , and  $1.2 \times 10^{-8}$ , respectively; unit Sv/Bq). More than half of this comes from short-lived  $^{242}\text{Cm}$ , so during the first year the dose could decrease noticeably. This can be compared with the dose from the Chernobyl derived  $^{137}\text{Cs}$ . Saxén (1987) has estimated the average intake of  $^{137}\text{Cs}$  in 1987 in Finland to be 4800 Bq/y, from which the dose of 0.06 mSv/y can be calculated with the dose factor of the IAEA ( $1.3 \times 10^{-8}$  Sv/Bq). The maximum dose from transuranic elements in fish at the same time was about 0.1% of this. Compared to the average annual total dose to Finnish people (about 4 mSv/y in 2001), the maximum dose from transuranic elements in freshwater fish is insignificant, about 0.001% of the annual dose (STUK 2002).

## 9 Conclusions

The use of activity ratios of transuranic isotopes offers a good tool for the estimation of sources and their effects on activity concentrations in sediments.

In the present study, concentrations of Pu isotopes were low in sediments, fish, and alga samples from the Barents, Kara, and Petshora Seas as well as in the outlets of Ob and Yenisey rivers. The highest concentrations of  $^{239,240}\text{Pu}$  were less than 5 Bq/kg in sediments, less than 0.3 Bq/kg in algae and below the detection limit in fish flesh, except in a bottom feeder fish. The  $^{238}\text{Pu}/^{239,240}\text{Pu}$  ratio in sediments showed that the source of TRUs was mainly the global fallout, which came to about 0.03 – 0.04.

In the Kola Bay areas, the concentration of sediments was also low but elevated  $^{238}\text{Pu}/^{239,240}\text{Pu}$  ratios, usually above 0.04, indicated that another source, apart from global fallout, must exist.

In the Thule accident area, plutonium and americium concentrations in sediments were from one to more than three orders of magnitude higher than the fallout level. The highest  $^{239,240}\text{Pu}$  concentration was about 7600 Bq/kg. The activity ratios both in sediments and in the separated particle showed that the origin of excess of transuranic elements was weapon-grade Pu. The mean ratio of  $^{238}\text{Pu}/^{239,240}\text{Pu}$  was 0.018,  $^{241}\text{Pu}/^{239,240}\text{Pu}$  was 0.72, and  $^{241}\text{Pu}/^{241}\text{Am}$  4.0 respectively. However, the large variation in all isotopic ratios indicates that the origin of Pu was not homogenous. A large and uneven amount of hot particles can prevent good estimations of inventory and accumulation calculations. The sediments in the area were quite mixed and contamination reached down to the depths studied.

In the northern part of the Baltic Sea, in the Baltic Proper, the Gulf of Finland and the Gulf of Bothnia, the effects of the Chernobyl accident could be seen in sediments. While the most part of  $^{239,240}\text{Pu}$  was from global fallout, the Chernobyl fallout could be seen from activity ratios of  $^{238}\text{Pu}/^{239,240}\text{Pu}$  and  $^{241}\text{Pu}/^{239,240}\text{Pu}$ , and from the excess amounts of  $^{241}\text{Pu}$ . The ratio of  $^{241}\text{Pu}/^{239,240}\text{Pu}$  was 13 at the highest. The portion of Chernobyl origin  $^{241}\text{Pu}$  was 5.5 times bigger than that originating from the global fallout at the highest. The peak of Chernobyl fallout year (1986) could be detected in vertical distribution in the undisturbed sediment core, but Chernobyl-derived Pu was still accumulated onto the surface of the bottoms.

In Finnish freshwater fish in the area of high TRU fallout and in the water of Lake Päijänne, the Chernobyl derived TRUs were observed as somewhat elevated concentrations. However, the concentrations in fish were



still low, those of  $^{239,240}\text{Pu}$  only few mBq per kilo. The annual maximum dose to people from transuranic elements in freshwater fish was insignificant, about 50 nSv/y, which was 0.001% of the total average annual dose to the Finnish people.

The results of freshwater fish indicate incomplete knowledge of the behaviour of different isotopes of Pu, Am and Cm in a fresh fallout situation. Some results suggested the preferential uptake of  $^{238}\text{Pu}$  when compared with that of  $^{239,240}\text{Pu}$  into fish, and also that the biological behaviour of Am and Cm was dissimilar in a fresh fallout situation. Whether this is a real situation or an experimental artefact remains unclear.

To get the valid results, it is important to choose proper methods, both for sampling and analysing, that are the most suitable for research according to all previous knowledge available. In this study, the anion exchange method was a good separation method for Pu determinations in all kinds of samples. Am and Cm were separated with a long but precise combined ion exchange and extraction method. For  $^{241}\text{Pu}$  determination, a reliable liquid scintillation method with tritium-based effectivity calibration was modified.

Great emphasis was laid on quality control during the entire research procedure. The results of intercomparisons and proficiency tests using the above methods were excellent. Only reliable, continuing quality assurance can guarantee competent results, especially when determining low-level concentrations and the small differences between them.

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Errata:

### **Publication III**

Page 343, eighth line in the text column should be:  
at Station 20, the next closest to the accident site (about

Page 343, thirteenth line in the text column should be:  
6000 Bq/kg at Station 20 and  $^{238}\text{Pu}$  Am and  $^{241}\text{Am}$  were