Development of analytical methods for the separation of plutonium, americium, curium and neptunium from environmental samples

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Academic Dissertation

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ABSTRACT

In this work, separation methods have been developed for the analysis of anthropogenic transuranium elements plutonium, americium, curium and neptunium from environmental samples contaminated by global nuclear weapons testing and the Chernobyl accident. The analytical methods utilized in this study are based on extraction chromatography.

Highly varying atmospheric plutonium isotope concentrations and activity ratios were found at both Kurchatov (Kazakhstan), near the former Semipalatinsk test site, and Sodankylä (Finland). The origin of plutonium is almost impossible to identify at Kurchatov, since hundreds of nuclear tests were performed at the Semipalatinsk test site. In Sodankylä, plutonium in the surface air originated from nuclear weapons testing, conducted mostly by USSR and USA before the sampling year 1963.

The variation in americium, curium and neptunium concentrations was great as well in peat samples collected in southern and central Finland in 1986 immediately after the Chernobyl accident. The main source of transuranium contamination in peats was from global nuclear test fallout, although there are wide regional differences in the fraction of Chernobyl-originated activity (of the total activity) for americium, curium and neptunium.

The separation methods developed in this study yielded good chemical recovery for the elements investigated and adequately pure fractions for radiometric activity determination. The extraction chromatographic methods were faster compared to older methods based on ion exchange chromatography. In addition, extraction chromatography is a more environmentally friendly separation method than ion exchange, because less acidic waste solutions are produced during the analytical procedures.
LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following five publications, which are referred to in the text by their Roman numerals (I-V).


III. Salminen, S. and Paatero, J. *Concentrations of $^{238}$Pu, $^{239+240}$Pu and $^{241}$Pu in surface air in Finnish Lapland 1963.* Accepted to Boreal Environmental Research.


V. Salminen, S., Paatero, J., Roos, P., Helariutta, K. *Deposition of $^{237}$Np in peat and lichen in Finland.* Accepted to Journal of Radioanalytical and Nuclear Chemistry.

Author’s contribution to the publications I-V

The author planned the study for publication I along with other authors, performed part of plutonium analysis and all data analysis, and wrote the manuscript. For publication II, the author was partly responsible for the plutonium analysis and data analysis, and she prepared the manuscript together with the first author Jukka Lehto. For publications III-V, the author drew up the research plans and performed all chemical separations and measurements independently. She did the data analysis for publications III-V with Jussi Paatero and was the lead author of the publications III-V.
1. INTRODUCTION

Transuranium elements plutonium, americium curium and neptunium have been introduced to the environment from atmospheric nuclear weapons testing, nuclear fuel reprocessing and single events, such as the Chernobyl accident. Transuranium nuclides generally have long half-lives and decay mainly by alpha emission. In addition, they often have several possible oxidation states that may change during time. Reduced actinides (III, IV) are more particle-reactive and therefore less mobile than oxidized actinides (V, VI). Therefore, these elements are long-term contaminants in environment and their bioavailability may change over time.

The aim of this work was to develop analytical methods for separating isotopes of Pu, Am, Cm and Np from different kinds of environmental samples contaminated by global nuclear test fallout and the Chernobyl accident. The separation methods used in this study were based on extraction chromatography and were optimized according to the sample type (air filter and peat). Activity concentrations of transuranium nuclides in air and peat were determined and compared to corresponding activity concentrations from other studies. Finally, contributions from different contamination sources to transuranium deposition in Finland were estimated.
2. TRANSURANIUM NUCLIDES AND THEIR SOURCES IN ENVIRONMENT

The radioactive elements having mass number of 89-103, from actinium to lawrencium, form the actinide series in periodic table. Electrons are filling the 5f electron shell of actinides, and with lanthanides the electrons fill the 4f electron shell. For this similarity in electron occupancy, actinides are analogous to lanthanides. The ionic radius is decreasing in the function of increasing nuclear charge with both actinides and lanthanides, this effect is called actinide or lanthanide contraction. Actinides can exhibit a variety of oxidation states, whereas with lanthanides, only one or two oxidation states are possible.

Transuranium nuclides, or actinides heavier than uranium, were first prepared during the Manhattan project in the 1940s. Most of the transuranium radionuclides decay by alpha emission, often having long physical and biological half-lives and enriching in the liver or bones if introduced to the human. The transfer in certain food chains is possible for plutonium, americium, curium and neptunium. These properties together make transuranium nuclides highly radiotoxic. Transuranium elements have been introduced to the environment from atmospheric nuclear weapons testing during 1950s and 1960s, nuclear fuel reprocessing, accidents of aircrafts carrying nuclear weapons and the Chernobyl accident in 1986. Transuranium nuclides are considered as artificial radionuclides and their half-lives are shorter than the age of the Earth. However, minute amounts of $^{244}$Pu ($t^{1/2} 8.08 \times 10^7$ a) originate on Earth from supernova explosions (Clark et al. 2006), where other transuranium nuclides have also been born, but due to their shorter half-lives, they no longer exist on Earth. In addition, trace amounts of neptunium and plutonium are born in uranium ores as a consequence of neutron capture due to cosmic radiation and spontaneous fission of uranium.
Table 1. Transuranium isotopes of this study and their half-lives (Chu et al. 1999), decay modes, energies and intensities of the strongest transitions (Chu et al. 1999). Possible oxidation states of elements are listed here (Clark et al. 2006, Lumetta et al. 2006, Runde&Schulz 2006, Yoshida et al. 2006), the most typical oxidation state is bolded. * indicates isotope used as a tracer nuclide during analysis. In the case of $^{235}$Np, intensity is the summed intensity of Auger electrons and X-rays of L-shell transitions.

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>$t_{1/2}$</th>
<th>Main decay mode</th>
<th>Decay energy</th>
<th>Intensity (%)</th>
<th>Oxidation states</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{237}$Np</td>
<td>2144a</td>
<td>α</td>
<td>4.788 MeV</td>
<td>47</td>
<td>3,4,5,6</td>
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<tr>
<td>$^{235}$Np*</td>
<td>396d</td>
<td>EC</td>
<td>11.87-21.49 keV</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td>$^{242}$Pu*</td>
<td>373a</td>
<td>α</td>
<td>4.901 MeV</td>
<td>77.5</td>
<td></td>
</tr>
<tr>
<td>$^{241}$Pu</td>
<td>14.35a</td>
<td>α</td>
<td>20.8 keV</td>
<td>&lt;99</td>
<td></td>
</tr>
<tr>
<td>$^{240}$Pu</td>
<td>6563a</td>
<td>α</td>
<td>5.168 MeV</td>
<td>72.8</td>
<td></td>
</tr>
<tr>
<td>$^{239}$Pu</td>
<td>24110a</td>
<td>α</td>
<td>5.157 MeV</td>
<td>73.3</td>
<td></td>
</tr>
<tr>
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<td>α</td>
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<td></td>
</tr>
<tr>
<td>$^{243}$Am*</td>
<td>7370a</td>
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<td>$^{241}$Am</td>
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<td>5.486 MeV</td>
<td>84.5</td>
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<tr>
<td>$^{244}$Cm</td>
<td>18.1a</td>
<td>α</td>
<td>5.805 MeV</td>
<td>76.4</td>
<td></td>
</tr>
<tr>
<td>$^{243}$Cm</td>
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<td>α</td>
<td>5.785 MeV</td>
<td>72.9</td>
<td></td>
</tr>
<tr>
<td>$^{242}$Cm</td>
<td>162.8d</td>
<td>α</td>
<td>6.113 MeV</td>
<td>74</td>
<td></td>
</tr>
</tbody>
</table>

2.1. Plutonium

Plutonium can exist at oxidation states +3, +4, +5, +6 and in rare conditions +7 (Table 1). The most typical oxidation state of plutonium in aquatic environment is +5, where the metal is in the form of the PuO$_2^+$ ion. In soils and sediments plutonium exists predominantly as +3 and +4. The energy differences between oxidation states of plutonium are very small, enabling plutonium to exist at several oxidation states in solution simultaneously. Therefore, the adjustment and stabilization of the oxidation state is essential in plutonium analysis.

The most important global plutonium source has been the atmospheric nuclear testing mainly by USSR and USA and to a lesser extent by Great Britain, France and China in the 1950-1960s (UNSCEAR 2000 Annex C). The total released activities during nuclear weapons testing have been estimated to be $6.52 \times 10^{15}$ Bq of $^{239}$Pu, $4.35 \times 10^{15}$ Bq of $^{240}$Pu.
and $1.42 \times 10^{17}$ Bq of $^{241}$Pu (UNSCEAR 2000 Annex C). Underground nuclear tests near the ground surface are sources of local plutonium contamination at the nuclear test sites like Semipalatinsk, Novaya Zemlya, Bikini and Enewetak. In 1964 a satellite with a SNAP-9A radioisotopic power source was destroyed over Mozambique, spreading $6.3 \times 10^{14}$ Bq of $^{238}$Pu globally to the atmosphere. The Chernobyl reactor accident in 1986 is a significant source of plutonium contamination, both globally and locally, releasing to environment $3.5 \times 10^{13}$ Bq of $^{238}$Pu, $3 \times 10^{13}$ Bq of $^{239}$Pu, $4.2 \times 10^{13}$ Bq of $^{240}$Pu and $\sim 6 \times 10^{15}$ Bq of $^{241}$Pu (UNSCEAR 2000 Annex J). Emissions from nuclear fuel reprocessing plants and accidents of aircraft carrying nuclear weapons, like at Thule (Dahlgaard et al. 2001) and Palomares (Iranzo et al. 1987), are important local contamination sources of plutonium.

Isotope and activity concentration ratios of plutonium isotopes give information about the origin of plutonium, because every nuclear event has basically individual isotopic composition. Therefore, isotopic ratios can act as fingerprints in detection of plutonium contamination sources. For example, $^{238}$Pu/$^{239+240}$Pu activity ratios for weapons grade plutonium, nuclear tests (before 1964 and SNAP-9A accident), releases from nuclear fuel reprocessing plants and the Chernobyl fallout are about 0.014, 0.026, 0.25 and 0.47, respectively (Holm et al. 1992). However, the $^{238}$Pu/$^{239+240}$Pu activity ratios in global nuclear test fallout and weapons-grade plutonium are nowadays so similar, that it is difficult to recognize a plutonium source by using this activity ratio, although it is still a useful method for distinguishing the influences from nuclear weapons testing and the Chernobyl fallout. The $^{240}$Pu/$^{239}$Pu mass ratio by ICP-MS is a better tool for identifying the origin of the plutonium from global fallout or weapons-grade plutonium, since the $^{240}$Pu/$^{239}$Pu ratio is clearly different for plutonium from nuclear testing ($\sim 0.18$) and weapons-grade plutonium (approximately 0.05) (Warneke et al. 2002).

### 2.2. Americium

$^{241}$Am, ($t_\frac{1}{2} = 432$ a), has ended up in the environment from either direct americium deposition, or, ingrowth from $^{241}$Pu ($t_\frac{1}{2} = 14.4$ a). From nuclear weapons testing,
1.2×10^{16} \text{ Bq of } ^{241}\text{Am has been ingrown from the decay of } ^{241}\text{Pu present in the original nuclear test fallout (Allard et al. 1984), although there was also a minor amount of direct } ^{241}\text{Am deposition. A total amount of } 4.8\times10^{12} \text{ Bq of } ^{241}\text{Am was released in the Chernobyl accident (Kashparov et al. 2003) and from } \sim 6\times10^{15} \text{ Bq of Chernobyl-derived } ^{241}\text{Pu (UNSCEAR 2000 Annex J), } 1.3\times10^{14} \text{ Bq of } ^{241}\text{Am has ingrown until 2009. In addition to these two sources, high amounts of } ^{241}\text{Am and } ^{241}\text{Pu have been discharged from nuclear fuel reprocessing facilities. Due to the constant ingrowth of } ^{241}\text{Am from } ^{241}\text{Pu, the fraction of } ^{241}\text{Am in the environment continues to grow relative to the fraction of } ^{239,240}\text{Pu.}

Americium has been found to be more bioavailable than plutonium in some studies (Paatero and Jaakkola 1998), although there are as many contradictory views. Americium appears typically as Am^{3+} in the environment (Table 1), resembling trivalent lanthanides and rare earth elements in its chemical behaviour.

### 2.3. Curium

Curium is similar to americium in many ways, with +3 as the most typical oxidation state (Table 1). The similar chemical behaviour of curium and americium makes it possible to determine both elements simultaneously, often with a single tracer (^{243}\text{Am}) (Paatero 2000). However, in some studies a minor difference in separation chemistry between Am and Cm has been observed (Ham 1995, Martin and Odell 1997, Rodriguez et al. 1997). The alpha energies of Am isotopes are sufficiently different from those of Cm isotopes, enabling the separation of Am and Cm peaks in an alpha spectrum. However, the alpha energies of ^{243}\text{Cm (5.785 MeV) and } ^{244}\text{Cm (5.805 MeV) are so close to each other that they cannot be separated by conventional alpha spectrometry. Still, } ^{243}\text{Cm (t}_{1/2} = 32 \text{ a) is a minor isotope compared to } ^{242}\text{Cm and } ^{244}\text{Cm (Schneider&Livingston 1984), therefore all } ^{243,244}\text{Cm can be assumed to be } ^{244}\text{Cm only.}

Nuclear fuel reprocessing has been the most important source of curium in the environment. The amount of the most abundant isotope in nature, ^{244}\text{Cm (t}_{1/2} = 18.1 \text{ a),
was insignificant in global nuclear weapons testing fallout (Holm & Persson 1978, Schneider & Livingston 1984). $^{242}\text{Cm}$ ($t_{1/2} = 164$ d) was the dominating alpha emitting nuclide in the Chernobyl fallout (Lancsarcics et al. 1988), $\sim 0.9 \times 10^{15}$ Bq of $^{242}\text{Cm}$ was released in the Chernobyl accident (UNSCEAR 2000, Annex J), but because of its short half-life it has quantitatively decayed to $^{238}\text{Pu}$. The behaviour of curium and activity concentration of curium in different environments is less studied than the corresponding properties of plutonium or americium.

2.4. Neptunium

Neptunium has the same main sources in the environment as the other transuranium nuclides. Nuclear weapons testing, nuclear fuel reprocessing and incidences like the Chernobyl accident have released $^{237}\text{Np}$, $^{241}\text{Am}$ (parent nuclide of $^{237}\text{Np}$) and $^{241}\text{Pu}$ (grandparent nuclide of $^{237}\text{Np}$). Compared to $^{239,240}\text{Pu}$ or $^{241}\text{Am}$, the activity inventory of $^{237}\text{Np}$ is orders of magnitude lower in the environment, but the amount of $^{237}\text{Np}$ is constantly increasing from both the direct $^{237}\text{Np}$ discharges and decay of $^{241}\text{Pu}$ and $^{241}\text{Am}$ to $^{237}\text{Np}$. Beasley et al. (1998) have estimated the globally released amount of $^{237}\text{Np}$ from atmospheric nuclear tests to be $\sim 39 \times 10^{12}$ Bq. The total of $8 \times 10^9$ Bq of $^{237}\text{Np}$ was emitted during the Chernobyl accident (UNSCEAR 2000 Annex J). Additional Chernobyl-derived $^{237}\text{Np}$ will build up from $^{241}\text{Pu}$ (and $^{241}\text{Am}$) released in the Chernobyl accident.

Neptunium has four easily changeable oxidation states, and is an even more redox-sensitive element than plutonium. The most typical valence state in the environment is Np$^{5+}$ (Table 1), existing as a highly soluble NpO$_2^+$ ion. Because of its pentavalent state, neptunium has been found to be more mobile in the environment than plutonium or americium. Due to a very low activity concentration of $^{237}\text{Np}$ in the environment, a long half-life of $^{237}\text{Np}$ and a low specific activity, neptunium has not been as extensively studied as other transuranium nuclides.
3. METHODS FOR DETERMINING TRANSURANIUM NUCLIDES

3.1. The main separation and sample preparation methods for Pu, Am, Cm and Np

3.1.1. Sample decomposition by wet-ashing

The organic and inorganic matrix of environmental samples can be destroyed by dry ashing and/or wet-ashing depending on the matrix and analyzed nuclides. The decomposition time by wet-ashing can vary between 30 minutes and several days, depending on the separation procedure. Wet-ashing can be performed either with a hot plate or with a micro-wave oven. Generally, sample digestion with a micro-wave oven is faster than traditional hot plate wet-ashing and smaller acid volumes are needed, but, on the other hand, only very small sample amounts (a few grams) can be handled in micro-wave ovens.

Concentrated HNO₃ is mainly used for destroying the organic components in the sample in addition to dry ashing and HCl for decomposing inorganic components. *Aqua regia* and other acid mixtures are utilized in sample decomposition as well. The undissolved residue (after HNO₃ and HCl treatments) is silica and other insoluble minerals, which can be digested by HF or by fusion with lithium borate, NaOH, NaOH+Na₂O₂ etc. The acid(s) used for decomposing the sample are chosen according to the sample type and the desired radionuclide fraction for analysis. For example, if the investigated radionuclide(s) is easily extractable at the surface of the particles, leaching of the sample with concentrated HNO₃ and HCl for a few hours is an adequate wet-ashing procedure. However, if the analyzed nuclide(s) is incorporated in the silica matrix, or there is some refractory material in the sample, then a total dissolution of the sample by HF or fusion is necessary. Hydrogen peroxide is often added in the end of wet-ashing for completing the leaching.
3.1.2. Liquid-liquid extraction

Liquid-liquid extraction is also known as solvent extraction. Liquid-liquid extraction can be employed either as a pre-concentration method for actinides or as a separation method for single actinides. Two insoluble phases, organic solvent and normally acidic aqueous solution, form the extraction system and depending on the pH, temperature, organic solvent, acid and the oxidation state of an actinide, the actinide ions form complexes with either phase. The method is fast and simple. The drawback of the method is the organic radioactive waste solution generated during the separation procedure, and problems with phase separation (third phase).

A variety of organic liquid-liquid extraction solutes are used in transuranium separation chemistry. Among the most utilized are HDEHP (di(2-ethylhexyl)ortho-phosphoric acid) (Jia et al. 1989, Ramebäck & Skalberg 1998), TTA (thenoyltrifluoroacetone) (Holm 1981, Holm & Nilsson 1981, Bunzl & Kracke 1987, Choppin 1991, Lindahl et al. 2004), Aliquat 336, TOA (tri-n-octylamine) (Hashimoto et al. 1979, Yu-fu et al. 1990), TIOA (tri-isooctylamine) (Butler 1968), TOPO (triocylphosphine oxide) (Jia et al. 1989, Kalmykov et al. 2004) and TBP (tri-n-butylphosphate), known from the PUREX process. The liquid extraction procedure is often repeated and/or combined with different liquid extraction, ion exchange or extraction chromatography.

3.1.3. Co-precipitation

Co-precipitation is used both as a pre-concentration method for actinides and as a method for preparing alpha counting samples. Lanthanide fluorides, such as LaF₃ (Magnusson & La Chapelle 1948, Lindahl et al. 2004) and NdF₃ (Rao & Cooper 1995), as well as CaC₂O₄ (Bunzl & Kracke 1987, Mietelski et al. 1993) have been extensively used for separating actinides from alkali metals, main part of transition metals, Fe³⁺ and anions disturbing extraction chromatographic separations, sulphate and phosphate. These co-precipitations will also separate tri- and tetravalent actinides from penta- and hexavalent actinides to some extent. Other co-precipitation media for actinides are
Fe(OH)$_3$ (Wong 1971), Nd(OH)$_3$ (La Rosa et al. 2005), MnO$_2$ (Wong et al. 1978, Sidhu 2003) and BiPO$_4$, the procedure developed during the Manhattan project by Thompson and Seaborg (Clark et al. 2006). Americium and plutonium have been co-precipitated with CaF$_2$ before separation by UTEVA® and TRU® resins (Varga et al. 2007). Co-precipitation of actinides especially with NdF$_3$ or CeF$_3$ is a common method for making the alpha preparate (Hindman 1983, Sill 1987) as an alternative to electrodeposition.

### 3.1.4. Anion exchange

Organic anion exchange resins like Dowex-1 and BioRad AG 1 are strongly basic, and composed of styrene-divinylbenzene polymers with quaternary amine groups. Hydroxyl or chloride ions attached to amine groups can be replaced by anionic complexes between actinide ion and nitrate or chloride. Anion exchange is a traditional separation method for transuranium nuclides with many remarkable qualities. The separation procedure is simple and can be automated, if needed. In ion exchange the very low quantities of radionuclides can be concentrated from large sample volumes. Ion exchange resins are highly specific and a high decontamination factor is achieved in appropriate circumstances. Still, ion exchange is slow compared to extraction chromatography. An important environmental detail is the production of large volumes of hazardous wastes due to the use of concentrated acid solutions during ion exchange operations. These wastes can even be contaminated with radionuclides.

The control of oxidation state of plutonium and/or neptunium is necessary before and during the ion exchange separation of transuranium nuclides. Plutonium is often stabilized as Pu$^{4+}$ with addition of NaNO$_2$ and heating before loading the sample solution to an exchange column. Plutonium can be reduced to Pu$^{3+}$ with NH$_4$I, hydroxylamine or hydrazine before or during the separation. The countless applications of anion exchange for analyzing transuranium nuclides from environmental samples include separation of Pu and Am from miscellaneous environmental samples (Yamato 1982), Pu and Am+Cm from peat and lichen (Reponen et al. 1993, Paatero et al. 1994, Paatero et al. 1998b), Np from lichen (Lindahl et al. 2004), Np and Pu from seaweed and seawater (Lindahl et al. 2004), Pu and Am from...
2005), Pu from litter (Mietelski and Wąs 1994), Am+Cm from litter and humus layers (Mietelski&Wąs 1997) and Pu and Am+Cm from mushrooms and soil (Mietelski et al. 1993).

3.1.5. Extraction chromatography

Extraction chromatography (EC) was taken to a large-scale utilization in the beginning of 1990s by Horwitz et al. and Eichrom. Extraction chromatography is a combination of liquid-liquid extraction and ion exchange. The grains of porous silica or organic polymer form the inert support, incorporated and surrounded by the stationary phase (Horwitz). The stationary phase is a liquid extractant. Nitric or hydrochloric acid passing the resin beads is the mobile phase. An actinide ion forms a complex with nitrate or chloride and this complex adsorbs to the stationary phase of the resin. Because the strength of retention depends on the acid solution (HNO₃/HCl), acid concentration, additional complexing agents (HF, H₂C₂O₄) and the oxidation state of an actinide ion, the retention and stripping of different nuclides can be controlled (Figure 1). Am+Cm, Th and U are at valence states +3, +4 and +6, respectively, in normal EC procedures, but Pu can be as +3 or +4 and Np as +4 or +5. The oxidation states of Pu and Np are typically adjusted by oxidation of Pu with NaNO₂ (Pu³⁺→Pu⁴⁺) and reduction of Pu (Pu⁴⁺→Pu³⁺) and Np (Np⁵⁺→Np⁴⁺) with ascorbic acid, ferrous sulphamate, hydroquinone, hydrazine, sulphamic acid or TiCl₃.

Extraction chromatography is a rapid and selective separation method for radionuclides, producing less acidic waste solutions than conventional ion exchange chromatography. However, the high costs of the resins compared to ion exchange resins, as well as analytical disturbances caused by the sample matrix (clogging of the column, foaming of the resin, poor recovery, leaking of an analyte to the wrong fraction etc.), where the sample contains high amounts of disturbing matrix components, limits the use of EC. The effect of flow rate is also important, in many EC methods the elution rate can be uncontrolled or gravity-controlled, but in some procedures the flow rate has to be adjusted. Extraction chromatographic resins can be used diversely: for separating and
pre-concentrating radionuclides with single column or sequentially with multiple EC resin columns, or in combination with ion exchange separation.

The extractant in the UTEVA® resin, diamyl, amylyphosphonate (DAAP) adsorbs tetra- and hexavalent actinides (Horwitz et al. 1992). UTEVA® can be used for separating trivalent nuclides Pu+Am as a group from U. UTEVA® is rarely used as a single column, but rather in combination with other EC resins in determination of transuranium nuclides. Instead, a single UTEVA® column can be used for separating Th and U (Pilvioï&Bickel 2000).

TRU® resin has a mixture of carbamoylmethylphosphine oxide derivative (CMPO) and tri-n-butyl phosphate (TBP) as the stationary phase. TRU® retains tri-, tetra and hexavalent actinides (Horwitz et al. 1993) and it can be used, for example, for separating Pu and Am+Cm. Pu, Am and Cm have been separated from nuclear power plant samples with a single TRU® column (Rodriguez et al. 1997). With this type of sample matrix, Fe interfered the separation of Pu and Pu interfered the separation of Am+Cm, which were seen as spectral interferences in LSC and alpha spectrometry. A method for separating Th, U, Np, Pu and Am from aqueous samples with low actinide concentrations consists of two TRU® column separations (Boll et al. 1997). A number of automated EC procedures based on separation with TRU® have been developed. For example, a flow-injection ICP-MS was utilized for separating Am and Pu (Egorov et al. 1998) and the separation of single and grouped actinides has been studied with a later generation SI (sequential injection) ICP-MS (Grate et al. 1999).

TEVA® resin has a trialkylmethylammonium nitrate (Aliquat 336) as the stationary phase (Horwitz et al. 1995). TEVA® retains tetravalent actinides and can be used for separating Pu, Np, Th and Tc. Another important application of TEVA® resin is the separation of Am+Cm from lanthanides. TEVA® is particularly applied in separation of Np from environmental samples for the determination by ICP-MS. Ayranov et al. (2009) used a lithium borate fusion as a pre-treatment before TEVA® separation of Np. There, measurement by double-focusing ICP-MS proved the method to be efficient enough for
separating Np from U. According to the method of Kenna (2002), even three sequential TEVA® column separations are needed for adequate purification of Pu and Np from U before determination by ICP-MS. Np and Pu have been separated simultaneously with TEVA® resin by automated SI ICP-MS equipment (Kim et al. 2004).

Figure 1. Nitric acid and hydrochloric acid dependencies of $k'$ (the resin capacity factor) for selected actinide ions with TRU resin (Horwitz et al. 1993).

Sequential column separations with two or more Eichrom resins together have been developed widely. Mellado et al. (2002) found out that, in sequential UTEVA® + TRU® + Sr resin® separation of Pu, Am, U and Sr from fish, part of U goes with the fraction
containing Pu+Am from UTEVA® column to TRU® column. This was due to the sample matrix. Sidhu (2004) has developed a method for analyzing Pu, Am, Cm and Sr from different environmental samples with Sr® and TRU® resins. Recently a comprehensive study for determining actinides simultaneously with UTEVA® and TRU® resins has been published, aiming eventually for a single-column separation of Am (Cm), Pu, Th, U (Np) by a TRU® column (Vajda et al. 2009).

3.2. Methods for measuring activity and mass concentration

3.2.1. Alpha spectroscopy

Alpha spectroscopy is a traditional method for determining activities of alpha emitting transuranium nuclides. The technique is widely used due to its simplicity, relatively low costs, easy availability and instrumental stability. Nowadays the most utilized alpha detector type is a PIPS (passivated implanted planar silicon) detector, which has an ion layer implanted with an accelerator, producing a rugged detector with a good energy resolution. Long counting times from days to weeks are needed for environmental samples with low activities. One limitation of alpha spectrometry in analysis of Pu isotopes is impossibility to determine \(^{239}\text{Pu}\) and \(^{240}\text{Pu}\) separately due to similar alpha energies of the isotopes.

Good radiochemical purity is essential when determining transuranium nuclides by alpha spectrometry for avoiding spectral interferences. Especially the members of natural uranium series can be problematic if the separation method is not efficient enough, due to typically high concentrations of U, Th, Po etc. in environmental samples and similar alpha energies of Pu, Am, Cm and Np compared to uranium series nuclides. A thin counting source is needed for prevention of self absorption of alpha particles to the sample. A thick alpha counting preparate, often due to lanthanides and iron in the sample, leads to broad and possibly overlapping peaks and peak shift to lower energies in the alpha spectrum. Alpha counting samples can be prepared by various techniques e.g. electrodeposition or co-precipitation of tri- or tetravalent actinides with lanthanide
fluoride. The oxidation state is typically adjusted, if needed, with reducing agent such as TiCl₃.

3.2.2. Liquid scintillation counting (LSC)

Liquid scintillation counting has been widely used for activity determination of beta emitter $^{241}$Pu in environmental samples because the method is fast and easy (Hakanen et al. 1984, Yamamoto et al. 1990, Paatero et al. 1994, Lee&Lee 1999, Mietelski et al. 1999). However, LSC is not a very useful method for determining activities of single alpha emitting nuclides due to relatively poor energy resolution and higher detection limit compared to alpha spectrometry (Yu-fu et al. 1990). The counting efficiency for alpha particles is close to 100% in LSC. For beta particles, the counting efficiency depends on several parameters, such as the beta energy of a nuclide, LSC cocktail and the quench level. LSC has been utilized for measuring X-rays and Auger electrons from nuclides decaying by electron capture, such as $^{55}$Fe. Neptunium has been studied by means of LSC by measuring alpha activity of $^{237}$Np (Aupiais et al. 1999), but no previous data about activity determination of $^{235}$Np by LSC exists.

3.2.3. Inductively coupled plasma-mass spectrometry (ICP-MS)

The introduction of inductively coupled plasma-mass spectrometry to the field of environmental radioactivity studies has opened new possibilities in determination of transuranium nuclides. Double-focusing sector field ICP-MS, often with a multi-collector array, is particularly suitable for measuring low concentrations of long-lived isotopes. The detection limit for actinides has been 0.02 pg/ml with a conventional quadrupole ICP-MS (Muramatsu et al. 2001) and at level of fg/ml or fg/g with sector field ICP-MS (Rodushkin et al. 1999, Pointurier et al. 2004, Varga et al. 2007) depending on the instrument and nuclide; the longer the half-life of the isotope, the lower the detection limit. The detection limits of alpha spectrometry and ICP-MS are comparable, but the clear benefits of ICP-MS are fastness, high sample throughput and the possibility for simultaneous determination of many nuclides from one measurement. Especially in the
case of $^{237}\text{Np}$ the determination by ICP-MS saves time remarkably compared to alpha spectrometry because the counting time by alpha spectrometry can easily be several weeks for sample with low $^{237}\text{Np}$ activity. The costs and availability of the adequately sensitive ICP-MS instrument, as well as the need for experienced maintenance people limit the utilization of the mass spectrometric methods. In addition, ICP-MS instruments are in a certain way unstable compared to alpha spectrometry, and the response of the instrument for the measured elements has to be checked by measuring standard solutions during every sample run. The radiochemical purity of a sample is even more essential with ICP-MS than with alpha spectroscopy, in particular, $^{238}\text{U}$ and its hydrides cause isobaric interference in the determination of Np and Pu. Furthermore, $^{238}\text{Pu}$ can not be determined by ICP-MS due to continuous presence of $^{238}\text{U}$ despite of all efforts for removing uranium from samples.

It should be noted that samples are consumed during ICP-MS analysis, whereas with alpha spectrometry it is possible after measurement to improve sample purification and/or re-measure the samples, if needed. Therefore, alpha spectrometry has an advantage of being a more non-destructive method compared to ICP-MS, which can be an important issue if the environmental samples investigated are unique. It has been concluded that ICP-MS cannot totally replace alpha spectrometry, but rather mass spectrometry and radiometric methods are complementary determination methods for radionuclides (Varga et al. 2007, Hou&Roos 2008, Ayranov et al. 2009).

4. EXPERIMENTAL

4.1. Samples

4.1.1. Air filter samples from Kazakhstan

Kurchatov (50.8 °N, 78.5 °E), 70 km northeast of the Experimental Field, was chosen for the sampling site due to its location near the former Semipalatinsk nuclear test site. Weekly air filter samples were collected at Kurchatov during almost one year (from week
14/2000 to week 9/2001) and later in more dusty conditions in Astana (51.2 °N, 71.4 °E) for three months (from week 15/2001 to week 33/2001). The aerosol samples were collected by the methods developed for Wide Area Environmental Sampling (WAES) in Finland (Valmari et al. 2002). The weekly sampled air amount at Kazakhstan was about 25000 m³. Sample filters were weighed before and after sampling to determine the weight of solid material collected onto the filter. Filters used in the Kazakhstan field trial were made of polyvinyl chloride, Petrianov FPP-15-1.5.

4.1.2. Air filter samples from Sodankylä

Daily aerosol samples were collected by filter sampling at the Sodankylä meteorological observatory (67°22’N, 26°39’E, $h = 179$ m above sea level) of Finnish Meteorological Institute (FMI). The air filters (Whatman 42) had an effective filtering area of 269 cm², the air flow rate was approximately 20.4 m³ h⁻¹ and the filtered air volume was typically 490 m³. After the decay of $^{222}$Rn to $^{210}$Pb and $^{220}$Rn to stable lead within five days, the total beta activities of the aerosol samples were measured in the FMI’s laboratory. Filter halves from year 1963 were retrieved from the sample archive, and analysed with HPGe gamma spectrometry to determine $^{137}$Cs. The daily air filter halves were combined to 176 samples each covering 1-3 days.

4.1.3. Peat samples

The Finnish National Public Health Institute collected 62 peat samples from commercially utilized peatlands on 12-14 May, 1986. An unknown portion of nuclear test fallout radionuclides had been removed from the peat material during the peat production before sampling. The sampling areas had been untouched since the peat harvesting season of 1985. A detailed description of the peat sampling procedure and preliminary results of gamma spectrometric analysis have been published by Jantunen et al. (1987). In addition to peat samples, some lichen samples from northern Finland were utilized, because lichen is known to be an excellent deposition indicator for transuranium nuclides (Tuominen&Jaakkola 1973, Paatero et al. 1998b, Lindahl et al. 2004).
4.2. Separation of $^{239+240}$Pu and $^{238}$U from Kazakhstan air filters by UTEVA® and TRU® resins

Air filters from Kazakhstan were ashed overnight at 400 °C. $^{242}$Pu and $^{236}$U tracers were added as yield determinants and the samples were wet-ashed with HNO$_3$. After filtration, evaporation and dissolution of the residue, plutonium and uranium were separated from each other, from other radionuclides and matrix with Eichrom’s UTEVA® and TRU® extraction chromatography resins (Fig. 2). Before column separation, plutonium was reduced to Pu$^{3+}$ with ascorbic acid and ferrous sulphamate solution. The plutonium-containing fraction was eluted from the UTEVA® column with the load solution and then it was loaded to a TRU® column to separate plutonium from americium and other trivalent nuclides. Uranium fraction was eluted from UTEVA® column and it was stored for later use. Plutonium was eluted from TRU® with 0.02 M TiCl$_3$ + 4 M HCl and it was co-precipitated with 70 μg of NdF$_3$ (50 μg of Nd) according to the method of Hindman (1983). The solution was filtered through a membrane filter for preparing the alpha counting sample.
4.3. Separation of $^{239+240}$Pu, $^{241}$Am and $^{90}$Sr from Sodankylä air filters by TRU® and Sr® resins

Plutonium, americium and strontium were separated from air filters with Eichrom’s TRU® resin and Sr-resin® (Fig. 3). Americium was analyzed from air filters for determining $^{241}$Pu by ingrowth of $^{241}$Am since sampling time. The separation method was modified and combined from methods used by Spry et al. (2000), Nygren et al. (2001) and Sidhu (2004). After ashing $^{242}$Pu and $^{243}$Am tracers and the strontium carrier were
added to the residue. The samples were wet-ashed with HNO₃ and HCl. After evaporation the residue was dissolved in 10-15 ml of 3 M HNO₃ + 0.1 M sulphamic acid – 0.1 M ascorbic acid – 0.5 M Al(NO₃)₃. Plutonium, americium and strontium were first separated from each other by TRU® column. Strontium was collected from the column with the load solution. Americium was eluted from TRU® column with 9 M and 4 M HCl and plutonium was eluted with 4 M HCl + 0.02 M TiCl₃. Americium and plutonium were co-precipitated with 70 μg of NdF₃ onto a membrane filter for alpha counting (Hindman 1983).

The strontium fraction was further purified from ⁹⁰Y, the daughter nuclide of ⁹⁰Sr, with Sr-resin®. The strontium fractions eluted from Sr-resin® column were stored for two weeks to allow the ingrowth of ⁹⁰Y in the samples. The activity of ⁹⁰Sr was determined by measuring the activity of ⁹⁰Y by liquid scintillation counting and the recovery of strontium was determined by ion chromatography III (Salminen et al. 2008).
Sample
+ tracers ($^{242}$Pu, $^{243}$Am) and Sr-carrier (10 mg)
Ashing 400 °C
wet-ashing (30 ml conc. HNO₃ + 10 ml HCl)
Evaporation
Dissolving the residue in 10-15 ml 3 M HNO₃ – 0.1 M sulphamic acid – 0.1 M ascorbic acid – 0.5 M Al(NO₃)₃
($\text{Pu}^{4+} \rightarrow \text{Pu}^{3+}$)

TRU (conditioned with 5 ml 3 M HNO₃)

Sr-resin (conditioned with 5 ml 3 M HNO₃)

sample loading
rinse with 10 ml 3 M HNO₃
wash 10 ml 3 M HNO₃ + 0.1 M NaNO₂
($\text{Pu}^{3+} \rightarrow \text{Pu}^{4+}$)

evoke Sr with 15 ml 0.05 M HNO₃
wash 5 ml 3 M HNO₃ + 0.02 M TiCl₃

Am evaporation
evaporation with
aqua regia and conc. HNO₃
dissolution in 1 M HNO₃
cooprecipitation with NdF₃
measurement of alpha activity

evoke Pu with 10 ml 4 M HCl + 0.02 M TiCl₃

Pu
cooprecipitation with NdF₃
measurement of alpha activity

Sr after two weeks activity measurement
of $^{90}$Y by Quantulus 1220 (Cherenkov counting mode)

Figure 3. The method used for separating plutonium, americium and strontium from air filters collected at Sodankylä (III).

4.4. Separation of $^{241}$Am+$^{244}$Cm from peat by TRU® and TEVA® resins

20-130 g of dried and homogenized peat was used in analysis. The separation procedure for plutonium, americium and curium in peat and lichen samples had been previously started with the addition of $^{242}$Pu and $^{243}$Am tracers (Reponen et al. 1993). Am and Cm have been proven to behave similarly during the separation procedure (Paatero 2000) and therefore $^{243}$Am was used as a tracer for both $^{241}$Am and the Cm isotopes. Pu, Am and Cm were separated from the sample matrix and other alpha emitting nuclides by ashing, wet-ashing, co-precipitations and anion exchange (IV Fig. 1, Paatero 2000). The fraction in 8 M HNO₃ containing Am and Cm was stored in plastic bottles for further purification of Am and Cm.
After 12 years, Am+Cm fractions from earlier plutonium separations (Reponen et al. 1993, Paatero et al. 1994) were analyzed and Am and Cm were separated from interfering nuclides (lanthanides, iron, and traces of thorium and polonium) by extraction chromatography (Fig. 4). The separation method was slightly modified from the method by Outola (2003). The fractions in 8 M HNO₃ were first evaporated and diluted, then Am and Cm were co-precipitated as oxalates. The precipitate was calcinated and the CaCO₃/CaO ash containing Am and Cm was dissolved into 1 M Al(NO₃)₃ + 3 M HNO₃-solution for separating Am and Cm from other interfering nuclides with TRU® and TEVA® resins (Eichrom Technologies). Am and Cm were first separated from tetra- and hexavalent impurities (traces of Th, U and Pu) in a TRU® column. The Am and Cm fraction was collected and evaporated, and the residue was dissolved into 2 M NH₄SCN + 0.1 M formic acid. The solution was loaded onto a TEVA® column to purify Am and Cm from lanthanides. The collected fraction containing Am and Cm was evaporated and treated with concentrated acids to decompose the remains of resin, and finally Am and Cm were co-precipitated with 50 μg of Nd as trifluorides (Hindman 1983). The NdF₃-precipitate was filtered on a membrane filter for alpha counting.

4.5. Separation of ²³⁷Np from peat by TEVA® resin

20-100 g of dried and homogenized peat sample was ashed at 400 °C. A ²³⁵Np tracer solution was added to the samples for recovery determination before wet-ashing with concentrated acids. After wet-ashing the solution was filtrated and then evaporated to a smaller volume. Neptunium was co-precipitated with calcium oxalate for reducing the concentration of disturbing elements (e.g. iron, aluminum and phosphate ions) in samples before extraction chromatography. Neptunium was reduced to Np⁴⁺ with ascorbic acid before co-precipitation for precipitating neptunium quantitatively. The oxalate precipitate containing Np was calcined at 600 °C. The CaCO₃/CaO ash was dissolved with 3M HNO₃+1M Al(NO₃)₃ solution for a TEVA® column separation by the method of Eichrom (2005) (Figure 5). Np was reduced to Np⁴⁺ with ferrous sulphamate solution and ascorbic acid before loading sample to the column. Possibly interfering elements uranium, plutonium, americium, thorium and polonium were eluted first, and finally neptunium...
was eluted with 10 ml of 0.02 M HNO₃ + 0.02 M HF. 1 ml of the neptunium fraction was used for recovery determination by liquid scintillation counting. The rest of the neptunium fraction was used for measuring ²³⁷⁴Np by HR-ICP-MS. V

Figure 4. Am and Cm separation from peat samples with TRU and TEVA resins (IV).
20-100 g peat (dried, homogenised)

**Ash** 400°C 1-3 days, add $^{235}$Np-tracer

**Wet-ash**: 30-100 ml conc. HNO$_3$ 6h + 10-30 ml conc. HCl 6h, filtration (Whatman GF/A)

Undissolved residue

Solution

Evaporation -> 30ml

Dilute with H$_2$O to 700 ml, add 200 mg Ca$^{2+}$ + 5-10 g ascorbic acid + 10 g oxalic acid

Solution

Add 25 % NH$_3$ until pH 1.5-2, heating (t<50°C to not destroy ascorbic acid), filtration (Whatman 42 Ashless)

Precipitate

Evaporate, dissolve the residue to 10-20 ml 3M HNO$_3$+1M Al(NO$_3$)$_3$, add 2 ml 0.6 M Fe-sulphamate solution and 150-200 mg ascorbic acid (Pu$^{4+}$->Pu$^{3+}$ and Np$^{5+}$->Np$^{4+}$)

Load sample solution, wash the beaker with 10 ml 2.5 M HNO$_3$+ 0.1 M Fe-sulphamate (add to column), wash column with 25 ml 2.5 M HNO$_3$ + 0.1 M Fe-sulphamate (U, Pu$^{3+}$, Am)

Wash with 20 ml 9 M HCl and 5 ml 6 M HCl (Th and Po)

Elute Np with 10 ml 0.02 M HNO$_3$ + 0.02 M HF

Evaporate and dissolve to 5-10 ml 5 % HNO$_3$ (s. p.)

1/10 of Np-fraction for yield determination by LSC

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Figure 5. Separation scheme for the determination of neptunium from peat and lichen samples. The recommended second TEVA separation is marked with a dash line to the original scheme (V).

### 4.6. Determination of $^{239+240}$Pu and $^{241}$Am$^{+244}$Cm by alpha spectroscopy

Activities of $^{238}$Pu, $^{239+240}$Pu and $^{241}$Am in membrane filters containing NdF$_3$ precipitates were measured by model A450 PIPS alpha detectors (nominal resolution 20 keV for 5.486 MeV peak of $^{241}$Am) using counting times of between five and seven days (Fig. 6) L,II,III,IV. A typical counting time was 10 000 minutes. With this counting time the detection limit $D_L$ (Currie 1968) was 0.05 mBq/air filter sample for $^{238}$Pu and $^{239+240}$Pu L,II,III and 0.90 mBq/kg for $^{241}$Am and $^{244}$Cm IV.
Figure 6. A typical alpha spectrum of Am and Cm in peat samples (IV). The counting time was 10450 minutes.

Detection limit $D_L$ is calculated with Currie’s formula (Currie 1968)

$$D_L = \frac{2.71 + 4.66\sigma_B}{T \cdot E},$$  \hspace{1cm} (1)

where $\sigma$ is standard deviation of the background, $T$ is the counting time and $E$ is the counting efficiency. In the case of $^{241}$Am, the $^{243}$Am tracer often contains $^{241}$Am as impurity due to the tracer preparation process. This results in extra counts at the alpha peak region of $^{241}$Am in the spectra of blank and real americium samples, elevating the detection limit of $^{241}$Am. Therefore, the standard deviation of the blank sample, containing $^{241}$Am due to $^{243}$Am tracer, has been used for calculating the detection limit of $^{241}$Am instead of the standard deviation of the background.
4.7. Activity determination of $^{241}$Pu and $^{235}$Np by LSC

4.7.1. $^{241}$Pu in NdF$_3$ precipitates

After alpha counting, the membrane filter containing Pu isotopes was wetted with 0.6 M H$_3$BO$_3$ + 0.1 M HCl and liquid scintillation cocktail (Optiphase HiSafe 3 or Ultima Gold LLT) was added. Activity of the beta active isotope of plutonium, $^{241}$Pu, was measured with a low-level liquid scintillation counter Quantulus 1220 (Wallac Ltd) using $\alpha/\beta$ separation and counting time of 600 min. For $^{241}$Pu, at a counting time of 600 min, the detection limit (DL) is 8 mBq (Currie 1968). The efficiency calibration of Quantulus 1220 for $^{241}$Pu was performed using $^3$H standard; the energy of $^3$H ($E_{\text{max}}$ 18.6 keV) is sufficiently similar to the energy of $^{241}$Pu ($E_{\text{max}}$ 20.8 keV) for efficiency calibration (Yamamoto et al. 1990).

4.7.2. $^{235}$Np in fraction from TEVA® separation

1 ml of Np fraction (total volume of 10 ml) was transferred to a plastic scintillation vial and 20 ml of scintillation cocktail OptiPhase HiSafe 3 was added. The activity concentration of $^{235}$Np was determined by measuring L-shell transitions of the low-energy X-rays and Auger electrons (12–21 keV) from $^{235}$Np with the liquid scintillation counter Quantulus 1220 (Wallac Ltd.) for 10 hours (Figure 7).

The efficiency of Quantulus 1220 for $^{235}$Np was determined with both $^3$H ($E_{\beta_{\text{max}}} = 18.6$ keV) and $^{55}$Fe. $^{55}$Fe decays by electron capture, emitting both X-rays and Auger electrons at the energy range of 0.6–6.5 keV. The counting efficiency was 29.8(±0.1)% for $^3$H and 33(±1)% for $^{55}$Fe, in other words, being approximately the same for both the low-energy beta particles and the X-rays/Auger electrons. It was decided to use $^{55}$Fe in efficiency calibration of $^{235}$Np samples due to the similar decay mode of $^{55}$Fe and $^{235}$Np. $^3$H is not necessarily the most suitable nuclide for efficiency calibration when measuring low-energy X-rays and Auger electrons from electron capture (Ceccatelli and Felice 1999).
4.8. Mass concentration measurement of $^{237}\text{Np}$ by ICP-MS

The samples in 5% HNO$_3$ (supra pure) were measured with high-resolution ICP-MS (Micromass Plasma Trace 2) with a double-focusing reverse Nier-Johnson geometry, an ultrasonic nebulizer as an injector and a peristaltic pump for transferring the sample solution to the nebulizer $^V$. $^{242}\text{Pu}$ standard solution was added to every sample as a yield tracer for mass concentration measurement of $^{237}\text{Np}$. Solution blanks (5% supra pure HNO$_3$) were analyzed between samples during ICP-MS-measurements. The counts from solution blanks were subtracted from sample counts. The limit of detection $D_L$ for $^{237}\text{Np}$ by HR-ICP-MS was ca. 10 fg. MDA of a single sample was higher than the instrumental detection limit for the sample because of the extra $^{237}\text{Np}$ introduced in the sample within the tracer solution.

![Graph](image.png)

Figure 7. Spectra of $^{235}\text{Np}$ tracer ($A = 0.73$ Bq) and similarly prepared background sample measured by Quantulus 1220 ($^V$). The peak at energy region of 12–21 keV (channels 1-300) consists of L-shell transitions of $^{235}\text{Np}$ producing X-ray and Auger electron radiation.
5. RESULTS AND DISCUSSION

5.1. Reliability and functionality of the separation methods

5.1.1. The method for separating plutonium and uranium from Kazakhstan air filters

The recovery for plutonium varied between 40% and 100%, the median value being 78%, with air filters from Kazakhstan. Uranium recovery was 46–100%. The concentrations of polonium and thorium in air are usually several orders of magnitude higher than the concentration of plutonium. At the beginning of the Kazakhstan field trial the ammonium oxalate solution was used for eluting plutonium from the TRU® column. However, in many samples, $^{210}$Po disturbed the $^{239}$Pu determination and the method needed modification. Two methods were tested for removing polonium from plutonium fraction (1, Table 1). First, spontaneous electrodeposition of polonium onto crushed silver from hydrochloric acid solution was used for removing polonium before the separation of plutonium with UTEVA® and TRU®. Secondly, plutonium was eluted from the TRU® column with TiCl$_3$ + HCl solution instead of ammonium oxalate solution. Both methods gave plutonium fraction free of polonium, but the TiCl$_3$ elution was utilized with air filters, because it produced greater yields than crushed silver handling and because silver handling is more laborious.

The presence of thorium in plutonium samples results in overestimated activity of $^{238}$Pu and further erroneously high $^{238}$Pu/$^{239+240}$Pu activity ratio, since the alpha energies of $^{228}$Th and $^{238}$Pu are similar (5.423 MeV and 5.499 MeV, respectively). The possible incomplete separation of thorium from plutonium was investigated in three ways. Two plutonium alpha samples with high $^{238}$Pu/$^{239+240}$Pu ratio were measured again one month after the extraction chromatographic separation, in order to observe the possible ingrowth of $^{224}$Ra (half-life 3.66 d) from mother nuclide $^{228}$Th (half-life 1.91 a). However, $^{224}$Ra was not seen in the plutonium spectrum. Finally, the thorium tracer experiment and analyses of lichen and reference sediment, with known $^{238}$Pu/$^{239+240}$Pu activity ratios,
proved that the UTEVA® + TRU® method separates thorium from plutonium efficiently and the presence of thorium can be ruled out as the reason for high $^{238}\text{Pu}^{239+240}\text{Pu}$ ratios.¹

Filter blank and reagent blank analyses were performed for finding possible contamination from reagents, glassware and cross-contamination between samples during the analytical procedure. In plutonium spectra of the blank samples there were counts only from the tracer $^{242}\text{Pu}$. Two samples of reference sediment IAEA-135 were analyzed to confirm the reliability of the separation procedure. All the results for $^{238}\text{Pu}$, $^{239+240}\text{Pu}$, $^{234}\text{U}$ and $^{238}\text{U}$ agreed well with the recommended values for IAEA-135 sediment (I, Table 2).

5.1.2. The method for separating plutonium, americium and strontium from Sodankylä air filters

The median recovery values for plutonium, americium and strontium were 90%, 65% and 49%, respectively, with the method used for analyzing air filters from Sodankylä. The developed method was tested with standard reference sediment IAEA-135 before analyzing the air filter samples. Activity concentrations of $^{238}\text{Pu}$ and $^{239+240}\text{Pu}$ in IAEA-135 sediment corresponded well the recommended values by IAEA (III, Table 1). However, activity concentrations of $^{241}\text{Am}$ in IAEA-135 samples exceeded the confidence interval given by IAEA, probably due to ingrowth of $^{241}\text{Am}$ from $^{241}\text{Pu}$ in the sediment since the reference date of the sediment (1 January 1992).

Filter blank samples were analyzed to detect possible contamination from reagents, glassware and other sources during the analytical procedure. None or only few counts were observed in alpha spectra of plutonium and americium blank samples in the energy regions of $^{238}\text{Pu}$, $^{239+240}\text{Pu}$ and $^{241}\text{Am}$.

The separation method used for Sodankylä air filter samples produced plutonium samples of sufficient purity for alpha spectrometry, but if the plutonium samples are to be measured by mass spectrometry, an extra U/Pu-separation is recommendable III.
5.1.3. The method for separating americium and curium from peat samples

The separation method for americium and curium based on extraction chromatography is one or two working days shorter, and more user-friendly with less steps, compared to conventional separation methods for Am and Cm by anion exchange. The median recovery of $^{243}$Am in peat samples was 59\%, possibly it could have been higher without the long storage time, twelve years, of sample solutions in plastic bottles.

The functionality of the TRU® + TEVA® method for peat samples was tested with the certified reference material IAEA-135 sediment before analyzing the real samples. Reagent blank samples were analyzed to investigate possible contamination during the Am and Cm purification process. $^{243}$Am tracer solutions often contain some $^{241}$Am as an impurity. The few counts within the region of the $^{241}$Am alpha peak in the alpha spectra of Am blank samples were then subtracted from the $^{241}$Am peak counts in the spectra of actual samples. $^{243}$Am tracers often contain also $^{244}$Cm, but in the spectra of blank samples there were no counts from $^{244}$Cm.

Am and Cm were expected to behave similarly during the separation and purification process according to earlier study (Paatero 2000). However, in some studies the different behaviour of Am and Cm in TRU® separation has been observed, where the recovery was lower for Cm than for Am (Ham 1995, Martin&Odell 1997, Rodriguez et al. 1997). An overestimated recovery of Cm would result in underestimated activity of Cm in a sample. Therefore, especially in routine analysis of samples, a separate Cm tracer might be useful. However, with these peat samples the most important uncertainty sources in analyses were the inhomogeneity of samples and low activity concentrations of Am and Cm. The peat samples had varying composition with possibly some hot particles deposited from the Chernobyl accident. The low activity concentrations of Am and Cm cause high statistical errors of radioactivity in alpha counting.

Peaks in americium alpha spectra of some peat samples were not well-resolved. A probable reason for this was the excess amount of lanthanides on the co-precipitated
alpha counting preparate. In those cases the second TEVA® separation was performed for extra purification of Am from lanthanides. The alpha spectra of once more co-precipitated samples were reasonable with adequately separated americium peaks after the second TEVA® separation. Electrodeposition could be the better alpha counting sample preparation method for americium than co-precipitation, if the original sample matrix, such as many peat types, has high lanthanide concentrations.

5.1.4. The method for separating neptunium from peat samples

At the moment, there is no certified reference material available for $^{237}$Np, although at least reference sediments IAEA-135, IAEA-384 and SRM-4350B have been analyzed for determining activity concentration of $^{237}$Np in reference materials (Kenna 2002, Kim et al. 2004). The separation method was first tested with tracer experiments, where the radiochemical recovery of $^{235}$Np was close to 100%. With actual peat samples the recovery of Np was 18–100%, the median value was 79%.

Two incongruous limitations, large sample mass and only sparingly added $^{235}$Np tracer, together make the separation procedure of neptunium challenging. Large sample mass is needed for the analysis due to the low concentration of $^{237}$Np in environmental samples. On the other hand, peat often contains massive bulk of iron and other disturbing matrices possibly causing problems during the analytical procedure. However, the $^{235}$Np tracer amount added to the sample had to be as low as possible due to $^{237}$Np impurity in the tracer solution. Thus, a high radiochemical recovery is needed in order to detect the fairly low activity of $^{235}$Np tracer by LSC.

Determination of $^{237}$Np by mass spectrometry is interfered by $^{238}$U, if the sample has high uranium concentration, as is often the case with environmental samples. $^{238}$U peak tails partly or totally over $^{237}$Np peak in mass spectrum, if the Np/U separation has not been efficient enough. The analyzed twelve peat and lichen samples had clearly separate $^{237}$Np and $^{238}$U peaks in mass spectra, approving the separation method and decontamination of neptunium from uranium to be sufficient. However, with some later analyzed peat
samples with higher uranium concentration, interference from $^{238}$U was observed. Therefore, a second TEVA® column separation is strongly recommended for minimizing uranium concentration in the sample before ICP-MS measurement of $^{237}$Np.

Besides interfering with ICP-MS measurements of $^{237}$Np, $^{238}$U also disturbs the determination of $^{235}$Np by LSC. Like $^{235}$Np, $^{238}$U and its daughter radioisotopes (e.g. $^{234}$Th and $^{234m}$Pa) emit low-energy X-rays and Auger electrons. If uranium and its daughters are present in a sample in substantial amounts, the low-energy region peak in the LSC spectrum is piled up from X-rays and Auger electrons of Np, U and its daughters, due to the poor energy resolution of LSC. This would lead to an erroneous value for neptunium recovery. On the other hand, if the sample contains measurable activity of uranium, an alpha peak in the high-energy region of a LSC spectrum would exist, as uranium isotopes decay mainly by alpha emission. There were no marks from other nuclides than $^{235}$Np in the LSC spectra of peat and lichen samples, due to the very low specific activity of $^{238}$U and the successful separation of uranium and its daughter nuclides from neptunium$^\text{V}$.

An additional factor causing problems with the method development was the relatively high background count rate of scintillation cocktail Optiphase HiSafe 3 (1.5 cpm at spectrum channels 1–300). Some other liquid scintillation cocktail with lower background count rate, especially at the low-energy region of LSC spectrum, and ultra-low level vials, are essential for enabling the detection of low $^{235}$Np activities, as well as contamination from $^{238}$U.

5.2. Plutonium in air at Kurchatov

The activity concentrations of $^{238}$Pu and $^{239+240}$Pu in air filters of Kurchatov were $7.2(\pm 2.9) – 960(\pm 51)$ nBq/m$^3$ (median value 34 nBq/m$^3$) and $13.4(\pm 4.2) – 2490(\pm 90)$ nBq/m$^3$ (median value 98 nBq/m$^3$), respectively$^\text{I,II}$. Expressed per mass of collected dust, the corresponding activities were $0.198(\pm 0.085) – 16.42(\pm 0.87)$ Bq/kg for $^{238}$Pu and $0.67(\pm 0.15) – 228(\pm 7)$ Bq/kg for $^{239+240}$Pu (I, Figs. 4 and 5). The median values for
activities were 1.26 Bq/kg for $^{238}$Pu and 3.25 Bq/kg for $^{239+240}$Pu. The wide variation in activity concentrations of plutonium was caused by changing dust composition and dust amount on the filter, depending on varying wind directions and wind velocity. Hot particles, solid fragments coated by radioactive material, in the dust have probably resulted in the highest plutonium activity concentrations. For comparison, $^{239+240}$Pu activity concentration in surface air has been 1.4 nBq/m$^3$ in Germany (Rosner&Winkler 2001) and 33 nBq/m$^3$ in USA (Pan&Stevenson 1996) during 1990s. In the Semipalatinsk area, $^{239+240}$Pu activity concentration in the surface soil has been reported to be $1.45(\pm0.07) - 202(\pm6)$ Bq/kg (Voigt et al. 2001), being at the same magnitude as our results.

Activity ratio $^{238}$Pu/$^{239+240}$Pu varied from $0.011(\pm0.003)$ to $2.42(\pm0.43)$ (Fig. 8). The variation in activity ratio, as well as in activity concentration, was due to variations in the resuspension conditions, source areas and atmospheric transport and dispersion conditions. It is very difficult to estimate the source of plutonium contamination in samples collected near Semipalatinsk, because there has been conducted over 120 atmospheric and over 300 underground nuclear tests. In addition to nuclear weapons testing, other nuclear activities have also been performed at the Semipalatinsk area. Thus, plutonium sampled with the dust on air filter is a mixture from various sources with individual isotope ratios.

![Figure 8. $^{238}$Pu / $^{239+240}$Pu activity ratio in air filter samples from Kurchatov (I).](image)
The two air samplers K1 and K2P were identical except that sampler K2P had an impactor-type pre-separation unit that removed particles of cut-diameter over 13 μm with 50% efficiency. There was no clear difference between the $^{239+240}$Pu activities in samples collected with the two air samplers (I, Fig. 4), leading to a conclusion that plutonium is attached to particles under 13 μm.

The samples from Astana had lower plutonium activity concentration than samples from Kurchatov due to the increased distance from the Semipalatinsk test site. Activity concentrations of $^{238}$Pu and $^{239+240}$Pu were $4.6(±2.3) – 23(±6)$ nBq/m$^3$ and $5.0(±1.4) – 131(±32)$ nBq/m$^3$, respectively.$^1$

5.3. Plutonium in air at Sodankylä

Activity concentrations of $^{238}$Pu, $^{239+240}$Pu and $^{241}$Am ($^{241}$Pu) in air of Sodankylä were elevated during spring and summer in 1963 (Figure 9, III, Figs. 2, 3 and 5). This spring maximum was observed with the total beta activity as well (Helminen&Mattson 1964) and it is caused by the seasonally enhanced transport of radionuclides from the stratosphere down to the troposphere. Activity concentrations of $^{238}$Pu and $^{239+240}$Pu (Fig. 9) were $<0.1 – 3.6(±0.5)$ μBq/m$^3$ and $0.4(±0.1) – 95(±3)$ μBq/m$^3$, respectively, during 1963. The activity concentrations of $^{239+240}$Pu in Sodankylä and Helsinki, northern and southern Finland, were found to be at the same level$^{III}$ (Jaakkola et al. 1979), on the contrary to earlier assumptions based on the 1/3 lower precipitation amount in northern Finland compared to southern Finland. The atmospheric plutonium activity concentration in Finland has been at the same magnitude as in Hanford Nuclear Reservation, Richland, USA ($^{239+240}$Pu 11 μBq/m$^3$ and $^{238}$Pu 0.6 μBq/m$^3$) (Pan&Stevenson 1996) and at Chilton, UK ($^{239+240}$Pu 26 μBq/m$^3$) (Cambray et al. 1974) during 1963.

The $^{238}$Pu/$^{239+240}$Pu activity ratio in air filters of Sodankylä was $0.014(± 0.003) – 0.32(± 0.11)$. Most of the samples had a $^{238}$Pu/$^{239+240}$Pu ratio of $~0.03$ (III, Fig. 4), corresponding to the activity ratio of 0.024 in global nuclear testing fallout before 1964 and SNAP-9A accident (Hardy et al. 1973). The high activity ratios in the middle of June 1963 are
caused by very low plutonium concentrations resulting in high statistical errors of activity. Some very low activity ratio values could indicate weapons-grade plutonium, but this could not be confirmed by the $^{241}\text{Pu}/^{239+240}\text{Pu}$ activity ratio.

The activity of $^{241}\text{Pu}$ was determined by the ingrowth of $^{241}\text{Am}$ in samples. The activity concentration of $^{241}\text{Pu}$ was $< 16 – 1730(\pm 70) \mu\text{Bq/m}^3$ in 1963. The $^{241}\text{Pu}/^{239+240}\text{Pu}$ activity ratio varied between $7.6(\pm 1.2)$ and $41(\pm 8)$ (decay-corrected to year 1963), the median value of 18 corresponding to the reported value for global fallout plutonium, 16 (Holm 1995). Some higher values for the ratio are probably due to nuclear tests conducted by USA in 1950s, producing higher $^{241}\text{Pu}/^{239+240}\text{Pu}$ ratio than later tests by USSR (Koide&Goldberg 1981). The $^{241}\text{Pu}/^{239+240}\text{Pu}$ activity ratio for weapons-grade plutonium has been $0.75–7.5$ (Irlweck&Hrnecek 1999). Some low values for $^{241}\text{Pu}/^{239+240}\text{Pu}$ ratio in samples of Sodankylä could indicate weapons-grade plutonium, but the low $^{238}\text{Pu}/^{239+240}\text{Pu}$ and $^{241}\text{Pu}/^{239+240}\text{Pu}$ ratios did not coincide for the same days.
The decrease of $^{238}\text{Pu} / ^{239+240}\text{Pu}$ ratio was observed during 1963, while the $^{241}\text{Pu} / ^{239+240}\text{Pu}$ ratio increased (III, Fig. 7). The ratio of total beta activity concentration (Helminen & Mattson 1964) to $^{239+240}\text{Pu}$ decreased continuously as the fission products decayed during 1963 (III, Fig. 8). The two different decay curves in Figure 8 of publication III are due to change in the source of airborne $^{239+240}\text{Pu}$ and total beta activities. In January-March 1963 the artificial radioactivity in arctic troposphere was originated from the debris of nuclear tests made at the Novaya Zemlya on Christmas 1962, just before the partial nuclear test ban treaty started. The fission product mixture was relatively fresh in winter due to minimal atmospheric convection and precipitation (Paatero et al. 2003). In spring the exchange of air masses between stratosphere and troposphere increased, bringing an older mixture of radionuclides to troposphere and further down to the surface air.

5.4. Americium and curium in peat

The total activity concentration of $^{241}\text{Am}$ in peat samples was $0.011 (\pm 0.002) - 0.81 (\pm 0.03)$ Bq/kg corresponding to $0.059 (\pm 0.011) - 6.27 (\pm 0.22)$ Bq/m² on 1.5.1986 IV. In Poland the activity of $^{241}\text{Am}$ in litters, collected in 1991, varied between 0.18 and 5.04 Bq/kg (1.5.1986) (Mietelski & Was, 1997), the activities being higher in Poland than in Finland. The highest value was obtained from so-called “Chernobyl plutonium area” in northeast Poland. The total $^{241}\text{Am} / ^{239+240}\text{Pu}$ ratio in peat samples was 0.17–1.88 (1.5.1986). The ratio has such a high maximum value because the ingrowth from $^{241}\text{Pu}$ was included in the total activity value for $^{241}\text{Am}$.

The total $^{241}\text{Am}$ activity in peat, before 1990 and the separation of Am and Pu, originates from four different sources: 1) direct $^{241}\text{Am}$ deposition from atmospheric nuclear tests in the 1950-1960s, 2) $^{241}\text{Am}$ ingrown from $^{241}\text{Pu}$ deposited from nuclear tests, 3) direct $^{241}\text{Am}$ deposition from the Chernobyl accident and 4) $^{241}\text{Am}$ ingrown from Chernobyl-derived $^{241}\text{Pu}$. In order to separate the Chernobyl-originated direct $^{241}\text{Am}$ deposition from total $^{241}\text{Am}$ activity, a value of 0.211 for the $^{244}\text{Cm} / ^{241}\text{Am}$ activity ratio in Chernobyl fallout was derived from activity ratio medians $^{244}\text{Cm} / ^{242}\text{Cm} = 0.0053$ (Paatero et al. 1998b), $^{241}\text{Am} / ^{239+240}\text{Pu} = 0.42$ (Paatero et al. 1998b) and $^{242}\text{Cm} / ^{239+240}\text{Pu} = 16.7$ (Paatero et
Therefore, the activity of Chernobyl-derived $^{241}\text{Am}$ is obtained from the equation

$$A (^{241}\text{Am})_{\text{Chernobyl-fallout}} = A (^{244}\text{Cm}) / 0.211$$

Activities of $A (^{241}\text{Am})_{\text{Chernobyl-fallout}}$ and $^{244}\text{Cm}$ are decay-corrected to the reference date of this work, 1.5.1986. The activity concentration of Chernobyl-derived $^{241}\text{Am}$ by Eq. 2 was $0.0024(\pm0.0001) – 1.207(\pm0.042)$ Bq/kg and $0.0115(\pm0.0003) – 9.32(\pm0.33)$ Bq/m² (1.5.1986) (IV, Table 1). Activity concentration of $^{241}\text{Am}$ in deposition samples collected 1.–30.4.1986 in Finland has been reported to be $0.012–0.170$ Bq/m² (Saxén et al. 1987), the values for deposition being much lower than for peat samples. However, the sampling period of Saxén et al. was before the time of maximum Chernobyl deposition, therefore the values might have been higher with a later sampling time.

The activity concentration of $^{244}\text{Cm}$ in peat samples varied between $<0.0005$ and $0.255(\pm0.017)$ Bq/kg of dry weight, which corresponds to deposition values $<0.002 – 1.97(\pm0.13)$ Bq/m² (1.5.1986) (IV, Table 1). Previously determined activity concentration of $^{244}\text{Cm}$ in lichens in Finland has been $0.025$ Bq/m² at most (Paatero et al. 1998b), one tenth of the maximum value of present study. The regional variation in activity concentrations was, however, high in both studies. The activity of $^{244}\text{Cm}$ has been $0–0.31$ Bq/kg (corrected to our reference date 1.5.1986) in litter samples in Poland, collected in 1991 (Mietelski&Wąs, 1997). These values correspond well to our values in Finland, although the activity concentrations in Poland might be even higher if the samples were collected a few years earlier. Compared to Chernobyl-derived plutonium deposition, $^{244}\text{Cm}$ is only a marginal factor in total transuranic radioactivity from the Chernobyl accident to Finland: $^{241}\text{Pu}$ and $^{239+240}\text{Pu}$ activities were $0–412$ Bq/m² (Paatero et al. 1994) and $0–7.71$ Bq/m² (Reponen et al. 1993), respectively, in 1.5.1986. $^{242}\text{Cm}$ was not seen in alpha spectra, but with larger sample mass or earlier Am+Cm purification process it might have been possible to observe the supported $^{242}\text{Cm}$ produced by long-lived $^{242m}\text{Am}$ ($t_{1/2} = 141$ a). The production of supported $^{242}\text{Cm}$ has been previously observed in
Chernobyl-contaminated samples (Mitchell et al. 1998, Holm et al. 2002) and with nuclear fuel reprocessing plants (Mitchell et al. 1998).

The fraction of Chernobyl-derived $^{241}\text{Am}$ / total observed $^{241}\text{Am}$ in peat varied between 0.9% and 100% the average value being 34% (IV, Table 2 and Fig. 4). It can be seen from Fig. 4 in publication IV, that $^{241}\text{Am}$ originates mainly from the nuclear weapons testing fallout, containing both $^{241}\text{Am}$ and $^{241}\text{Pu}$. The highest values for Chernobyl-derived fractions of $^{241}\text{Am}$ are caused by partial removal of weapons testing fallout in peat during peat production before 1986. In Sweden, only 12% of $^{241}\text{Am}$ in lichen and moss originated from the Chernobyl accident (Holm et al. 1992). Also in Poland the main source of $^{241}\text{Am}$ in forest litter was the global nuclear fallout (Mietelski&Wąs, 1997).

5.5. Neptunium in peat

The activity concentration of $^{237}\text{Np}$ in peat was 0.48 ($\pm$0.01) – 3.84 ($\pm$0.08) mBq/kg and 1.98 ($\pm$0.05) – 14.1 ($\pm$0.3) mBq/m² (V, Table 1). In Sweden the corresponding values in lichen collected in 1986-1988 were 0.08 ($\pm$0.01) – 2.08 ($\pm$0.17) mBq/kg (Lindahl et al. 2004). In lichen samples from northern Finland, the $^{237}\text{Np}$ concentration was below the MDA, which was 0.76 mBq/kg for both samples L1 and L2 V. Compared to other transuranium nuclides in peat, the activity concentration of $^{237}\text{Np}$ is orders of magnitude lower (Table 2). On the other hand, the mass concentration of $^{237}\text{Np}$ in peat is practically as high as that of $^{239+240}\text{Pu}$, and significantly higher than those of $^{241}\text{Am}$ and $^{244}\text{Cm}$.

The $^{237}\text{Np}/^{239+240}\text{Pu}$ activity ratio in the global nuclear testing fallout and the Chernobyl fallout can be calculated to be 0.0037 and 0.000125, respectively (Beasley et al. 1998, UNSCEAR 2000 Annexes C&J). In peat samples the $^{237}\text{Np}/^{239+240}\text{Pu}$ activity ratio varied between 0.00145 ($\pm$0.00009) and 0.00286 ($\pm$0.00010) (V, Table 1). The activity ratio in peat in Finland is dominated by the nuclear weapons testing in the 1950s and 1960s. In contrast, the $^{237}\text{Np}/^{239+240}\text{Pu}$ activity ratio in forest litter in a remote area of southern Poland has been 0.00033 ($\pm$0.00025) – 0.00046 ($\pm$ 0.00003), calculated from the activity
concentrations of $^{237}\text{Np}$ and $^{239+240}\text{Pu}$ by La Rosa et al. (2008). This area has a typical composition of nuclides from the Chernobyl accident. At areas contaminated with hot particles in northeastern Poland the corresponding ratio was $0.00077(\pm0.00012) – 0.00146(\pm0.00014)$ (La Rosa et al. 2008). The $^{237}\text{Np}/^{239+240}\text{Pu}$ activity ratio is clearly higher in peat in Finland than in litter in Poland.\(^V\)

The Chernobyl-derived component of total deposition of $^{237}\text{Np}$ can be calculated from $^{237}\text{Np}/^{239+240}\text{Pu}$ ratios 0.0037 and 0.000125 in nuclear test fallout and the Chernobyl fallout, respectively (Beasley et al. 1998, UNSCEAR 2000 Annexes C&J), and from total $^{239+240}\text{Pu}$ deposition from nuclear testing fallout to the latitudes of Finland (Hardy 1973, Hardy et al. 1973). The fraction of Chernobyl-originated $^{237}\text{Np}$ from the total $^{237}\text{Np}$ deposition in peat samples was 0.1–13% (V, Table 2). The corresponding value of the Chernobyl-originated fraction of Np in Sweden was 5–30% at the most heavily $^{137}\text{Cs}$-contaminated areas (Lindahl et al. 2004). Therefore, the Chernobyl-derived fraction of $^{237}\text{Np}$ is at the same level both in Sweden and in Finland.\(^V\)

Table 2. The activity and mass concentrations of transuranium nuclides in peat in Finland. The reference date for activities is 1.5.1986.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>A (mBq/kg)</th>
<th>A (Bq/m²)</th>
<th>m (pg/kg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{239+240}\text{Pu}$</td>
<td>22(±3) – 1780(±90)</td>
<td>0.17±(0.02) – 17.9(±1.2)</td>
<td>10(±1) – 780(±40)</td>
<td>Reponen et al. 1993</td>
</tr>
<tr>
<td>$^{241}\text{Am}$</td>
<td>11(±2) – 810(±30)</td>
<td>0.059±(0.011) – 6.27(±0.22)</td>
<td>0.09±(0.02) – 6.4(±0.2)</td>
<td>IV</td>
</tr>
<tr>
<td>$^{244}\text{Cm}$</td>
<td>&lt;0.5 – 255(±17)</td>
<td>&lt;0.002 – 1.97(±0.13)</td>
<td>&lt;0.0002 – 0.085(±0.006)</td>
<td>IV</td>
</tr>
<tr>
<td>$^{237}\text{Np}$</td>
<td>0.48±(0.01) – 3.84(±0.08)</td>
<td>0.00198(±0.00005) – 0.0141(±0.0003)</td>
<td>18.4(±0.4) – 148(±3)</td>
<td>V</td>
</tr>
</tbody>
</table>
5.6. Regional distribution and the Chernobyl-derived component of transuranium nuclides in peat in Finland

The regional distribution of Chernobyl-originated $^{244}$Cm, $^{241}$Am and $^{237}$Np deposition in Finland is depicted in Figures 10-12. The interpolation of $^{241}$Am and $^{244}$Cm deposition was made with the inverse distance weighing method (IDW) taking into account the local amount of precipitation. The highest deposition values for all nuclides were found from a relatively narrow sector from the southwestern coast to northeast. This has been correlated with the air mass trajectory associated with the initial release of radionuclides from the Chernobyl reactor (Pöllänen et al. 1997). The deposition patterns resemble those of other refractory nuclides, e.g. plutonium isotopes, $^{95}$Zr and $^{141}$Ce (Arvela et al. 1990, Reponen et al. 1993, Paatero et al. 2002).

Percentage fractions of Chernobyl-derived activity concentrations of $^{239+240}$Pu (Reponen et al. 1993), $^{241}$Pu (Paatero et al. 1994), $^{241}$Am $^{IV}$ and $^{237}$Np $^{V}$ (Table 3) show that $^{239+240}$Pu, $^{241}$Pu, $^{241}$Am and $^{237}$Np were deposited mainly from the nuclear weapons testing fallout. The fraction of the Chernobyl-derived deposition of $^{237}$Np is lower than for other transuranium nuclides. Fractions of $^{241}$Am, $^{239+240}$Pu and $^{241}$Pu activities originating from the Chernobyl accident vary greatly among peat samples depending on the location of the peat bog. Again, the highest values can be explained by skimming off varying amounts of old nuclear test fallout during the years of peat production (Paatero et al. 1994).

### Table 3. The percentage fractions of Chernobyl-derived transuranium nuclides in peat in Finland. All $^{244}$Cm in the peat samples was originated from the Chernobyl accident.

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>$A_{\text{Chernobyl}}/A_{\text{total}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{239+240}$Pu</td>
<td>0-100</td>
</tr>
<tr>
<td>$^{241}$Pu</td>
<td>10-99</td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>0.9-100</td>
</tr>
<tr>
<td>$^{237}$Np</td>
<td>0.1-13</td>
</tr>
</tbody>
</table>
Figures 10-12. Regional deposition of Chernobyl-derived $^{241}$Am, $^{244}$Cm and $^{237}$Np based on IDW analysis for selected peat and lichen samples in Finland.
5.7. Total estimated transuranium depositions from atmospheric nuclear weapons testing and Chernobyl accident to Finland

The estimations of total activities of transuranium nuclides from two main sources to Finland are summed in Table 4 and the basis of these calculations is listed below:

- $^{237}$Np from the Chernobyl accident: $1 \times 10^{11}$ Bq of total $^{239+240}$Pu activity from Chernobyl to Finland (Reponen et al. 1993) and inventories of $^{237}$Np and $^{239+240}$Pu in the reactor core at the time of the accident, $2.6 \times 10^{11}$ Bq and $2.46 \times 10^{15}$ Bq, respectively (UNSCEAR 2000, Annex J)

- $^{237}$Np from nuclear weapons testing: $2 \times 10^{13}$ Bq of $^{239+240}$Pu from the global fallout to latitudes of Finland (Hardy et al. 1973), the total activity of $^{237}$Np released during nuclear weapons testing, 40 TBq (Beasley et al. 1998), and $^{237}$Np/$^{239+240}$Pu activity ratio in global fallout, 0.0037 (Beasley et al. 1998, UNSCEAR 2000 Annex C)

- $^{238}$Pu and $^{241}$Pu in weapons testing fallout: Activity ratios $^{238}$Pu/$^{239+240}$Pu 0.03 (Hardy et al. 1973) and $^{241}$Pu/$^{239+240}$Pu 16 (Holm 1995) and a value of $2.0 \times 10^{13}$ Bq (Hardy et al. 1973) for $^{239+240}$Pu activity in Finland

- $^{239}$Pu and $^{240}$Pu from the Chernobyl accident: Previously estimated $^{239+240}$Pu deposition of $1 \times 10^{11}$ Bq in Finland (Reponen et al. 1993), and a calculated $^{240}$Pu/$^{239}$Pu activity ratio of 1.6 (Zaritskaya et al. 1979)

- $^{238}$Pu from Chernobyl to Finland: Previously estimated $^{239+240}$Pu deposition of $1 \times 10^{11}$ Bq in Finland and an observed $^{238}$Pu/$^{239+240}$Pu activity ratio of 0.54 ($\pm 0.02$) (Paatero et al. 1998b)

- $^{241}$Pu from Chernobyl to Finland: Previously estimated $^{239+240}$Pu deposition of $1 \times 10^{11}$ Bq in Finland and an observed $^{241}$Pu/$^{239+240}$Pu activity ratio of 95 (Paatero et al. 1994)
- $^{241}$Am from global nuclear test fallout (ingrown activity excluded): Activity ratio $^{241}$Am/$^{239+240}$Pu of 0.107 from nuclear weapons testing in Finland in 1963–1965 (Jaakkola et al. 1981) and $2.0 \times 10^{13}$ Bq of $^{239+240}$Pu in Finland from nuclear weapon test fallout IV

- $^{241}$Am from the Chernobyl accident: Geometric mean of $^{241}$Am deposition at grid points obtained from IDW analysis multiplied by the total area of Finland, 337000 km$^2$ IV

- $^{242}$Pu from Chernobyl to Finland: Previously estimated $^{239+240}$Pu deposition of $1 \times 10^{11}$ Bq in Finland and a calculated $^{242}$Pu/$^{239+240}$Pu activity ratio of 0.0085 (Zaritskaya et al. 1979) IV

- $^{244}$Cm from the Chernobyl accident: Geometric mean of $^{244}$Cm deposition at grid points obtained from IDW analysis multiplied by the total area of Finland, 337000 km$^2$ IV

- $^{242}$Cm from Chernobyl to Finland: Estimated $^{244}$Cm deposition of $8.2 \times 10^9$ Bq in Finland (IV) and an observed $^{244}$Cm/$^{242}$Cm activity ratio of 0.0053(±0.0013) (Paatero et al. 1998b)

As can be seen from Table 4, the effect of Chernobyl-derived deposition has been low on the total amounts of transuranium nuclides to Finland. Only fractions of percentages or few percentages of transuranium depositions are due to the Chernobyl accident.
Table 4. Estimated total activities from nuclear weapons testing and Chernobyl to Finland, the percentage fractions of global fallout of total deposition and masses of transuranium nuclides fallen from the Chernobyl accident to Finland.

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>A (Bq) from nuclear weapons testing</th>
<th>A (Bq) from the Chernobyl accident</th>
<th>A_{global fallout}/A_{total} (%)</th>
<th>m (g) from Chernobyl to Finland</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{237}$Np</td>
<td>$7.4 \times 10^{10}$</td>
<td>$1.1 \times 10^{7}$</td>
<td>99.985</td>
<td>0.42</td>
</tr>
<tr>
<td>$^{238}$Pu</td>
<td>$6.0 \times 10^{11}$</td>
<td>$5.4 \times 10^{10}$</td>
<td>91.74</td>
<td>0.083</td>
</tr>
<tr>
<td>$^{239}$Pu</td>
<td></td>
<td>$3.8 \times 10^{10}$</td>
<td></td>
<td>16</td>
</tr>
<tr>
<td>$^{240}$Pu</td>
<td></td>
<td>$6.2 \times 10^{10}$</td>
<td></td>
<td>7.1</td>
</tr>
<tr>
<td>$^{239+240}$Pu</td>
<td>$2.0 \times 10^{13}$</td>
<td>$1 \times 10^{11}$</td>
<td>99.50</td>
<td></td>
</tr>
<tr>
<td>$^{241}$Pu</td>
<td>$3.2 \times 10^{14}$</td>
<td>$9.5 \times 10^{12}$</td>
<td>97.12</td>
<td>2.4</td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>$2.1 \times 10^{12}$</td>
<td>$3.7 \times 10^{10}$</td>
<td>98.27</td>
<td>0.29</td>
</tr>
<tr>
<td>$^{242}$Pu</td>
<td></td>
<td>$8.5 \times 10^{8}$</td>
<td></td>
<td>5.8</td>
</tr>
<tr>
<td>$^{242}$Cm</td>
<td></td>
<td>$1.5 \times 10^{12}$</td>
<td></td>
<td>0.012</td>
</tr>
<tr>
<td>$^{244}$Cm</td>
<td></td>
<td>$8.2 \times 10^{9}$</td>
<td></td>
<td>0.0027</td>
</tr>
<tr>
<td>SUM</td>
<td>$1.1 \times 10^{13}$</td>
<td></td>
<td>32.1</td>
<td></td>
</tr>
</tbody>
</table>

6. CONCLUSIONS

The first part of this work, the method development for analyzing plutonium from air filters collected in Kazakhstan, produced a functional separation procedure based on extraction chromatography. Nevertheless, the complex sampling environment with hundreds of different plutonium sources at Semipalatinsk test site, having some Chernobyl-originated plutonium as well, made nearly impossible to identify the origin of plutonium in weekly filters. Plutonium in air of Sodankylä was deposited from global nuclear test fallout in 1963. No weapons-grade plutonium was observed in Sodankylä. The majority of activities of americium, curium and neptunium in peats in Finland is from nuclear weapons testing, although the Chernobyl-derived fraction of transuranium nuclide varies widely and local high Chernobyl-originated activities has been observed. Compared to previously determined plutonium isotopes in peats (Reponen et al.)
1993, Paatero et al. 1994), the deposition patterns of $^{241}\text{Am}$, $^{244}\text{Cm}$, $^{237}\text{Np}$, $^{239+240}\text{Pu}$ and $^{241}\text{Pu}$ resemble each others.

Hot particles from nuclear weapons testing and the Chernobyl accident were probably present in all investigated samples, because the variation in activity concentrations and activity ratios was great for air filters from Kazakhstan and Sodankylä, as well as for peat samples from southern and central Finland. Hot particles give further information about the origin, composition and magnitude of radioactive contamination. It would have taken much more time to isolate single hot particles from various analyzed samples, therefore it was not possible to include the particle analysis to routine analyses.

The activity of transuranium nuclides from the Chernobyl accident to Finland, and furthermore the impact of Chernobyl-derived transuranium contamination on the radiation dose in Finland, is minor compared to the deposition of natural radionuclides. The total annual deposition of natural alpha and beta emitters $^{210}\text{Pb}$ and $^{210}\text{Po}$ is still a hundredfold higher (Paatero et al. 1994b) than the total transuranium deposition from Chernobyl, which was essentially a single event IV.

The advantages of extraction chromatography compared to ion exchange are the rapidness, smaller volumes of acidic waste solutions and the possibility to determine several nuclides at the same time. However, there are certain problems depending on the sample type (matrix effects) and according to the author’s experience of the two techniques, the radiochemical recovery has wider variation in extraction chromatography than in ion exchange chromatography. The four separation methods developed in this thesis worked well, although some additions, like extra purifications of samples for mass spectrometry and possibly electrodeposition instead of co-precipitation for americium alpha samples, might be necessary.

The separation method for determining $^{237}\text{Np}$ should be optimized according to improving means presented in publication V, because $^{237}\text{Np}$ in an important radionuclide and even dominating transuranium element in environment in the future. The
concentration of $^{237}\text{Np}$ in environment increases constantly from the decay chain beginning from $^{241}\text{Pu}$, and from nuclear fuel reprocessing and other possible sources. The knowledge of environmental behaviour of $^{237}\text{Np}$ is essential concerning the safety of nuclear waste repositories. Still, the research dealing with neptunium was essentially at the same point in 1999 as were studies of plutonium and americium in the late 1960s (Assinder 1999), so a great deal of exploration of neptunium is to be done.
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