



## Speciation Analysis of Radionuclides in the Environment - NSK-B SPECIATION project report 2009

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# Speciation Analysis of Radionuclides in the Environment

## - NSK-B SPECIATION project report 2009

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October 2009

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## Abstract

The second stage of the NKS-B project SPECIATION was complemented in 2008-2009, which mainly focus on three aspects: (1) Further improvement and development of methods for speciation analysis of radionuclides; (2) Investigation of speciation of some radionuclides in the environment (water, sediments, particles); and (3) Intercomparison exercise for speciation analysis of radionuclides in soil and sediment. This report summarizes the work completed in the project partners' laboratories, Method developments include: Development of a rapid and in-suit separation method for the speciation analysis of  $^{129}\text{I}$  in seawater samples; Development of a simple method for the speciation analysis of  $^{129}\text{I}$  in fresh water and seawater samples; Development of an on-line HPLC-ICP-MS method for the direct speciation analysis of  $^{127}\text{I}$  in water and leachate samples; Speciation of radionuclides in water includes: Speciation of  $^{129}\text{I}$  and  $^{127}\text{I}$  in time-series precipitation samples collected in Denmark 2001-2006 and its application for the investigation of geochemistry and atmospheric chemistry of iodine, Speciation of radionuclides in Ob and Yenisey Rivers, and Speciation of  $^{129}\text{I}$  and  $^{127}\text{I}$  in Lake Heimdalen water. Speciation of radionuclides in soils and sediments includes: Sequential extraction of radionuclides in sediments and of trace elements in soil samples. Sequential extraction of radionuclides in aerosols and particles has also been performed. Further-more, sorption experiments have been performed to investigate the association of Pu, Am and Cs with different geological materials. The intercomparison exercises included sequential extraction of Pu,  $^{137}\text{Cs}$ , U, Th, and  $^{129}\text{I}$  in one soil and one sediment standard reference materials (NIST-4354, IAEA-375) and Pu in sediment collected from the Lake Heimdalen, Norway.

## Key words

Speciation, radionuclides, radioecology, radioanalytical chemistry, Iodine-129, plutonium, fractionation, intercomparison, water, sediment, soil, aerosol, precipitation

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15<sup>th</sup> October 2009

# **Speciation Analysis of Radionuclides in the Environment**

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## **Abstract**

The second stage of the NKS-B project SPECIATION was complemented in 2008-2009, which mainly focus on three aspects: (1) Further improvement and development of methods for speciation analysis of radionuclides; (2) Investigation of speciation of some radionuclides in the environment (water, sediments, particles); and (3) Inter-comparison exercise for speciation analysis of radionuclides in soil and sediment. This report summarizes the work completed in the project partners' laboratories, Method developments include: Development of an rapid and in-suit separation method for the speciation analysis of  $^{129}\text{I}$  in seawater samples; Development of a simple method for the speciation analysis of  $^{129}\text{I}$  in fresh water and seawater samples; Development of an on-line HPLC-ICP-MS method for the direct speciation analysis of  $^{127}\text{I}$  in water and leachate samples; Speciation of radionuclides in water includes: Speciation of  $^{129}\text{I}$  and  $^{127}\text{I}$  in time-series precipitation samples collected in Denmark 2001-2006 and its application for the investigation of geochemistry and atmospheric chemistry of iodine, Speciation of radionuclides in Ob and Yenisey Rivers, and Speciation of  $^{129}\text{I}$  and  $^{127}\text{I}$  in Lake Heimdalen water. Speciation of radionuclides in soils and sediments includes: Sequential extraction of radionuclides in sediments and of trace elements in soil samples. Sequential extraction of radionuclides in aerosols and particles has also been performed. Furthermore, sorption experiments have been performed to investigate the association of Pu, Am and Cs with different geological materials. The intercomparison exercises included sequential extraction of Pu,  $^{137}\text{Cs}$ , U, Th, and  $^{129}\text{I}$  in one soil and one sediment standard reference materials (NIST-4354, IAEA-375) and Pu in sediment collected from the Lake Heimdalen, Norway.

**Keywords:** Speciation, radionuclides, radioecology, radiochemistry, fractionation, sequential extraction, intercomparison,  $^{129}\text{I}$ , plutonium

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## 1. Introduction

The NKS-B project – SPECIATION was launched in 2007, and through this project a close collaboration among Nordic laboratories on speciation of radionuclides was established. The experiences on the speciation analysis of radionuclides obtained in the individual laboratory were exchanged and shared. The progress and output of the SPECIATION project 2008 were published in a NKS-report (Hou et al. 2008, NKS-176). This project continued in 2008-2009, and in the second phase, the aims of the project (SPECIATION 2008-2009) were: (1) Further development and improvement of analytical methods for speciation of some important radionuclides in the environment; (2) Comparison, optimization, and harmonization of separation techniques for radionuclide speciation developed in Nordic laboratories, especially focused on operationally defined speciation procedures. (3) Organization of an inter-comparison on the speciation analysis of radionuclides such as  $^{137}\text{Cs}$ ,  $^{129}\text{I}$ ,  $^{127}\text{I}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ , uranium and thorium in soil and sediment samples. (4) Investigation of speciation of the some radionuclides in specific Nordic environments and the behaviour of radionuclides from European reprocessing facilities. The project was completed in October 2009, and the results and output are summarized this report.

### *Speciation concept and definitions*

Naturally occurring and artificially produced radionuclides in the environment can be present in different physico-chemical forms (i. e. radionuclide species) varying in size (nominal molecular mass), charge properties and valence, oxidation state, structure etc. (Salbu, 2009). Low molecular mass (LMM) species are believed to be mobile and potentially bioavailable, while high molecular mass (HMM) species such as colloids, polymers, pseudocolloids and particles are considered inert but can be retained in filtering organisms. The system is dynamic and the transition between categories is gradual, although the categories usually are defined according to fractionation techniques applied (Fig. xx).

The definition of radionuclide species applies to a modified version of the IUPAC trace metal nomenclature (Templeton et al., 2000): *chemical species* of a radionuclide are defined according to their physico-chemical properties such as nominal molecular mass, charge properties and valence, oxidation state, structure and morphology, density etc. (Salbu, 2009). *Speciation analysis* is defined by IUPAC 2000 as the analytical activities of identifying and/or measuring the quantities of one or more individual chemical species in a sample, and *speciation of an element* is defined as the distribution of an element amongst defined chemical species in a system. However, IUPAC 2000 differentiates between fractionation techniques and speciation techniques, where fractionation is defined as “the process of classification of an analyte or a group of analytes from a certain sample ac-



ording to physical (e.g., size, solubility) or chemical (e.g., bonding, reactivity) properties”. As the activity concentrations for most radionuclide species in the environment are too low for any specie-specific methods to be applied, fractionation techniques are needed and fractions must be concentrated prior to measurements (Salbu, 2000). Thus, *speciation analysis* of radionuclides should be defined as the analytical activity of fractionating, isolating, identifying and quantifying one or more individual radionuclide species in a sample, and should include *in situ*, *at site*, *on line*, *in laboratory* fractionation techniques applied prior to analysis.

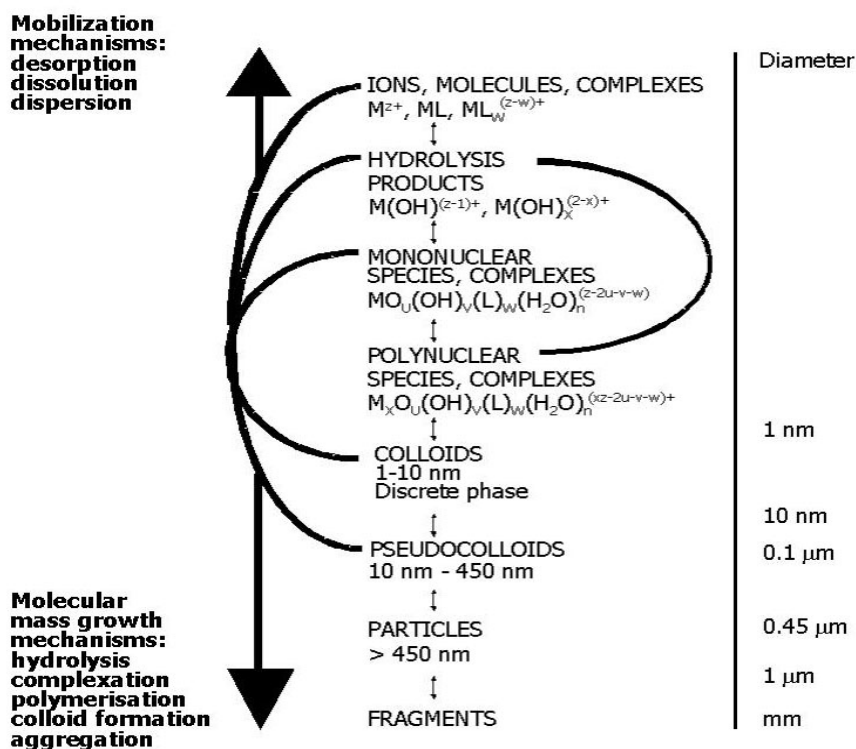


Figure 1. Size classes for different physico-chemical forms of radionuclides. Transformation processes changing the distribution of species are indicated (Salbu, 2000).

Furthermore, radioactive particles in the environment are defined as localised aggregates of radioactive atoms that give rise to inhomogeneous distribution of radionuclides significantly different from that of the matrix background. In soils and sediments grain size separation into sand and silt fractions is useful, and particles larger than 2 mm should be referred to as fragments. Following environmental chemistry, particles in aquatic systems are defined as entities having diameters larger than 0.45  $\mu\text{m}$ , as these are expected to sediment in still water due to gravity. Colloids or pseudocolloids are defined as localised heterogeneities ranging in size from about 1 nm to 0.45  $\mu\text{m}$ , i.e. entities which do not settle in still water due to mutual repulsion and Brownian movements. Hence, ra-

dionuclide species with nominal molecular mass less than 1-10 kDa (diameters less than about 1 nm) should be referred to as low molecular mass species (LMM). In air, radioactive particles ranging from submicrons in aerosols to fragments are classified according to their aerodynamic diameters, where particles less than 10 µm are considered respiratory.

A series of fractionation techniques are available for radionuclides in water, soils and sediments (Salbu and Oughton, 1995). However, all techniques suffer from disadvantages, and care should be taken when results are interpreted (Salbu, 2009). In the present report redox agents as well as hollow fibre ultrafiltration have been applied to distinguish between radionuclides in water. For radionuclides in soils, sediments and particles different sequential extraction techniques have been applied. For the radionuclide or element which mainly exists in ion form, such as iodine isotopes ( $^{129}\text{I}$  and  $^{127}\text{I}$ ), iodide and iodate are separated using chromatographic method. Then, radionuclides associated with obtained fractions are determined using alpha-, gamma-spectrometry, ICP-MS and AMS.

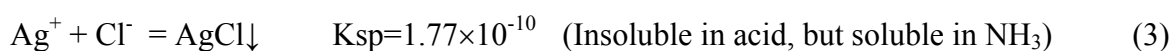
## 2. Progress in the method development for speciation of radionuclides

### 2.1. Development of a rapid and in-situ separation method for the speciation analysis of $^{129}\text{I}$ in seawater samples

A method for the speciation analysis of  $^{127}\text{I}$  and  $^{129}\text{I}$  in seawater and fresh water has been developed and successfully used for the investigation of  $^{129}\text{I}$  speciation in the North Sea water and precipitation (Hou et al., 2008, NKS-176). This method based on the separation of iodide and iodate using anion exchange chromatography, and solvent extraction using  $\text{CCl}_4$  for separation of iodine from matrix and interferences. The separated iodine was precipitated as AgI target for AMS measurement. This method was confirmed to be a very good method for the speciation of  $^{129}\text{I}$  and  $^{127}\text{I}$  in seawater as well as fresh water. However, the analytical procedure is relative long and time consuming, which is not suitable for the application in-situ on board.

In environmental water samples, iodine exists as iodide, iodate and some organic iodine species. A rapid and simple speciation method on the in-situ speciation separation of  $^{129}\text{I}$  in seawater was developed under this project. The method is based on the specific precipitation of iodide as AgI in the high concentration of chlorine, while iodate cannot precipitate under this condition. Iodide and iodate, as well as chloride, forms precipitate with silver ion following reactions and solubility products are shown below:





Here,  $M_m A_n = m M^+(aq) + n A^-(aq) \quad K_{sp} = [M^+]^m [A^-]^n$  (solubility production)

The very low solubility product of AgI compared to AgIO<sub>3</sub> implies that iodide may be primary precipitated when silver ions are added to the samples. The results (Figure 2 a,b) show that (1) Iodide can be quantitatively separated from iodate by co-precipitation of AgI with AgCl; (2) A molecular ratio of Ag<sup>+</sup> to Cl<sup>-</sup> in the sample (Ag/Cl) as low as 0.01 is enough for quantitative precipitation of iodide in 1.0 liter seawater, only 0.3-0.5 g Ag<sup>+</sup> is needed; (3) At Ag/I value of less than 200, and Ag/Cl ratio of less than 0.1, less than 2.0 % of iodate is precipitated with iodide; (4) Salinity does not effect the precipitation of iodide, but the amount of associated iodate precipitation (AgIO<sub>3</sub>) increases with the decreasing of salinity; (5) When salinity is lower than 5 (or Ag/Cl higher than 0.05), iodate starts to be precipitated (as AgIO<sub>3</sub>) with iodide (AgI). Based on these results, a separation procedure was developed for the separation of iodide and determination of iodide, iodate and total inorganic iodine (Figure 4).

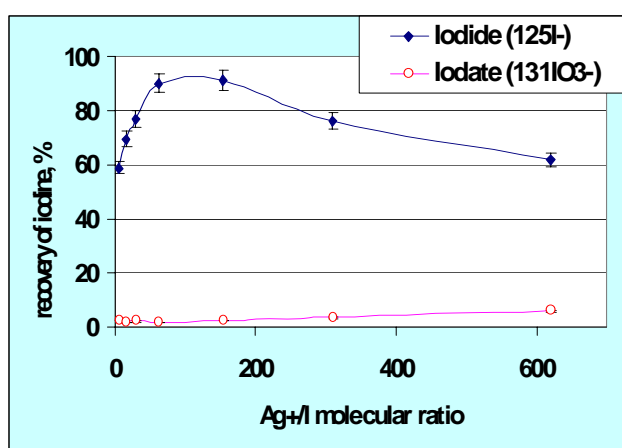


Figure 2a. Effect of Ag<sup>+</sup>/I<sup>-</sup> ratio on the precipitation of iodide and iodate in seawater sample (3.5% NaCl water)

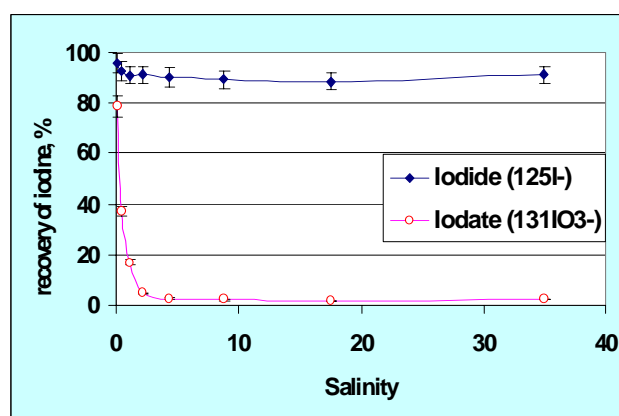


Figure 2b. Effect of salinity on the separation of iodide from iodate by AgI precipitation

In the procedure described above, iodide carrier (1-2mg) is first added to the seawater (0.1-2 liters), and pH is adjusted to 5-7 using HCl, and then 0.2-2 ml of 1mol/L AgNO<sub>3</sub> is added (Cl:Ag >10 mol/mol), the solution is stirred for 30 min. and the precipitate is separated by centrifuge. 25 % of NH<sub>3</sub> is then added to the precipitate to dissolve the AgCl, and the separated AgI is directly used for AMS measurement of iodide-129. For total I-129, after addition of iodine carrier and HCl to pH<2, NaHSO<sub>3</sub> solution is added to reduce iodate to iodide, then total iodine is separated by the same procedure as for iodide. The iodate-129 is calculated by the difference between iodide-129 and total iodine-129. The analytical results showed that the recovery of iodine is more than 80 % and the

crossover of iodate in the iodide fraction is less than 2 %. Because more samples can be treated simultaneously (>10 sample /h), the method is rapid and very suitable for the in situ separation on board of research vessels.

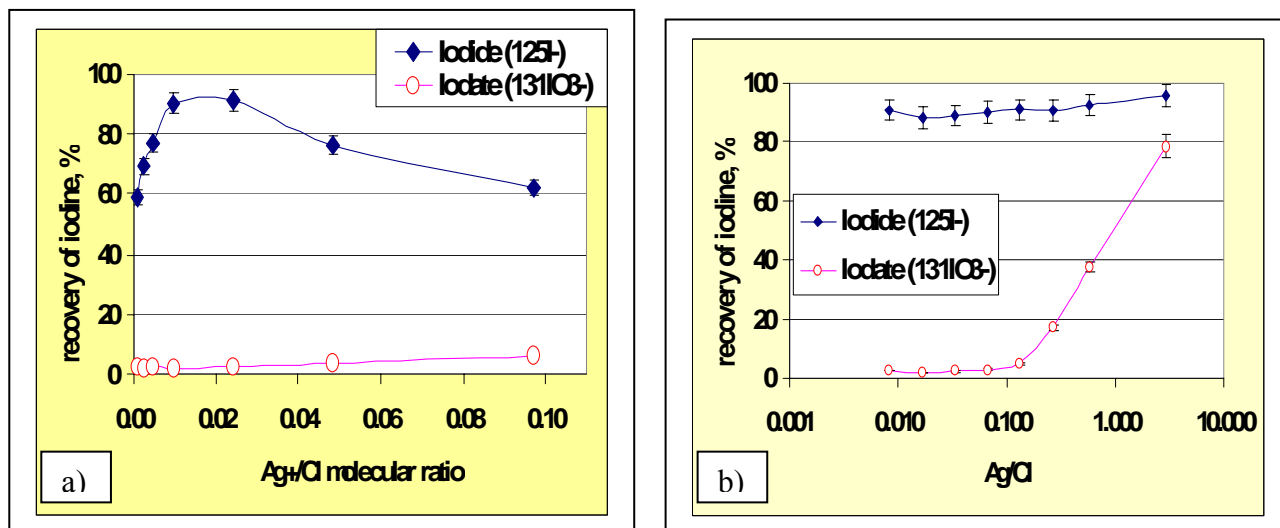


Figure 3. Effect of  $\text{Ag}^+/\text{Cl}^-$  ratio on the precipitation of iodide and iodate in water sample (a) salt water with 3.5 % NaCl; (b) water with different NaCl concentration (0.01-3.5 %)

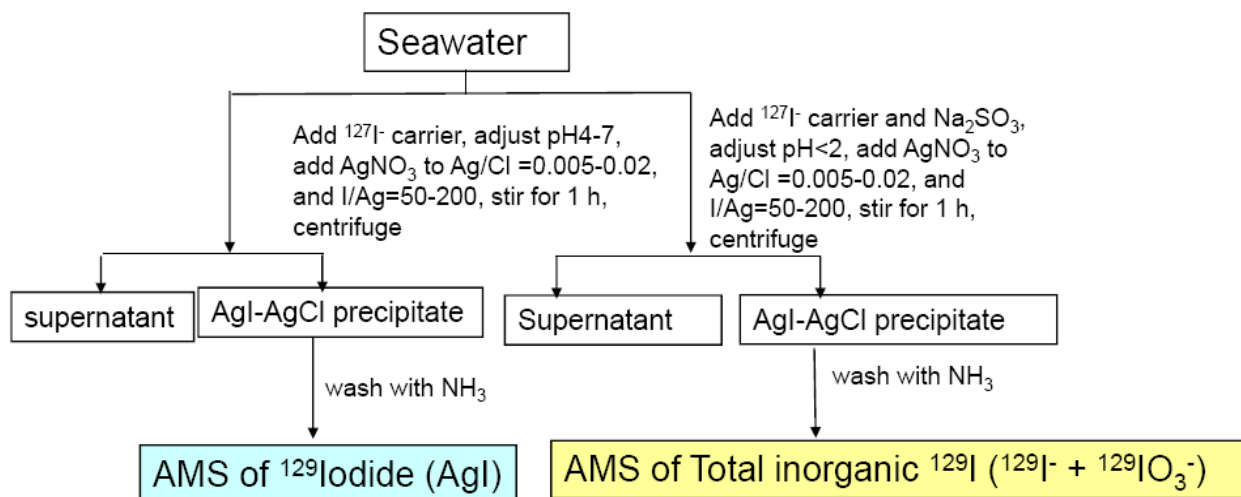


Figure 4. Flow chart showing chemical procedure for the speciation analysis of  $^{129}\text{I}$  in seawater

## 2.2 Development of a simple method for the speciation analysis of $^{129}\text{I}$ in fresh water and seawater samples

The developed co-precipitation method is rapid and suitable for the speciation separation of iodine in seawater *in situ* on board ships. However, it cannot be used for the speciation separation of

iodine in fresh water which contains low chlorine and often high concentrations of organic material (humic substances). A new procedure based on selective oxidization of iodide to elemental iodine in water using  $\text{NaClO}$ , while leaving iodate in the water. The produced element iodine is then extracted using  $\text{CCl}_4$  or  $\text{CHCl}_3$ , and separated from iodate.

In the conventional separation procedure for iodine, iodine is first converted to iodide, and the iodide is then oxidized to molecular iodine with  $\text{NaNO}_2$  or  $\text{H}_2\text{O}_2$ , and is then extracted into organic solvent  $\text{CCl}_4$  or  $\text{CHCl}_3$ . An alternative method is to convert iodine species to iodate, which is then reduced to molecular iodine by hydroxylamine hydrochloride. Therefore iodide can be separated from iodate by selective oxidizing iodide or selectively reducing iodate to molecular iodine, which is then extracted to organic and separated from each other.

However, the results (Figure 5, 6) show that for oxidizing iodide to  $\text{I}_2$  using  $\text{NaNO}_2$ , the sample solution has to be adjust to  $\text{pH} < 2$ . In this case, iodide reacts with iodate to form  $\text{I}_2$  and extracted into the organic phase. Oxidation of iodide to  $\text{I}_2$  using  $\text{H}_2\text{O}_2$  occurs at  $\text{pH} 5$ , while to obtain a high recovery ( $>40\%$ ), the solution has to be adjusted to  $\text{pH} < 4$ , and quantitative extraction of iodide require solution of  $\text{pH} 2$ . At  $\text{pH} 4$ , the recovery of iodide is only  $44\%$ , and a crossover extraction of iodate is less than  $3\%$ , while more than 4 extractions need to be repeated. These results indicate that using both  $\text{NaNO}_2$  and  $\text{H}_2\text{O}_2$  as oxidant reagent for separation of iodide from iodate is not suitable.

A method of reduction of iodate to  $\text{I}_2$  with hydroxylamine hydrochloride was also investigated for the separation of iodate from iodide. The result shows that the reduction occurs only at  $\text{pH} < 2$ . It is the same as oxidation of iodide, at  $\text{pH} < 2$ , the iodate reacts with iodide to form  $\text{I}_2$ , which makes the separation of iodate from iodide impossible.

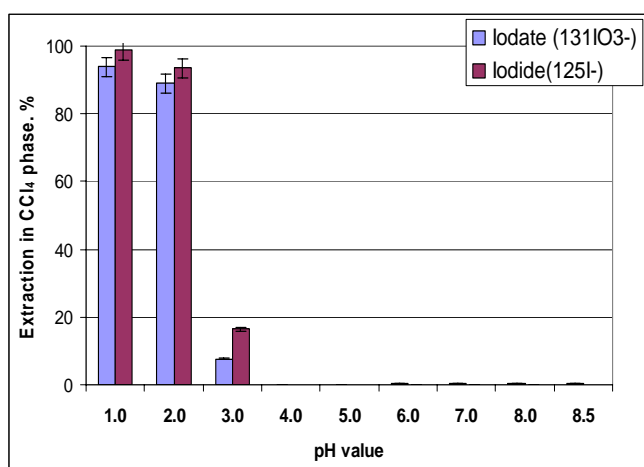


Fig. 5 Separation of iodide from iodate by oxidizing iodide to  $\text{I}_2$  using  $\text{NaNO}_2$  and extraction with  $\text{CCl}_4$

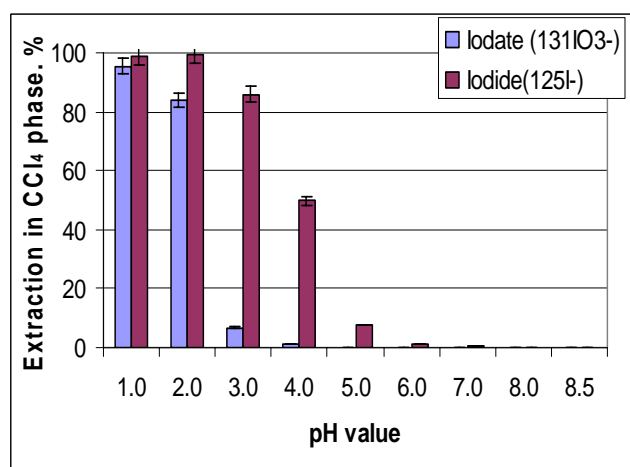


Fig. 6 Separation of iodide from iodate by oxidizing iodide to  $\text{I}_2$  using  $\text{H}_2\text{O}_2$  and extraction with  $\text{CCl}_4$

NaClO is a strong oxidant reagent and has been widely used to oxidize iodine to high oxidation state ( $\text{IO}_3^-$  or  $\text{IO}_4^-$ ) in alkali medium. Using NaClO as oxidant to iodize iodide to  $\text{I}_2$  was investigated. The results (Fig. 7) show that at  $4 < \text{pH} < 8$ , iodide can be quantitatively oxidized to  $\text{I}_2$  and extracted into the organic phase, while iodate (<1%) remains in solution. However, a suitable amount of NaClO should be added, because excessive NaClO may directly oxidize  $\text{I}^-$  to  $\text{IO}_3^-$  at high pH.

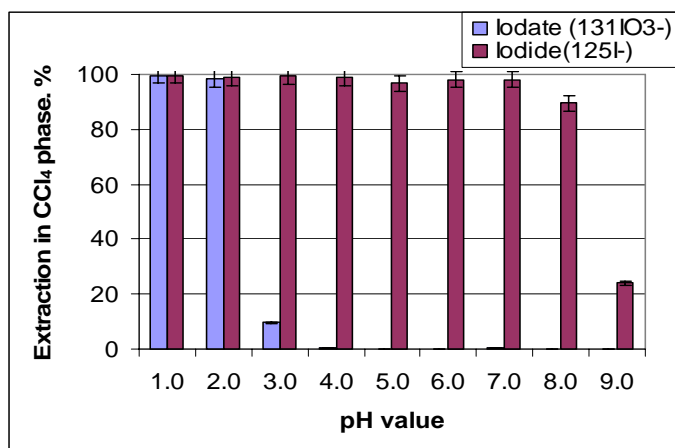


Figure 7. Separation of iodide from iodate in water using NaClO as oxidant.

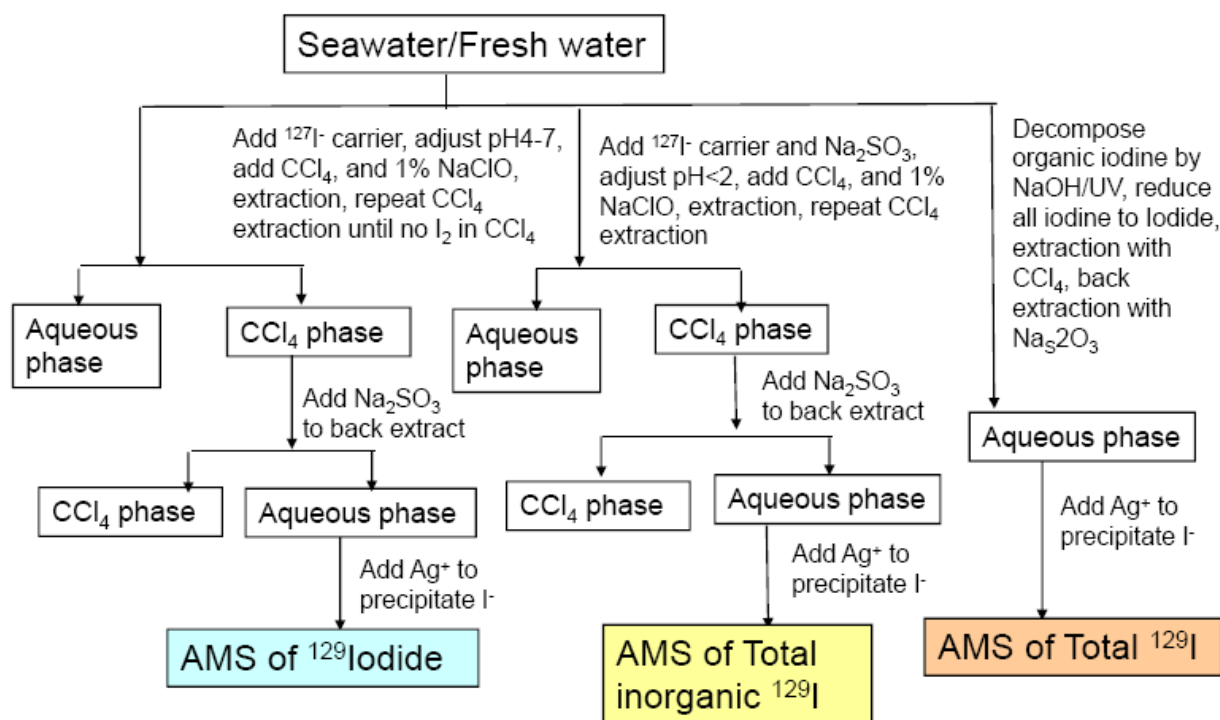


Figure 8. Chemical procedure for separation iodide and inorganic iodine using NaClO as oxidant and chemical speciation analysis of  $^{129}\text{I}$  in water samples

Based on this investigation, a chemical procedure (Fig. 8) was developed for separation of iodide from iodate in both seawater and fresh water. The two procedures (Fig.4 and 8) have been used for the analysis of environmental samples, and the results (Table 1) show that the data are comparable with the traditional method using anion exchange for separation of iodide and iodate.

Table 1 Comparison of two methods with the traditional anion exchange method for the chemical speciation analysis of  $^{129}\text{I}$  in environmental samples.

Separation method	Seawater, English Channel, $10^{10}$ at/L		Seawater, Kattegat (Denmark) $10^{10}$ at/L	
	$^{129}\text{I}^-$	$^{129}\text{IO}_3^-$	$^{129}\text{I}^-$	$^{129}\text{IO}_3^-$
Ion Exchange	28.7±1.6	37.5±1.2	3.59±1.36	2.57±1.13
AgI-AgCl precipitate	26.9±1.8	38.8±1.9	3.29±1.16	2.87±1.47
$\text{CCl}_4$ extraction with $\text{NaClO}$ oxidation	29.4±1.3	36.8±1.2	3.46±1.31	2.77±1.43

### 2.3 Development of an on-line HPLC-ICP-MS method for the direct speciation analysis of $^{127}\text{I}$ in water and leachate samples

In our previous investigation, the speciation analysis of  $^{127}\text{I}$  in the liquid sample was carried out by chemical separation of different species of iodine using ion exchange chromatography and off line measurement of iodine in the separated fractions using ICP-MS or neutron activation analysis. Although this method has been successfully used in the analysis of seawater, precipitation and water leachate of soil and sediment, the method is time consuming and indirect, especially the information of organic iodine could not be obtained. A direct analytical method based on the HPLC separation and ICP-MS measurement of iodine was developed: Since HPLC is coupled with ICP-MS, the speciation analysis of  $^{127}\text{I}$  in liquid samples can be carried out in on-line model.

In this work, Ion PAC AS11 column (2.0 mm id × 250 mm length, 13  $\mu\text{m}$  particle size, Dionex) was used in HPLC for the separation of iodide and iodate in liquid sample. An Ion PAC AG11 (2×50 mm) guard column was applied to remove the particle and impurities in the load sample for improving the performance of the separation column. AS11 is a weakly basic anion exchange column, the separation of iodide and iodate on this column is based on the significantly different affin-

ity of iodide and iodate, and the eluting behaviours of iodide and iodate on the column by encounter anions, such as  $\text{CO}_3^{2-}$ . A large sample loop with a capacity of 1.5 ml was used to load the sample to the column, which insures the accurate measurement of low concentration of iodide or iodate species in the effluent and eluate. An auto-sampler was employed in the HPLC, which is used to load the sample to the column automatically, therefore complete an automated determination of iodine species in as much as 60 samples. The effluent and eluate from the HPLC column is directly injected to the plasma of ICP-MS (Thermal) through nebulizer, and iodine concentration in the effluent and eluate is then on-line monitored, measured and recorded.

**Table 2 Experimental parameters of HPLC-ICPMS for the speciation analysis of 127I in liquid**

HPLC experimental conditions	
Column	Ion pac AS11 Dionex (2.0 mm id × 250 mm length, 13 um particle size), and an AG11 (2×50 mm) guard column
Mobile phase	0.03 mol/L $(\text{NH}_4)_2\text{CO}_3$
Flow rate	0.50 mL min <sup>-1</sup>
Volume sample loaded	100µl
ICP –MS parameters	
Forward power	1.45 kW
Plasma gas flow rate	1.0 min <sup>-1</sup>
Auxiliary gas flow rate	1.0 min <sup>-1</sup>
Carrier gas flow rate	1.0 min <sup>-1</sup>
Dwell time	30 ms

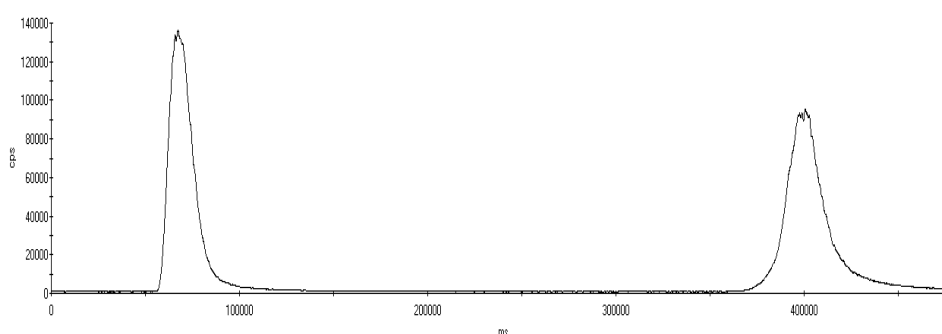


Fig. 9 HPLC-ICP-MS chromatogram for standard solution containing 5 ppb of  $\text{I}^-$  and 5 ppb  $\text{IO}_3^-$ .

Figure 9 shows the chromatogram of the HPLC-ICP-MS for iodine species standard, it can be seen that the retention times for iodate and iodide are 1.66 min. and 6.70min., respectively. The peak of iodide is wider than that of iodate, this is attributed to the longer eluting time of iodide. A series of iodine species standards were prepared using KI and  $\text{KIO}_3$ , and measured using the sys-



tem, and calibration curves for iodide and iodate are shown in Figure 10. A good line correlation between the prepared concentration and corresponding signal strength were observed for both iodide and iodate. By this method, iodide and iodate can be directly measured, and the concentration of total iodine in the sample can be directly measured using ICP-MS without the coupled to HPLC. Since the inorganic iodine in the environmental samples is mainly exist as iodide and iodate, the difference of total iodine and inorganic iodine (iodide plus iodate) is considered to be the sum of organic iodine. By running the standard with different concentration of iodide and iodate, natural water samples with different level of iodine and blank samples (deionised water) can be analysed, No memory effects were observed and a good reproducibility was achieved.

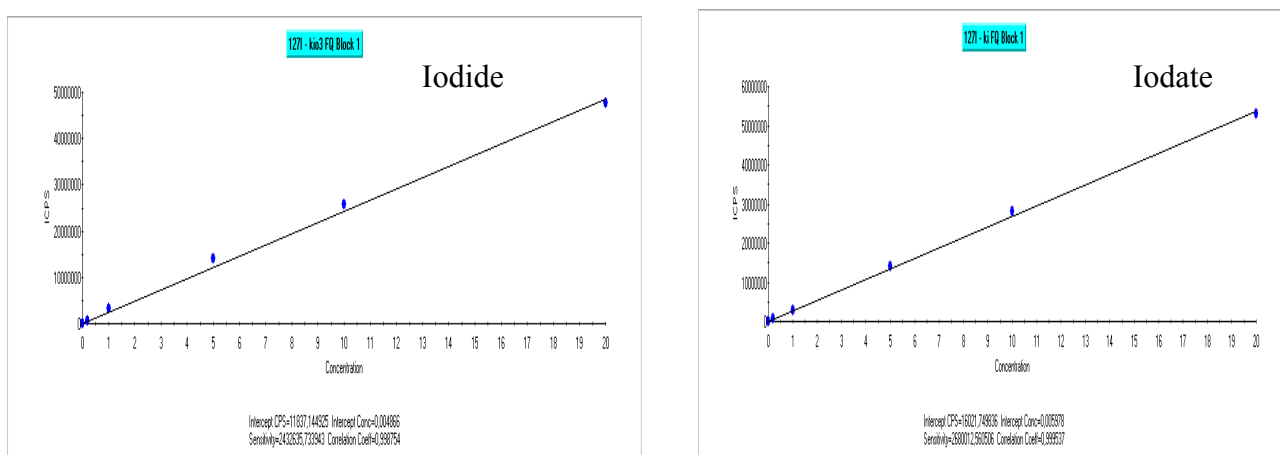


Fig. 10 HPLC-ICP-MS calibration curves for iodide and iodate

Table 3 Analytical results of iodine species in natural water samples collected in Denmark and analysed by HPLC-ICPMS

Sample	Location	Sampling date	pH	Total iodine (nM)	I- (nM)	IO3- (nM)	Organic iodine (nM)
Seawater	Færøerne Havvand	11-12-2008	6.5	411,1	103,78	253,54	53,78
Rain water	Ejby	03-02-2009	5	6,55	0,78	0,4	5,37
Lake	Hostrup Sø	26-01-2009	5.5	47,2	0,99	0,88	45,32
River	Suså	03-02-2009	7	74,5	1,16	4,05	70,45
Groundwater	EJ BY	27-01-2009	7	42,71	1,55	15,44	27,27

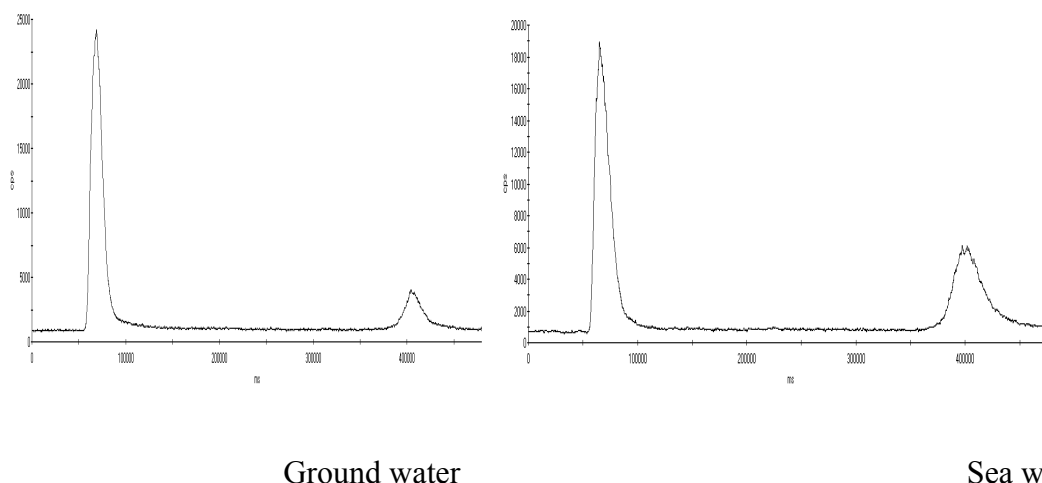


Fig. 11 HPLC-ICP-MS chromatogram of iodine species in ground water (left) and seawater (right).

Using the developed method, some water samples including seawater, rain, lake water, river water, and ground water (Table 3) have been analysed. These samples are first filtered through a 0.45  $\mu\text{m}$  membrane, and then prepared to 0.03 mol/L  $(\text{NH}_4)_2\text{CO}_3$  solution. The prepared sample was loaded to the HPLC column and measured by ICP-MS. Figure 11 shows the chromatogram of HPLC-ICPMS for iodine in seawater and ground water are similar to the chromatogram observed in standard (Figure 9, 11). Table 3 shows the analytical results of iodine species in these samples.

### 3. Speciation of the some radionuclides in water

#### 3.1 Speciation of $^{129}\text{I}$ and $^{127}\text{I}$ in time-series precipitation samples collected in Denmark 2001-2006 and its application for the investigation of geochemistry and atmospheric chemistry of iodine

Speciation analysis of  $^{129}\text{I}$  and  $^{127}\text{I}$  in precipitations collected from Roskilde, Denmark in 2000-2006 was implemented, and the variations of concentrations of iodide, iodate, total iodine for  $^{129}\text{I}$  and  $^{127}\text{I}$  are show in Fig. 12-15. The concentrations of total  $^{129}\text{I}$  in precipitation vary from 0.28 to  $5.63 \times 10^9$  atoms  $\text{L}^{-1}$  with an average of  $(2.34 \pm 1.43) \times 10^9$  atoms  $\text{L}^{-1}$ , and the annual deposition flux of  $^{129}\text{I}$  is  $(1.25 \pm 0.30) \times 10^{12}$  atoms  $\text{m}^{-2}$ . Iodide is the major species of  $^{129}\text{I}$ , which accounts for 50-99% of total  $^{129}\text{I}$  with an average of 92%. The concentrations of total  $^{127}\text{I}$  vary from 0.78 to 2.70  $\text{ng mL}^{-1}$  with an average of  $1.63 \pm 0.47$   $\text{ng mL}^{-1}$ , and annual deposition of  $^{127}\text{I}$  is  $0.95 \pm 0.26$   $\text{mg m}^{-2}$ . Unlike  $^{129}\text{I}$ , iodate is the major species of  $^{127}\text{I}$ , which accounts for 43-93% of total  $^{127}\text{I}$  with an average of 68%, and the concentrations of non-ionic iodine and iodate are lower. The  $^{129}\text{I}/^{127}\text{I}$  atomic values for total iodine vary from 5.04 to  $76.5 \times 10^{-8}$  atom/atom with an average of  $(30.1 \pm 16.8) \times 10^{-8}$ ,

while these values are 10 times lower for iodate with an average of  $(2.95 \pm 3.13) \times 10^{-8}$ . A similar seasonally variations of  $^{129}\text{I}/^{127}\text{I}$  values as well as  $^{129}\text{I}$  concentration are observed with higher value in spring and lower one in summer-autumn period.

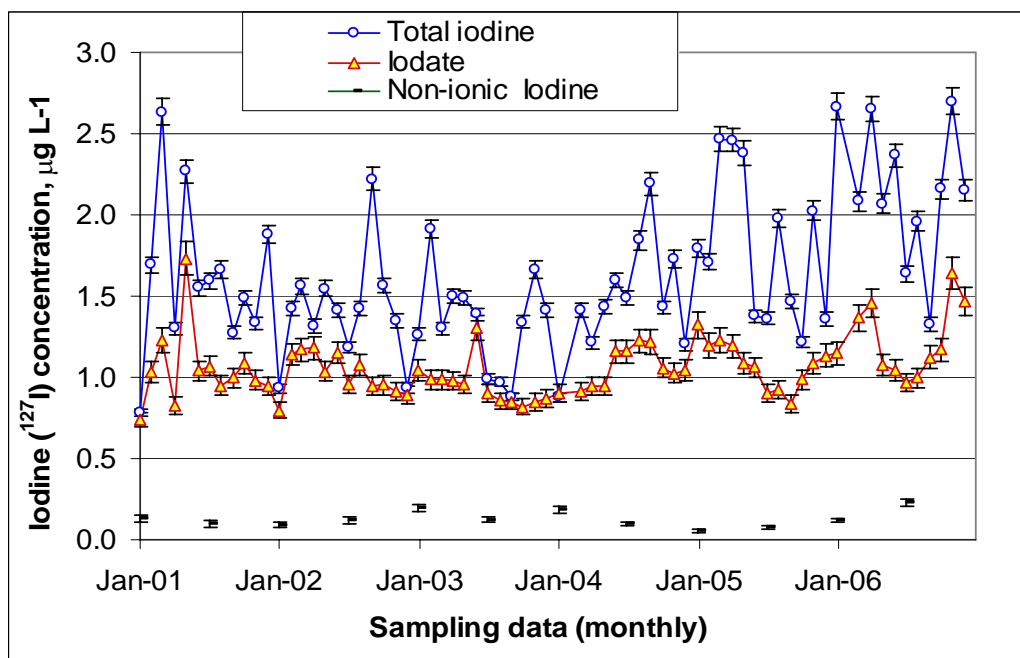


Figure 12. Variation of concentrations of  $^{127}\text{IO}_3^-$ , and non-ionic and total  $^{127}\text{I}$  in precipitation from Roskilde, Denmark in 2001-2006 (the error bar shows the analytical uncertainty).

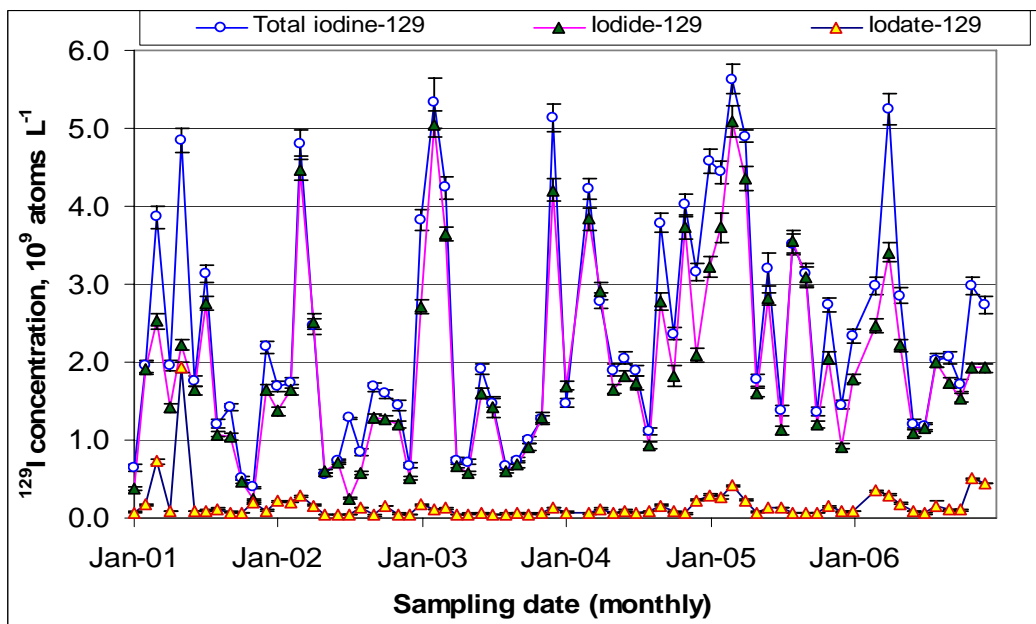


Figure 13. Variation of concentrations of  $^{129}\text{I}$ ,  $^{129}\text{IO}_3^-$ , and total inorganic  $^{129}\text{I}$  in precipitation from Roskilde, Denmark in 2001-2006 (the error bar shows the analytical uncertainty).

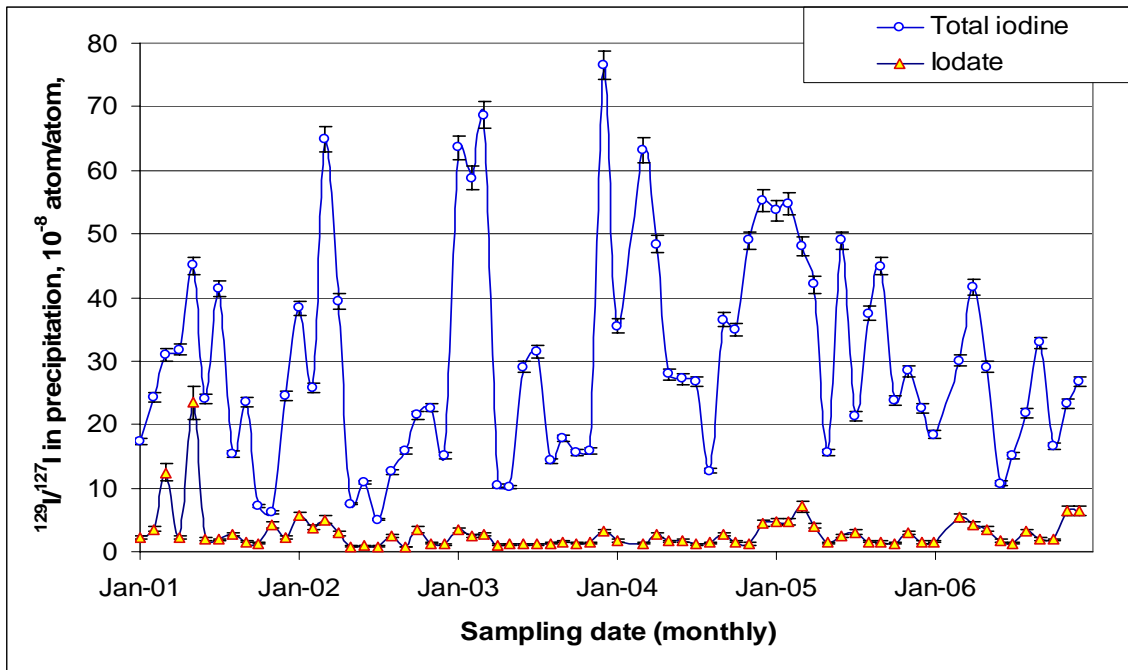


Figure 14. Variation of  $^{129}\text{I}/^{127}\text{I}$  values ( $10^{-8}$  atoms/atoms) for iodate and total iodine in precipitation from Roskilde, Denmark in 2001-2006 (the error bar shows the analytical uncertainty).

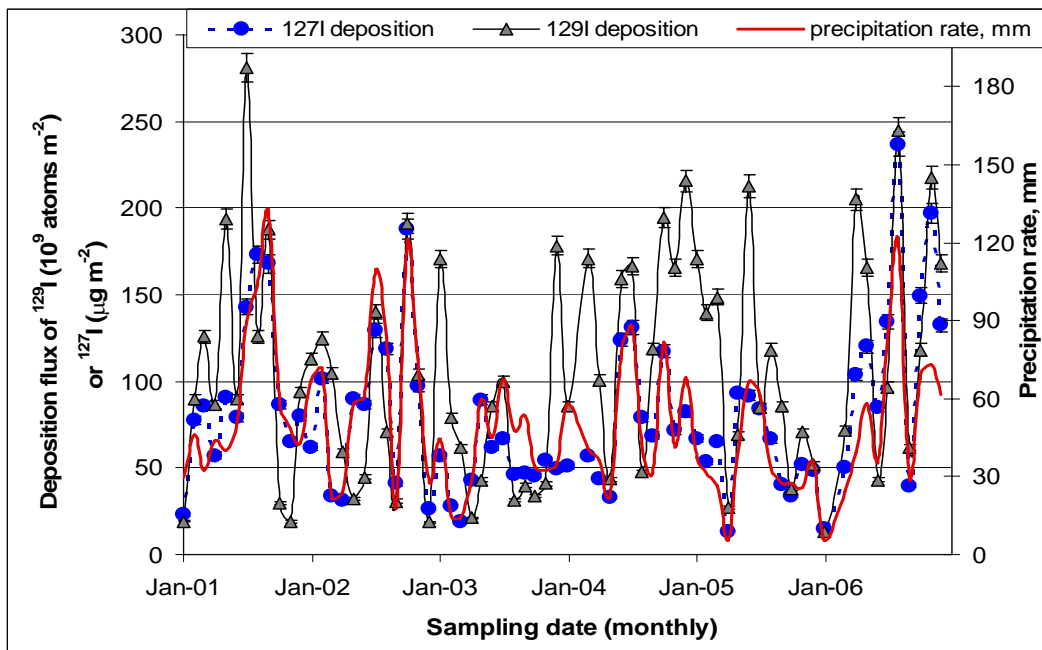


Figure 15. Variation of deposition flux of  $^{129}\text{I}$  and  $^{127}\text{I}$  ( $10^9$  atoms  $\text{m}^2$ ) by precipitation collected with a  $1 \text{ m}^2$  collector at Roskilde, Denmark in 2001-2006, the deposition rates (mm) are show as a solid line(red).

Based on these results, it is concluded that (1) an increased  $^{129}\text{I}$  level in precipitation is attributed to the release of  $^{129}\text{I}$  from reprocessing plants at La Hague and Sellafield, in which marine discharges is the major source of  $^{129}\text{I}$  through the re-emission of  $^{129}\text{I}$  discharged to the seas, particularly from the coastal areas. (2) Iodide as the dominant species of  $^{129}\text{I}$  is mainly attributed to the re-

emission of  $^{129}\text{I}$  from the coastal water in the English Channel, Irish Sea, North Sea, Kattegat and Norwegian Sea. While, iodate, as the major species of  $^{127}\text{I}$  in the precipitation, might results from its multi-origins, i.e. emission from the ocean as well as emission from terrestrial plants. (3) Based on the deposition fluxed of  $^{129}\text{I}$  and  $^{127}\text{I}$  measured in this work, an annual deposition of  $^{129}\text{I}$  over European can be estimated to be  $3.0 \text{ kg y}^{-1}$  in 2001-2006, and a total annual deposition of stable iodine on the surface of the earth to be about  $0.5 \times 10^{12} \text{ g y}^{-1}$ . (4) High concentrations of  $^{129}\text{I}$  in the coastal areas among the European seas and its specific origin from marine discharges of two European re-processing plants supply a unique environmental tracer. This work shows the potential application of  $^{129}\text{I}$  as tracer for the investigation of geochemical cycle and complex atmospheric chemistry of iodine.

### 3.2 Speciation of iodine in Lake Heimdalen, Norway

Lake water was collected from the Lake Heimdalen, Valdres, Norway, an area that was significantly affected by the Chernobyl fallout. The samples were subjected to fractionation shortly after collection in the laboratory using filtration ( $0.45 \mu\text{m}$  membranes), ultrafiltration with hollow fibre membranes having nominal molecular mass cut-off of 10 kDa and 3 kDa, respectively, and by using chromatography of non-polar (organic species retained by XAD-8 and XAD-4 resins). All fractions were submitted to the Risø laboratory for chemical separation of iodine and ICP-MS determination of  $^{127}\text{I}$ . The prepared targets were analysis by AMS in Uppsala University for determination of  $^{129}\text{I}$ .

The results show that both iodine isotopes are predominantly present as low molecular mass (LMM) species (Table 4, Fig. 16). Furthermore, a certain fraction of iodine (colloidal and LMM species) is associated with non-polar, organic species. The results indicate that the LMM fraction (less than 3 kDa) is somewhat more enriched in  $^{129}\text{I}$ , while the non-polar fraction seems to be somewhat more enriched in  $^{127}\text{I}$ .

Table 4. Activity concentrations of  $^{127}\text{I}$  and  $^{129}\text{I}$ , and the isotopic ratios of  $^{129}\text{I}/^{127}\text{I}$  in water fractions from Lake Heimdalen.

Fractions	$^{127}\text{I}$ conc., ng/ml	$^{129}\text{I}$ conc., $10^8$ at/L	$^{129}\text{I}/^{127}\text{I}$ , $10^{-8}$ at/at
Total	$0.31 \pm 0.01$	$15.5 \pm 0.9$	$10.4 \pm 0.7$
Total minus XAD 8 and 4	$0.27 \pm 0.01$	$13.1 \pm 0.6$	$10.0 \pm 0.6$
10 kDa	$0.27 \pm 0.01$	$13.8 \pm 0.7$	$10.6 \pm 0.6$
3 kDa	$0.27 \pm 0.01$	$14.9 \pm 1.3$	$11.5 \pm 1.1$

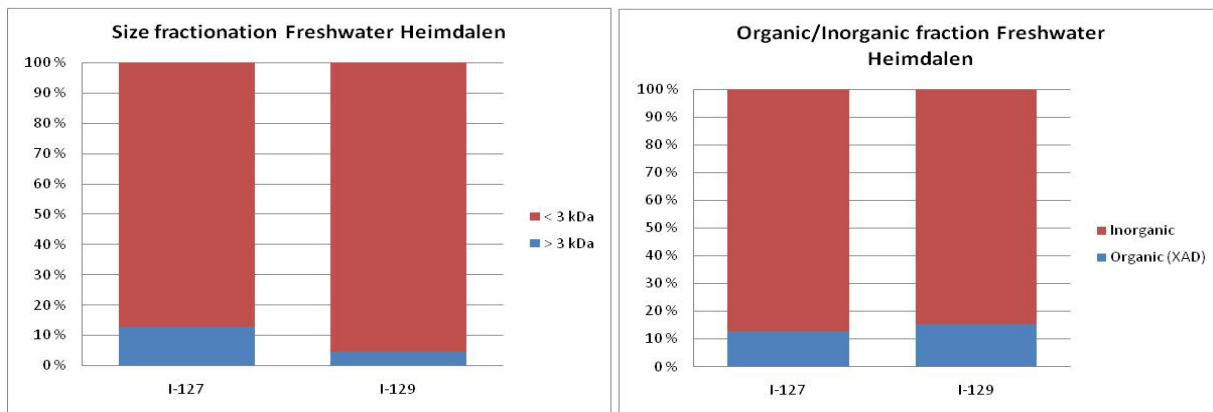
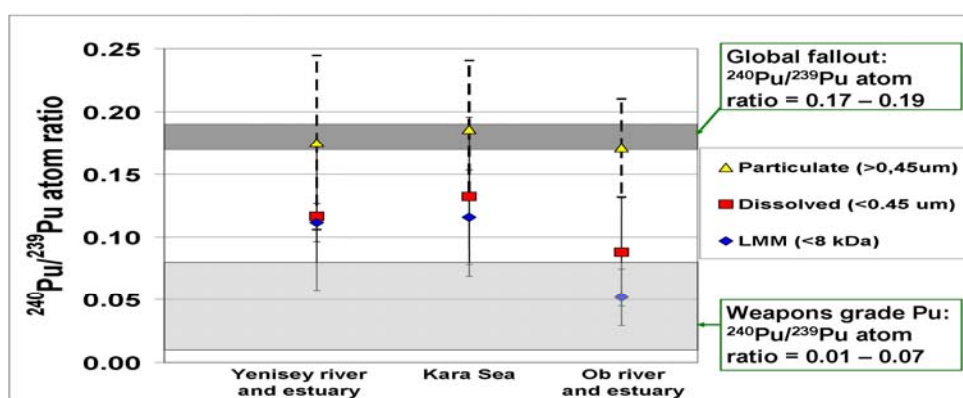


Figure 15. Relative distribution (%) of I-127 and I-129 present as LMM species (less than 3 kDa) and present as non-polar species (XAD-resins) in water from Lake Heimdalen.

### 3.3 Speciation of Pu in waters from River Ob and River Yenisey

Plutonium (Pu) isotope ratios can be used to differentiate between sources of Pu contamination such as nuclear weapon production, weapon fallout as well as accidental and routine releases from nuclear installations. To obtain information on the contamination level, speciation and sources of Pu in the Ob and Yenisey river systems (Siberia, Russia) and the adjacent Kara Sea, water samples collected in three areas were size fractionated onboard ship and the concentrations and atom ratios of  $^{240}\text{Pu}$  and  $^{239}\text{Pu}$  in obtained water fractions (i.e. particles, colloids and low molecular mass species) were determined by accelerator mass spectrometry (AMS). Results show a clear difference in speciation between high  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratio Pu derived from global weapon fallout and low  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratio Pu, presumably originating from weapons-grade Pu (Fig. 16).



**Figure 16.** Pooled  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios in the particulate, dissolved and LMM fractions in the Yenisey (river and estuary; particles  $n = 9$ ; dissolved  $n = 9$ ; LMM  $n = 4$ ), Kara Sea (particles  $n = 4$ ; dissolved  $n = 5$ ; LMM  $n = 3$ ) and Ob (river and estuary; particles  $n = 5$ ; dissolved  $n = 6$ ; LMM  $n = 5$ ), respectively.

In particular, the  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios ( $0.18 \pm 0.06$ ) for particles ( $>0.45 \mu\text{m}$ ) could not be distinguished from global fallout Pu ( $0.17 - 0.19$ ), whereas for low molecular mass (LMM;  $<8 \text{ kDa}$ ) species the Pu ratio was much lower than for global fallout Pu in both rivers. The difference was especially well pronounced in the Ob ( $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratio  $0.052 \pm 0.023$ ), where the difference was statistically significant (paired  $t$ -test,  $P=0.02$ ,  $n=4$ ). The low  $^{240}\text{Pu}/^{239}\text{Pu}$  atom ratios in filtered ( $<0.45 \mu\text{m}$ ) water and especially in the LMM fractions were observed at stations along the whole length of the two sampling transects, extending from the lower parts of the Ob and Yenisey Rivers and into the northern Kara Sea. This provides evidence of long range transport of Pu from low burn-up or non-civil sources into the Arctic Ocean. Pu appears to be predominantly in a dissolved form ( $<0.45 \mu\text{m}$ ) throughout the investigated area. The colloidal fraction ( $8 \text{ kDa} - 0.45 \mu\text{m}$ ) ranged within  $24 - 78 \%$  in the river systems and  $8 - 53 \%$  in the Kara Sea. Concentrations of  $^{239,240}\text{Pu}$  in filtered ( $<0.45 \mu\text{m}$ ) water were very low, ranging from  $2.6 - 40.6 \text{ mBq m}^{-3}$  in the rivers, somewhat higher than in the open Kara Sea ( $2.4 - 7.7 \text{ mBq m}^{-3}$ ) in agreement with previously reported values. The present results demonstrate how determination of concentrations and isotope ratios in individual fraction can provide a significant improvement in the interpretation of data compared to analysis of total samples.

## 4. Speciation of some radionuclides in sediments or soil

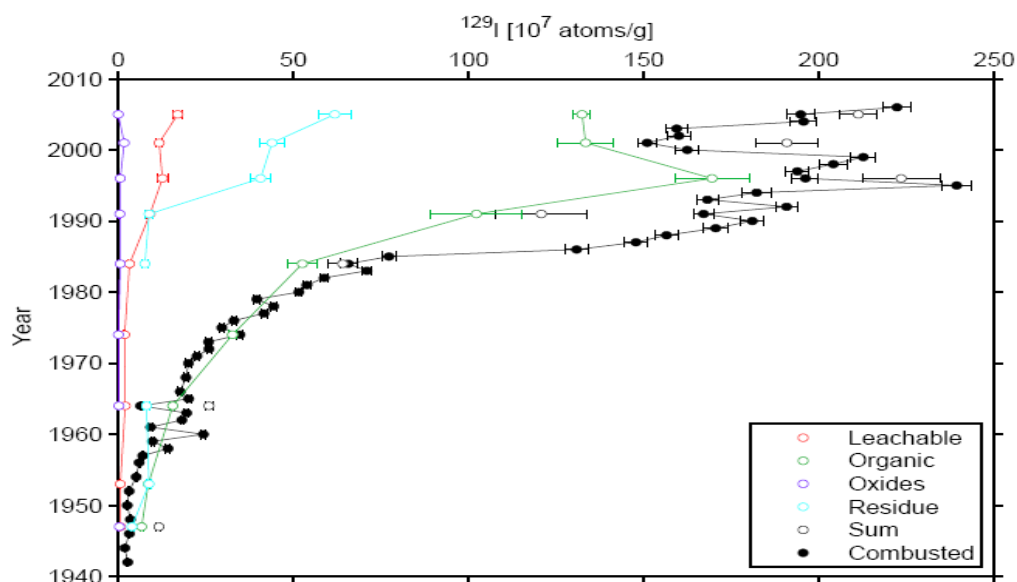
### 4.1 $^{129}\text{I}$ and $^{127}\text{I}$ and their speciation in lake sediment

Iodine is a biophilic element commonly occurring in trace to minor amounts in marine and terrestrial biota. Several radioactive isotopes of iodine have been released to the environment in relatively large amounts since the start of the atomic era during the 1940s. Although most of these isotopes decay within a short time, the long half-life (15.7 My) of  $^{129}\text{I}$  makes its geochemical behaviour comparable to the stable iodine. Presently, there are few data about the partitioning of the iodine isotopes in continental environment, which represent a large reservoir of the isotope. In the aim of capturing both the historical changes in  $^{129}\text{I}$  deposition since the start of the nuclear era and understand possible occurrence modes of iodine, we have measured  $^{127}\text{I}$  and  $^{129}\text{I}$  in a sequence of lake sediment located in central Sweden. The valve structure together with a well-defined Cs-137 Chernobyl peak provided constrained chronology of the sediment, which covers the period 1942-2006. All samples were measured for  $^{129}\text{I}$  and 9 selected samples were analyzed for the fractionation of  $^{129}\text{I}$  and  $^{127}\text{I}$  using the developed sequential leaching procedure (Fig. 17).

Scheme of the sequential extraction of iodine (both isotopes)

Speciation	Reagent	Temperature	Time
1. Leachable	1.0 M NaAc in 25% HAc (v/v), pH = 4	20° C	1 h.
2. Organic material*	0.3 M NaOH	60° C	4 h.
	5 - 6% NaOCl, pH = 12	96° C	1 h.
	0.3 M NaOH	60° C	30 min.
3. Reducible (Oxides)	0.04 M NH <sub>2</sub> OH.HCl and 0.01 M NaHSO <sub>3</sub> in 25% HAc (v/v)	80° C	6 h.
4. Residue*	NaOH fusion	550° C	8 h.

\* Iodine tracer (<sup>125</sup>I) was added for establishing recovery

Figure 17 Sequential extraction procedure for speciation of <sup>129</sup>I in sedimentFigure 18. Depth profile of <sup>129</sup>I concentrations for total iodine and different species of <sup>129</sup>I

The depth profile of <sup>129</sup>I in the sediment core (Figure 18) reflects impacts of the emission from the European nuclear reprocessing facilities since the early 1950's as well as that of the Chernobyl fallout in 1986. Results of the sequential leaching indicate that major part of both <sup>129</sup>I and <sup>127</sup>I is found within the organic fraction, whereas the reducible oxides fraction contains the lowest values (Figure 18, 19). The leachable and carbonate partitions show appreciable concentrations of both isotopes, but the values are lower than that found in the residual partition. The ratio of <sup>129</sup>I/<sup>127</sup>I in the different partitions shows a wide range reflecting mainly the two orders of magnitude difference in <sup>129</sup>I between post- and pre-Chernobyl period.



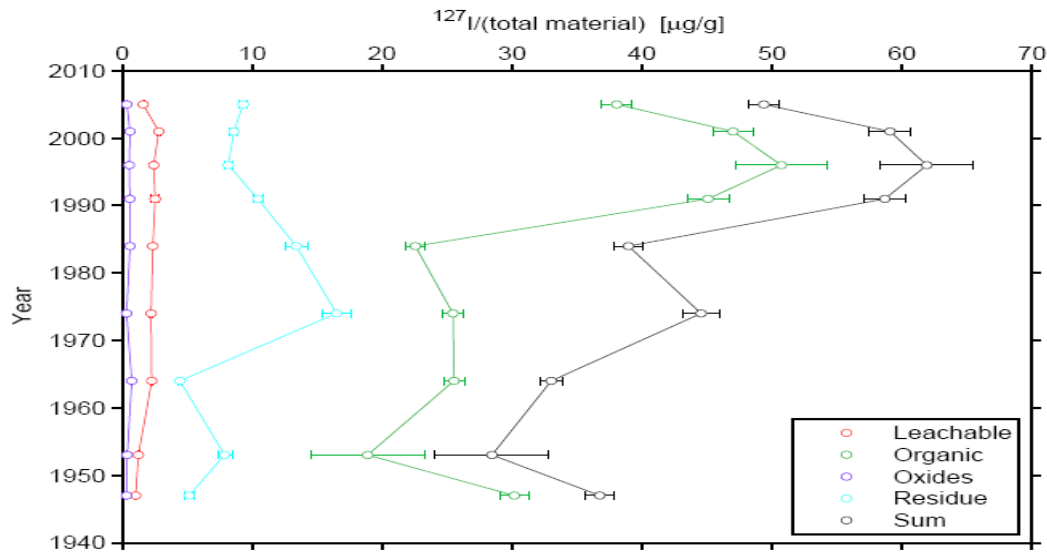


Figure 19. Depth profiles of  $^{127}\text{I}$  concentrations for total iodine and  $^{127}\text{I}$  associated with different extracted fraction

#### 4.2 Sequential extractions of soil samples for trace elements

In 2008, a large number of soil samples have been taken from various depths of three meter deep excavation holes in Finland. Soils of varying geotechnical character (organic soil, leaching horizons and undisturbed soil) were sieved to six grain size fractions. For each fraction, sequential extraction was carried out with a four steps process for chemical characterization of soils in Helsinki University. These tests are connected to a study where migration of long-lived anionic fission products of Tc, I etc. are being studied in soil.

The four step process is:

- Exchangeable fraction – 1M  $\text{BaCl}_2$
- Bound to carbonates - 30 ml of 1 M  $\text{CH}_3\text{COONH}_4$  in 25%  $\text{CH}_3\text{COOH}$  (pH 4)
- Bound to Fe and Mn oxides - 0.04 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25%  $\text{CH}_3\text{COOH}$  (pH 2)
- Bound to organics - 0.02 M  $\text{HNO}_3$  and 10 ml of 30%  $\text{H}_2\text{O}_2$
- Sparingly soluble – aqua regia

After each extraction concentrations Li, Na, Mg, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Sr, Mo, Cd, Cs and Pb were determined using ICP-MS.

#### 4.3 Sequential extraction of Ob and Yenisey sediments

The present study applied sequential extraction techniques to investigate the binding and mobility of plutonium in sediments from the rivers and estuaries of the Ob and Yenisey. As study sites,

the Ob and Yenisey are particularly interesting as both rivers have weapons-grade plutonium sources in their catchments areas, including the Russian plutonium production and reprocessing plants at Mayak, Tomsk-7 and Krashnoyarsk, and the Semipalantinsk nuclear weapons testing site in Kazakhstan. Plutonium activity and  $^{240}\text{Pu}/^{239}\text{Pu}$  ratios were determined using accelerator mass spectrometry (AMS). The main objective of the present study was to use sequential extraction to investigate the transfer and mobility of plutonium in the rivers and estuaries of the Ob and Yenisey. In the Yenisey River, a series of sediment samples were collected downstream from the KMCIC, to determine whether Pu speciation had changed with distance from the release point. Then, the speciation of Pu in river sediment samples was compared to that in the Yenisey estuary, wherein samples were also collected from areas having varying salinity and sediment composition.

Remobilisation of plutonium and other radionuclides from contaminated sediments, and subsequent transfer into water depends to a large extent upon their speciation, and particularly whether the contaminants are reversibly or irreversibly bound. In the present study, sequential extraction was applied to river and estuary sediments. The procedures, and the operationally-defined characterisation of the various fractions, are detailed below. Plutonium was extracted sequentially from dry sediment samples (10 g) using an established method (Oughton et al. 1992). All extractions were carried out by shaking the samples with 100 ml of extractants. The supernatant was separated from the solid by high-speed centrifugation (10000 g) and the solution filtered into a vial. The solid phases were washed (50 ml of distilled water) and centrifuged between each extraction step.

The extractants and conditions used were:

- Step 1, extract with sea water for 1 hr at room temperature (RT);
- Step 2, extract with ammonium acetate ( $\text{NH}_4\text{Ac}$ ) at sediment pH for 2 hr at RT;

Steps 1 and 2 remove the sediment pore water and easily exchangeable components.

- Step 3, extract with  $\text{NH}_4\text{Ac}$  at pH 5 for 2 hr at RT;
- Step 4, extract with hydroxylamine ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) at pH 2 (pH reduced with HCl) for 6 hr at  $80^\circ\text{C}$ ;

Steps 3 and 4 remove the redox sensitive and pH sensitive amorphous fractions from the sediments.

- Step 5, extract with hydrogen peroxide mixed with ammonium acetate ( $\text{H}_2\text{O}_2 + \text{NH}_4\text{Ac}$ ) and pH adjusted to pH 2 for 6 hr at  $80^\circ\text{C}$ ;

Step 5 is operationally defined as the extraction step that removes easily oxidized phases including organic material, or association with fuel particles.

- Step 6, extract by boiling the sediment in 7M  $\text{HNO}_3$  for 6 hr at  $80^\circ\text{C}$ .

This final step gives the irreversibly bound or "fixed" phase (slow kinetics, strong oxidation), while the residue would reflect that associated with mineral lattices.

The quality of the analytical results depends crucially on the details of the experimental procedure. If low-speed centrifugation is used to separate solid and supernatant, then colloidal material is included in the aqueous phase, whereas with high-speed ultra-centrifugation most of the colloidal material is included in the solid phase (Salbu 2000). Other factors influencing the analytical results can be solid/solution ratio, stirring, temperature, separation of phases and time of contact.

For all sediments studies, both estuarine and river, less than 15% of the plutonium was released in the first 4 extraction steps, with the majority being found in the H<sub>2</sub>O<sub>2</sub> and HNO<sub>3</sub> fractions. In these two fractions, Pu concentrations were greater than detection limits for all sediments analysed. For the estuarine sediments, Pu concentrations were below detection limits in the hydroxylamine fraction, hence the “lower” fractions were not analysed. For river sediments, levels were detectable in the initial fraction including hydroxylamine, and usually to the ammonium acetate fraction.

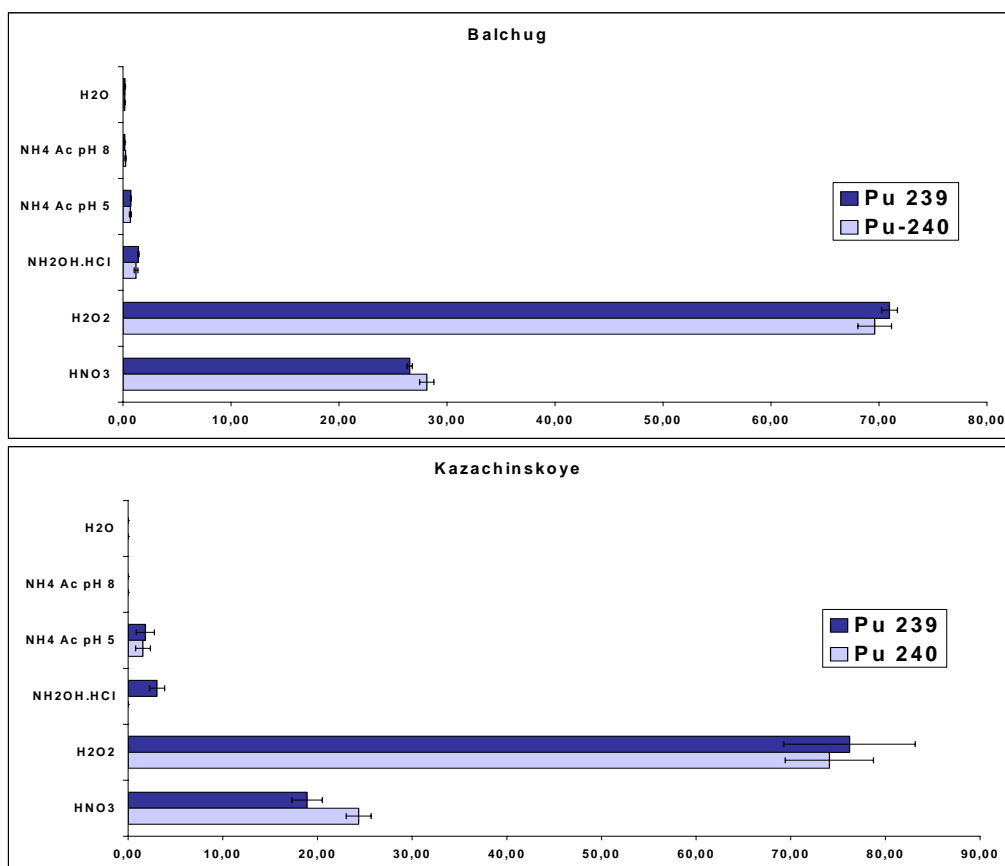


Figure 20 Sequential extraction results of Pu-239 and Pu-240 in sediment from Balchug and Kazachinskoye, Yenisey River.

Sequential extraction of the Yenisey River sediments indicated that up to 80 % of the plutonium was released in the H<sub>2</sub>O<sub>2</sub> fraction, which indicates that Pu is mobilized with weak oxidizing agents (Figure 20). Between 15 – 50 % of the Pu in Yenisey River sediments is associated with the irreversibly bound, HNO<sub>3</sub>-extractable fraction. Comparing river and estuarine sediments, the results

indicated a stronger binding of Pu to the estuarine sediments: in the latter case, between 60-100 % of the Pu was found in the HNO<sub>3</sub> fraction (Table 5).

Table 5. Sequential Extraction results Ob and Yenisey Estuaries samples

Sample site and extraction fraction	<sup>239,240</sup> Pu Bq/kg	<sup>239</sup> Pu Bq/kg	<sup>240</sup> Pu Bq/kg	% <sup>239</sup> Pu of total
Yenisey Estuary				
<b>Station 17</b>				
Total 0-1 cm	0.16 ± 0.02	0.116 ± 0.007	0.048 ± 0.008	
H <sub>2</sub> O <sub>2</sub> + NH <sub>4</sub> Ac, 6h, 80°C;	0.027 ± 0.003	0.024 ± 0.002	0.002 ± 0.001	10 ± 2
7M HNO <sub>3</sub> , 6h, 80°C	0.32 ± 0.02	0.227 ± 0.009	0.087 ± 0.009	90 ± 10
Total in extracts	0.34 ± 0.02	0.25 ± 0.01	0.09 ± 0.01	
<b>Station 21</b>				
Total 0-1 cm	0.61 ± 0.03	0.43 ± 0.01	0.18 ± 0.02	
H <sub>2</sub> O <sub>2</sub> + NH <sub>4</sub> Ac, 6h, 80°C;	0.47 ± 0.02	0.308 ± 0.008	0.16 ± 0.01	35 ± 2
7M HNO <sub>3</sub> , 6h, 80°C	0.83 ± 0.03	0.56 ± 0.02	0.26 ± 0.02	65 ± 4
Total in extracts	1.29 ± 0.05	0.87 ± 0.02	0.42 ± 0.02	

Although residues were not subjected to total digestion (e.g., alkali fusion or HF digestion), comparison of the sum of activities in extractions with the total activity determined in ashed and *aqua regia* digested sediments indicated Pu recoveries that were consistently higher than 100 %. This suggests that taking the sediments through the sequential extraction redox procedure may lead to a more efficient removal of Pu from sediment material. It is a well known problem that dry ashing can produce refractory oxides, which may lead to reduced solubility of Pu. On the other hand, wet ashing alone (i.e., direct digestion with strong acids or oxidising agents without dry ashing) is acknowledged to be a useful method when the organic content of sediments is not too high. One sample had a recovery in sequential extraction three times greater than that from dry ashing and *aqua regia* digesting, suggesting that direct wet ashing would have been preferable for analysis of the total activities in these sediments. Nevertheless, this discrepancy does not undermine the results and conclusions of the present paper. It is also possible that refractory PuO<sub>x</sub> may have remained in the residues from both sequential extraction and dry ashed sediments, however, previous methodological tests suggest that this is only a problem for samples contaminated by sources known to have a high initial refractory PuO<sub>x</sub> presence, such as those from weapon's testing.

Overall, the results are consistent with previously published data on Pu extractions, supporting a strong association of Pu with soils and sediments (Desideri et al. 2002; Skipperud 2005; Skippe-

rud et al. 2000a; Skipperud et al. 2000b). Both Yenisey River sediments (Figs 16) showed a high percentage within the H<sub>2</sub>O<sub>2</sub>-extractable fraction; from 47 to 80 %. This may reflect a high organic content of the soils and sediments, as H<sub>2</sub>O<sub>2</sub> is effective at dissolving organic material, as well as mobile Fe and Al oxides not dissolved by the previous extraction stages. Pavlotskaya (2002) found an important association of Pu with all the basic fractions (both humic and fulvic acids) of the total organic component of floodplain deposits and bottom sediments in the Yenisey River. Those results indicated that organic carbon was found in comparable amounts in all investigated bottom sediments in the river. They suggested that the fact that there is a positive correlation between Pu and total organic carbon (TOC) distributions illustrates the effect of organic matter on the migrational behaviour of plutonium. It is well known that transuranic elements can form stable complexes with humic and fulvic acids. These acids may either suppress (humic acids) or initiate (fulvic acids) migration of radionuclides (Pavlotskaya et al. 2003).

The high extractability into H<sub>2</sub>O<sub>2</sub> could also reflect the presence of Pu associated with UO<sub>x</sub> fuel particles, as uranium oxide is dissolved under oxidising conditions. For example, in Chernobyl-contaminated soils collected from close to the reactor, where the contamination was largely due to fuel particles, a relatively large fraction of all radionuclides was found to be associated with the H<sub>2</sub>O<sub>2</sub> fraction (Oughton et al. 1992). Officials from the Russian Ministry of Atomic Energy have declared that, unlike other similar Russian plants, the KMCIC has been accident-free since 1958, when the first reactor was started up. However, hot particles have been found in the Yenisey flood plain on several occasions (Bolsunovsky and Tcherjezian 2001). The ratios of Pu- and Cs-isotopes in the particles are indicative of their reactor origin, and closer studies of the different particles and their Pu- and Cs-isotope ratios has led to the conclusion that they were formed 30 and 20 years ago. This suggests that there have been at least two accidents or other “uncontrollable releases” from the KMCIC reactors, with part of the fuel released into the Yenisey River (Bolsunovsky and Tcherjezian 2001).

As evidence against the high H<sub>2</sub>O<sub>2</sub> extractability reflecting fuel particle content, the results showed no decrease in the H<sub>2</sub>O<sub>2</sub>-extractable fraction with increasing distance from plant. In most of the sediment samples, the <sup>240</sup>Pu/<sup>239</sup>Pu isotope ratios were relatively constant in all extraction fractions, but increased with distance from the plant, reflecting an increased influence from weapons testing sources. On the other hand, in a few samples there was a tendency for ratios to be lower in the H<sub>2</sub>O<sub>2</sub> fraction, which could reflect either the presence of particles or a strong initial association of Pu with organic material close to the source, and resistance of this material to weathering with transport downstream.

Although there was little change in Pu binding to river sediments downstream from the KMCIC, a marked increase in binding strength is apparent in the estuarine sediments. This transfer

of Pu from the H<sub>2</sub>O<sub>2</sub> fraction to the HNO<sub>3</sub> fraction could reflect a number of processes: i) a gradual fixation of Pu from organic components to the mineral component of the sediments; ii) an increased contribution from mineral-particle bound Pu from the catchment's run-off; iii) release of Pu due to weathering of fuel particles, or iv) a loss of Pu from organic components to the water phase as a result of the increased salinity and pH in the estuary, which may in turn be resorbed within amorphous Fe/Mn oxides/hydroxides. Again, information on isotope ratios can elucidate some of these hypotheses, particularly comparison of ratios and activities in the H<sub>2</sub>O<sub>2</sub> and HNO<sub>3</sub> fractions. Low Pu isotope ratios findings in colloids and low molecular mass fractions in water from the Ob and Yenisey Estuaries (Lind et al. 2006) support the latter theory (iv). Furthermore, remobilisation of elements from organic bound components has been demonstrated for other elements (like Al, Co, Cs, etc.) when freshwater meets higher salinity water (Oughton et al. 1997; Standing et al. 2002a; Teien et al. 2006); and enhanced collagulation and sedimentation of colloids in estuaries due to increased ionic strength is known to be an important chemical process in estuaries, as is the precipitation of Fe oxides and hydroxides. This also highlights the importance of understanding the macrochemical influence on trace levels of Pu in environmental systems, since both Pu chemical properties and the behaviour of the components to which it is bound or associated influence trace element mobility and speciation.

## 5. Speciation of some radionuclides in aerosols and particles

### 5.1 Iodine isotopes (<sup>127</sup>I and <sup>129</sup>I) in aerosols

Aerosols represent a potential carrier of iodine in the continental atmosphere where aerosol contribution to the iodine budget is scarce and even lacking for most parts of the world. We here present data on distribution of iodine isotopes (<sup>127</sup>I and <sup>129</sup>I) in aerosols covering the period 1983 to 2000 from two sites (67.84°N, 20.34°E and 56.08°N, 13.23°E) in Sweden. Aerosols have been collected by the Swedish Defence Research Institute (FOI) for the surveillance program of radioactivity in airborne particulate matters. Aerosols were weekly trapped in glass fibre filters (0.58 m×0.58 m) at an air-flow rate of 84 cm/s and a trapping efficiency > 99% for the > 0.3 μm particles.

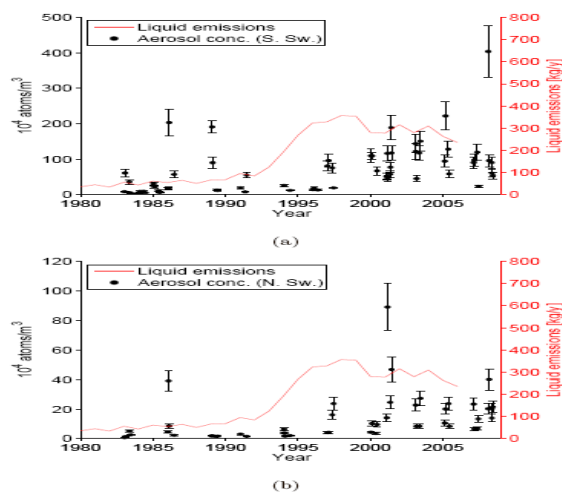
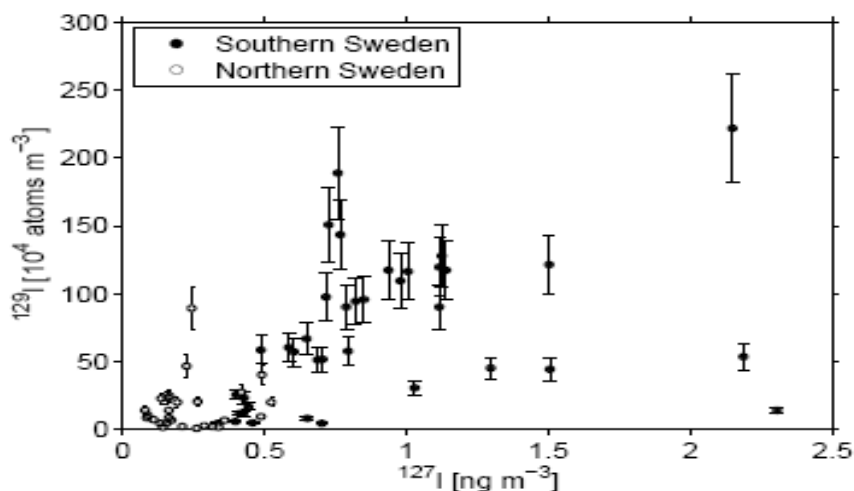


Figure 21 <sup>129</sup>I concentration in (1) southern Sweden (Ljungbyhed) and (b) northern Sweden (Kiruna) together with the liquid <sup>129</sup>I discharge from reprocessing plants at Sellafield and La Hague



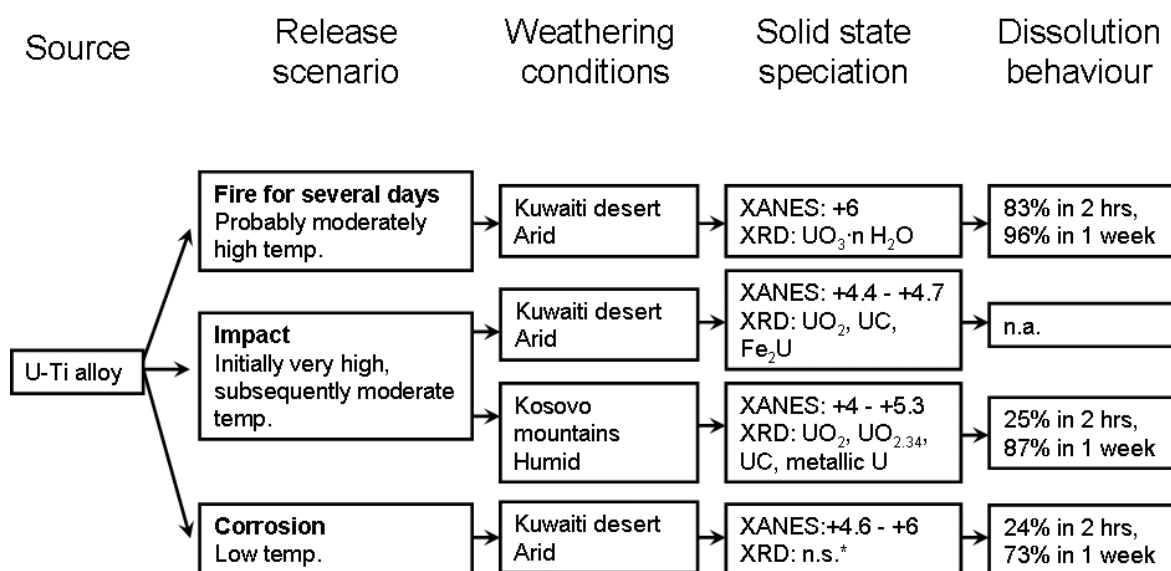
Figures 21 and 22 shows the variations of concentrations of  $^{129}\text{I}$  and  $^{127}\text{I}$  in the aerosol collected in Sweden from 1980 to 2008. Concentrations of  $^{127}\text{I}$  in the two sites vary between 0.14 and 2.31  $\text{ng/m}^3$  air while the range of  $^{129}\text{I}$  is  $(1 - 203) \times 10^4 \text{ atoms/m}^3$  air and isotopic ratios of  $^{129}\text{I}/^{127}\text{I}$  (atoms/atoms) range at  $(1 \text{ and } 23.9) \times 10^{-8}$ . Annual mean concentrations are consistently higher at the southern site with a significant difference in the relative concentrations between the sites, being 9 times higher for  $^{129}\text{I}$  and only 2 times for  $^{127}\text{I}$ . There is no clearly observable temporal trend and the correlation between the two isotopes is not strong ( $r^2=0.6$ ) suggesting effects from variable sources and complex atmospheric recycling. Both isotopes have anthropogenic sources (mainly fertilizers for  $^{127}\text{I}$  and nuclear fuel reprocessing for  $^{129}\text{I}$ ), but the natural source is dominant for  $^{127}\text{I}$  compared to  $^{129}\text{I}$ . A mixed proportion of sea surface volatilization and gaseous emission, particularly for the  $^{129}\text{I}$  suggest that aerosols fallout comprises not more than 35% and 25% of  $^{127}\text{I}$  and  $^{129}\text{I}$ , respectively, of the total fallout which is dominated by the wet (precipitation) component.

## 5.2 Speciation of radionuclides in radioactive particles

A combination of synchrotron radiation based X-ray microscopic techniques ( $\mu\text{-XRF}$ ,  $\mu\text{-XANES}$ ,  $\mu\text{-XRD}$ ) applied on single depleted uranium (DU) particles and semi-bulk leaching experiments have been employed to link the potential bioavailability of DU particles to site-specific particle characteristics. The oxidation states and crystallographic forms of U in DU particles have been determined for individual particles isolated from samples collected at different sites in Kosovo and Kuwait that were contaminated by DU ammunition during the 1999 Balkan conflict and the 1991 Gulf war. Furthermore, small soil or sand samples heavily contaminated with DU particles were subjected to simulated gastrointestinal fluid (0.16 M HCl) extractions. Characteristics of DU particles in Kosovo soils collected in 2000 and in Kuwait soils collected in 2002 varied significantly

depending on the release scenario and to some extent on weathering conditions. Oxidized U (+6) was determined in large, fragile and bright yellow DU particles released during fire at a DU ammunition storage facility and crystalline phases such as schoepite ( $\text{UO}_3 \cdot 2.25 \text{H}_2\text{O}$ ), dehydrated schoepite ( $\text{UO}_3 \cdot 0.75 \text{H}_2\text{O}$ ) and metaschoepite ( $\text{UO}_3 \cdot 2.0 \text{H}_2\text{O}$ ) were identified (Fig. 23).

As expected, these DU particles were rapidly dissolved in 0.16 M HCl indicating a high degree of potential mobility and bioavailability. In contrast, the extraction of samples contaminated with DU particles originating either from corrosion of unspent DU penetrators or from impacted DU ammunition appeared to be much slower as uranium was less oxidized (+ 4 to +6). Crystalline phases such as  $\text{UO}_2$ , UC and metallic U or U-Ti alloy were determined in impacted DU particles from Kosovo and Kuwait, while the  $\text{UO}_{2.34}$  phase, only determined in particles from Kosovo, could reflect a more corrosive environment. Although the results are based on a limited number of DU particles, they indicate that the structure and extractability of DU particles released from similar sources (metallic U penetrators) will depend on the release scenarios (fire, impact) and to some extent environmental conditions. However, most of the DU particles (73-96 %) in all investigated samples were dissolved in 0.16 M HCl after one week indicating that a majority of the DU material is bioaccessible.



**Fig. 23.** Summary of the results obtained in the present work.

The present results clearly indicate that although the sources are similar (DU penetrators), the release scenarios are of key importance; DU particles released during the fire in an ammunition storage facility fire are more oxidized and more bioaccessible than DU particles originating from impact or corrosion (Fig. 23).



## 6. Sorption experiments: association of Pu, Am and Cs with different geological materials

The development of nuclear energy resulted in accumulation of radioactive waste of different activity in various countries. The isolation of such waste for a long period of time requires reliable engineered and natural barrier systems where migration of radionuclides should be retarded through different physical and chemical processes. An understanding of geochemical processes affecting the contaminant transport is necessary for assessment of migration of radioactive contaminants in the repository environment. One of the most important issues of this is sorption to clay minerals. The fate and transport of dissolved contaminants in the geological environment to a great extent are determined by radionuclide interactions with mineral surfaces. The retardation of radionuclides depends on geochemical processes which include aqueous speciation, redox and interface reactions, precipitation and dissolution of minerals as well as colloids. Changes in geochemical conditions (mineral and solution composition, pH, Eh and temperature) can considerably affect the behavior of different radionuclides. To assess migration of radioactive contaminants in the repository environment it is essential to identify important geochemical processes affecting the contaminant transport.

The retardation and engineering extraction of cesium are difficult problems. For sorbing radionuclides, such as Cs, long time is required to reach steady-state conditions and its sorption-desorption behaviour in clay minerals is complicated (Kozak et al. 1999, Krumhansl et al. 2001).

The selective adsorption of Cs by mica-like minerals, such as illite  $\{(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,H_2O]\}$ , has been attributed to the large ionic radius, un-complexing nature and especially to its low hydration energy. Although cations with similar charge and ionic radii are expected to compete with cesium, the sequence of sorption ability of alkali elements  $Na^+ < K^+ < Rb^+ < Cs^+$  is in good agreement with the sequence of effective ionic radii of alkali elements and the sequence of single ion hydration enthalpies of alkali elements (Kemner et al. 1998). In the clay mineral muscovite, a fixed negative charge arises primarily from isomorphous substitution of  $Al^{3+}$  for  $Si^{4+}$  in the tetrahedral sheet comprising the siloxane site. In illite mineral whose composition is very close to that of muscovite, isomorphous substitution of  $Al^{3+}$  for  $Si^{4+}$  and partly of  $Fe^{2+}$  and  $Mg^{2+}$  for  $Al^{3+}$  enhances the stability of the  $Cs^+$ -siloxane surface complex. Strongly sorbed  $Cs^+$  on fractured edge sites (FES), external basal sites or within the interlayer exists as an inner-sphere, dehydrated surface complex, which is usually much more stable than outer-sphere complexes (Onodera et al., 1998).

Plutonium comprises only small part of total activities even in spent fuel, however, the toxic effect of  $^{239}Pu$  (half-life is 24 400 years) will be dominant for thousands of years after the decay of short-lived fission products. Plutonium can exist in 4 oxidation states under the conditions and pH

typically present in the natural environment. Plutonium exhibits a complicated redox behaviour that permits transformation of one oxidation state into another. Under oxidizing conditions, Pu(IV), Pu(V), and Pu(VI) are common, whereas, under reducing conditions, Pu(III) and Pu(IV) would exist (Silva et al, 1995). Am in ground water exists only as the trivalent  $\text{Am}^{+3}$  ion.  $\text{Am}^{+3}$  ions form positively charged or neutral hydroxo complexes  $\text{AmOH}^{+2}$ ,  $\text{Am}(\text{OH})^{2+}$ , and  $\text{Am}(\text{OH})_3$ ; in the presence of  $\text{CO}_3^{-2}$ , the species of  $\text{AmCO}_3^+$ ,  $\text{Am}(\text{CO}_3)^{2-}$  and  $\text{Am}(\text{CO}_3)_3^{-3}$  are characteristic (EPA, 1999). The insoluble hydrated carbonate  $\text{An}_2(\text{CO}_3)_3 \cdot 2-3\text{H}_2\text{O}$  can precipitate and reduce the An(III) concentration in solution at low pH with increasing carbonate concentration. In natural waters carbonates can compete with hydrolysis reactions and mixed hydroxocarbonates  $\text{An}(\text{III})(\text{OH})(\text{CO}_3)$  and  $\text{An}(\text{IV})(\text{OH})_2\text{m}(\text{CO}_3)_n$  can be limiting species for the solubility of actinides. Under conditions typical for cementitious repositories where calcite is the dominant alteration product the formation of carbonate and hydroxycarbonate species ( $\text{PuO}_2\text{CO}_3^-$ ,  $\text{PuO}_2(\text{CO}_3)_2^{3-}$ ,  $\text{PuO}_2(\text{CO}_3)_3^{5-}$ ,  $\text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$ ,  $\text{Pu}(\text{OH})_4(\text{CO}_3)_2^{4-}$ ) can affect plutonium adsorption. Under conditions of low pH and high concentrations of dissolved organic carbon, it appears that plutonium-organic complexes can control adsorption and mobility of plutonium in the environment. Plutonium can adsorb on different geological materials from low to extremely high affinities with  $K_d$  values typically ranging over 4 orders of magnitude (from 11 to 330 000 mL/g) (Choppin et al., 1997). The changes in oxidation state of plutonium considerably affect its mobility in the environment. The environmental mobility of Pu(IV) from 2 to 3 orders of magnitude is lower than the mobility of Pu(V) or Pu(VI). Pu(III) due to its negative potential at higher pH can be readily oxidized by water at even neutral pH levels (Sanchez et al., 1985; Duff et al., 1999). Therefore, it is supposed that plutonium exists in +4, +5 and +6 oxidation states in natural environment. Disproportionation reactions have negligible effect on the plutonium oxidation state in natural systems with typically low concentrations (Duff et al., 1999). However, interactions with various minerals (e.g., goethite ( $\square$ -FeOOH), manganite (Mn(III)O<sub>2</sub>H), hausmannite (Mn(II/III)<sub>3</sub>O<sub>4</sub>), pyrolusite ( $\square$ -Mn(IV)O<sub>2</sub>) and birnessite ( $\square$ -Mn(IV)O<sub>2</sub>) with different redox potentials can change plutonium sorption characteristics by either oxidizing or reducing the sorbed species (Morgenstem & Choppin, 2002; Panakl & Nitsche, 2001; Berthard & Chppin, 1985). The published material provides much useful information about the mobility of plutonium, but some of these publications are contradictory, especially regarding the oxidation state, speciation, coprecipitation and sorption of actinides on oxides and calcite minerals at high pH.

Recently in different publications the association of actinides with oxides and application of different methods for speciation determination have been discussed. Data on association of plutonium with geological material is rather contradictory. McDonald et al. found that plutonium is predominantly associated with Fe, Mn oxyhydroxides (43.9 %) and organic complexes (43.5%) in the Irish Sea sediments, whereas McCubbin et al. reported 37 % of Pu as upper limits for the fraction

associated with magnetic + nonmagnetic Fe minerals in samples collected at close area of the Cambrian coast (Turner & Sassman, 1996; Lujaniene et al. 2007). Data was obtained using different methods: sequential extraction and magnetic extraction technique. Using selective extraction procedures was shown that Pu was associated predominantly with Mn oxides. The dominant association with the Mn oxides occurred despite the fact that the Fe oxides were present at concentrations higher by factor from 2 to 30 in comparison with the Mn oxides.

X-ray absorption spectroscopy, in combination with microautoradiography, electron microprobe, and petrographic microscopy techniques were used to detect the spatial distribution of sorbed Pu on the zeolitic Topopah Spring Tuff sampled at Yucca Mountain. Large concentrations of sorbed Pu were associated with smectite and Mn oxide fracture minerals. Sorption of Pu to Fe-rich regions was not observed. In a similar experiment in which Tuff was used, Pu was concentrated in the zones of altered orthopyroxenes. These zones contained Fe-rich amorphous materials. Sanchez et al. found that adsorption Pu onto goethite is related to different hydrolytic character of Pu (IV) and Pu(V) in the solution and occurs for Pu (IV) at pH 3 to 5 and for Pu(V) at pH 5 to 7. It was determined also that an increase in ionic strength did not affect the adsorption of Pu on goethite (Morgenstern & Choppin, 2002). It was shown that Pu(V) and Pu(IV) sorption on  $\gamma$ -alumina and goethite generally increases as a function of pH. Pu(IV) sorption on goethite occurs at pH values between 2 and 6, whereas Pu(V) sorption on goethite occurs at pH values between 4 and 8. Pu(V) sorption on  $\gamma$ -alumina also occurs at pH values between 6 and 10 (Turner, 1995). Pu sorption on amorphous silica or on quartz is expected to occur at much lower pH values because of the much lower pH ZPC (the pH point of zero charge), at about 2, in contrast to that of the iron and aluminium hydroxides, which generally occurs between 7 and 9.

Unlike other heavy metals, Cs does not have affinity to sorb or co-precipitate with Fe-hydroxides. However, the coatings of organic matter, iron oxides and calcite usually present in natural environment can inhibit the caesium sorption to clay minerals. The mechanisms of these interactions are poorly understood. The aim of this study was the determination of Cs, Pu and Am  $K_d$  values and to study behaviour of radionuclides under conditions expected at the site.

In this work, samples of loam originated from the Galilaukė site (Galilaukė clay) and Triassic clay from industrial Šaltiškiai quarry (Šaltiškiai clay) selected as a candidate for the engineered barrier of Lithuanian near-surface repository were taken for laboratory investigations. X-ray diffraction analyses show about 14 % of montmorillonite in Šaltiškiai clay. The mineral composition of Šaltiškiai clay was estimated as follows: SiO<sub>2</sub> – 45.51%, Al<sub>2</sub>O<sub>3</sub> – 13.49%, Fe<sub>2</sub>O<sub>3</sub> – 5.17% MgO – 2.99%, CaO- 12.88%, Na<sub>2</sub>O – 0.28 %, K<sub>2</sub>O – 5.02%, TiO<sub>2</sub> – 0.43%, total S – 0.16%, loss on ignition 13.95% (Rauret et al. 1999). Samples of the natural groundwater (GW) and the synthetic rain water (SRW) (filtered through the 0.45  $\mu$ m membrane filter) were put into contact with the solidi-

fied locally available Portland cement (from “Akmenės cementas”) to obtain the extracts of groundwater - cement water (GWCW) and synthetic rainwater - cement water (SRWCW) solutions. The laboratory batch method was used for the determination of  $K_d$  values. The protocol of the standard method used at Pacific Northwest National Laboratory for measuring laboratory batch  $K_d$  values was applied (Rauret et al. 1999). Two sets of solutions were prepared for batch experiments.

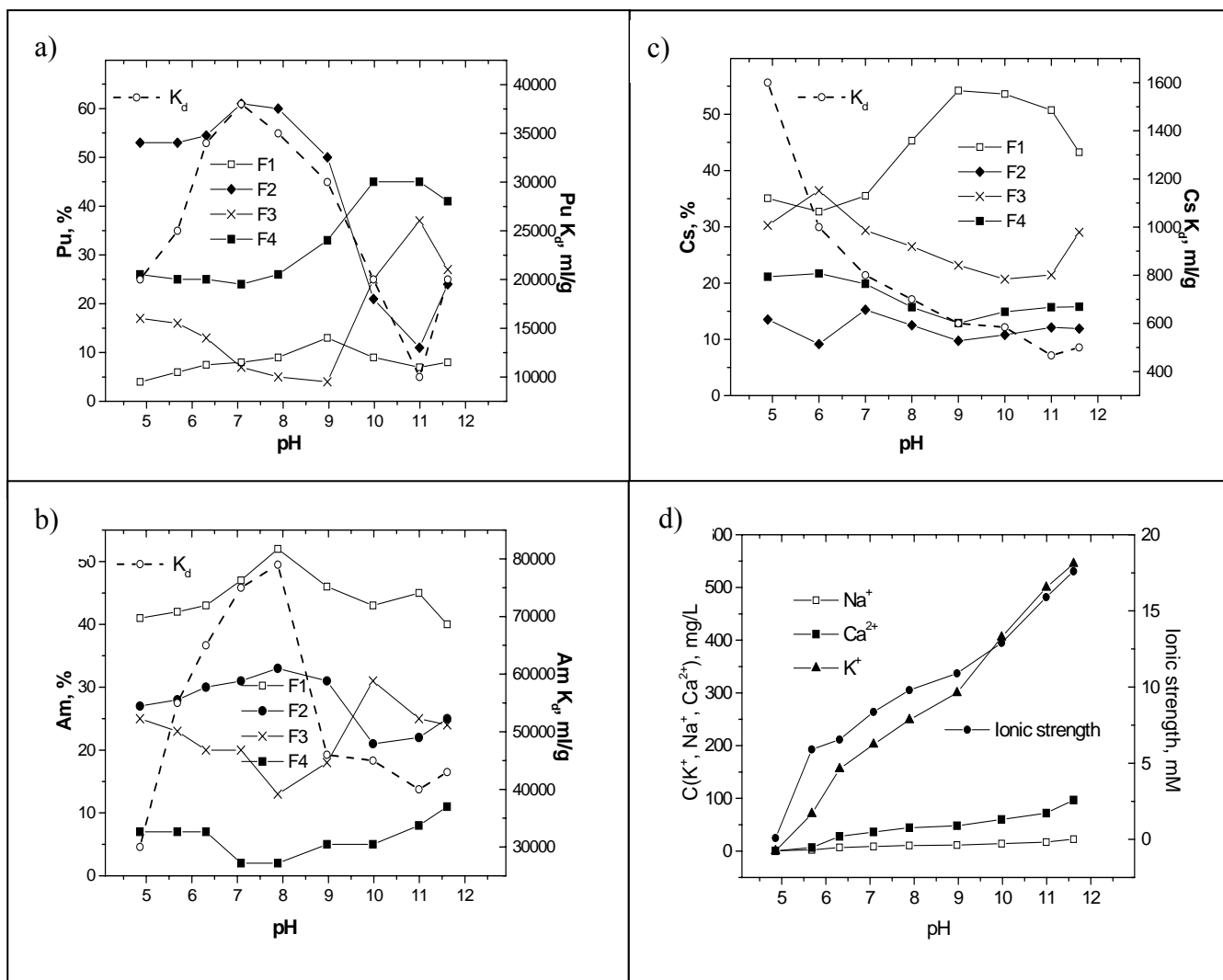


Figure 24. Effect of pH on sorption of Pu and Am and Cs to Treassic clay: a)b)c)  $K_d$  values and Pu/Am speciation in clay (F1 – exchangeable and carbonates; F2 – oxides; F3 – organic matter; F4 – residue) d) ionic strength and initial composition of sorption solution.

The tests were performed under atmosphere conditions at 25°C. The sample was disaggregated by an ultrasonic method. The total concentration of cesium in solutions was  $2.30 \times 10^{-10}$  mol/L and the solutions were labeled by  $^{134}\text{Cs}$ .  $^{134}\text{Cs}$  activities were measured with an intrinsic germanium detector (resolution 1.9 keV/1.33 MeV and the relative efficiency 42 %). Measuring time varied according to sample activities. An efficiency calibration of the system was performed using calibra-

tion sources (prepared from a solution supplied by Amersham, UK) of different densities and geometry that were close to measured samples. Accuracy and precision of analysis were tested in intercomparison runs, organized by the Riso National Laboratory, Denmark. Precision of  $^{134}\text{Cs}$  measurements by gamma spectrometry was  $\leq 3\%$ . The sorption of cesium on centrifuge bottle walls was detected to be less than 2 %.

Pu(IV) was used in sorption experiments. The oxidation state purity of Pu(IV) stock solution was analyzed by solvent extraction at pH 0.5 using 0.5 M TTA as extractant (Dumat & Staunton, 1999). Typically  $96 \pm 3\%$  of the total plutonium was found in the tetravalent state.

From 1 to 12 % of Pu(IV) and from 5 to 15% Am were found adsorbed to the tube walls for samples containing geological materials. The initial concentration of Pu(IV) and Am was adjusted by this fraction.

Pu(IV) and Am spikes were added for a final concentration of  $\sum\text{Pu} = 1.10 \times 10^{-9}$  mol/L and  $\text{Am} = 3.20 \times 10^{-11}$  mol/L. Solids were separated from the liquid by centrifugation for twenty minutes at 10,000 g after 10, 15 and 45-days contact. Plutonium in the solution and the geological material were determined after radiochemical separations based on the extraction chromatography. The UTEVA and TRU columns from Eichrom Industries were used and activities were measured by alpha spectrometry.  $^{242}\text{Pu}$  and  $^{243}\text{Am}$  were used as tracers in the separation procedure.  $K_d$  values of Cs and Pu were determined from three replicates. Details of experiment are described in previous publication (Lujanienė et al. 2003).

The association of sorbed Cs, Pu and Am in geological material was determined using sequential extraction procedure (Ewais et al. 2000; Lujanienė et al. 2005). Exchangeable and carbonate bound Cs was extracted using 1M  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  pH 5  $\text{CH}_3\text{COOH}$  extracting agent.

Sorption experiment (Fig.24) with synthetic rain water (SRW) and natural clay was undertaken in order to estimate conditions as close as possible to natural ones at low and intermediate waste repository when the rain water breakthrough can cause dissolution of cement. Composition of synthetic water was evaluated on the bases of long-term observations performed at the site. Local Portland cement which will be used in the repository was solidified, crashed and applied for cement water preparations. Cement-rain water solutions of different dilutions having characteristic gradient of pH, ionic strength and concentrations Ca, Na, K, and other ions were prepared. It was supposed that in natural conditions an increase in pH (up to 10-13) would be accompanied with an increase in ionic strength and concentration of main ions, and this integrated impact can be different from that of usually observed under laboratory experiments, when pH dependences are obtained under simplified fixed ionic strength conditions. Obtained Cs  $K_d$  values was in good agreement with presented ones in various publications and ranged from 9700 to 450 ml/g. The highest values were detected for natural groundwater. The Šaltiškiai clay exhibited the high retention capacity towards cesium.

During interaction of precipitation and ground water with cements and concrete the leached NaOH, KOH and later Ca(OH)<sub>2</sub> result in increase of pH (up to 10-13) and concentrations of K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, NH<sub>4</sub><sup>+</sup> ions in the surrounding solution. The retardation of Cs can be effected by the dissolved cations. The low K<sub>d</sub> values were expected under alkaline conditions (pH 11-13), however, comparatively low K<sub>d</sub> values determined in experiments using SRW indicated that acid rainwater can affect the cesium retention. It is generally recognised now that the sorption of <sup>137</sup>Cs by soil and sediments is mainly determined by specific sorption onto illite clay minerals, but such parameters as pH and organic matter were found to play less important role in the adsorption of Cs. Actually, a trace amount of illite can effectively immobilise caesium even in the presence of a high content of organic substances (up to 80%) in soil and bottom sediments. Cs extracted and found in the exchangeable, carbonate bound fraction can be regarded as sorbed to the surface, planar and to wedge sites from which it can be desorbed by NH<sub>4</sub><sup>+</sup> ions. Cs found in residual fraction can be attributed as specifically and strongly bound as well as really fixed which was not extracted even with aqua regia.

Pu and Am K<sub>d</sub> values obtained for Triassic clay from industrial Šaltiskiai quarry ranged from 15000 to 21000 ml/g and from 15000 to 80000 ml/g, respectively. Pu(IV) was used in sorption experiments. Experiment carried out with SRWCW solutions (pH 5-12) and Triassic clay indicated variations in PuK<sub>d</sub> values from 38000 to 10000 ml/g (Fig. 24). The highest values were observed at pH 6 -8. To understand better the sorption behaviour of plutonium isotopes, their association with geological material was studied using sequential extraction method. The information on speciation is especially important for evaluation of the mobility and bioavailability of radionuclides. However, the direct determination of speciation or binding forms of radionuclides is difficult and often hardly possible due to very low concentrations of radionuclides typically found in the environment. Therefore, the determination of physicochemical forms or fractions in practice, using sequential extraction methods, is a reasonable compromise to evaluate the associations of radionuclides in the environmental samples (e.g. with carbonate minerals, Fe/Mn oxides and organic substances). Recently obvious advantages were achieved in analyses of speciation of heavy metals (McDonald et al., 2004). The most widely used sequential procedure proposed by Tessier et al.(1979) was modified in order to avoid the mentioned problems by changing the extraction time, the extractant-sample ratio, the reagent concentration and the extraction temperature. However, no standardized sequential extraction protocol currently exists for determination of actinide associations. Therefore, the standard sequential extraction procedure protocol of the Standards, Measurements and Testing Programme (formerly BCR) of the European Commission was applied (Rauret et al., 1999).

Results of sequential extractions showed variations in association of Pu with different geochemical fractions (Fig. 24). The received fraction distribution can be explained by combined ef-

fects of adsorption, co-precipitation on Fe, Al and Mn oxyhydroxides as well as ion exchange reactions with clay minerals. Large amount of plutonium (from 10 to 62 %) was found to be associated with reducible fraction and it decreased with an increase of pH. Moreover, Pu  $K_d$  values correlated with amount of Pu associated with mentioned fraction ( $R=0.88$ ) (Lujaneiene et al. 2007). Recently the association of actinides with oxides and application of different methods for speciation determination have been discussed in different publications. Data on association of plutonium with geological material is rather contradictory. McDonald et al. found that plutonium is predominantly associated with Fe, Mn oxyhydroxides (43.9 %) and organic complexes (43.5%) in the Irish Sea sediments, whereas McCubbin et al. reported 37 % of Pu as upper limits for the fraction associated with magnetic + nonmagnetic Fe minerals in samples collected at close area of the Cumbarian coast (McDonald et al., 1990, 2004). Data was obtained using different methods: sequential extraction and magnetic extraction technique. Using selective extraction procedures was shown that Pu was associated predominantly with Mn oxides. The dominant association with the Mn oxides occurred despite the fact that the Fe oxides were present at concentrations higher by factor from 2 to 30 in comparison with the Mn oxides (Means et al., 1978).

X-ray absorption spectroscopy, in combination with microautoradiography, electron microprobe, and petrographic microscopy techniques were used to detect the spatial distribution of sorbed Pu on the zeolitic Topopah Spring Tuff sampled at Yucca Mountain (Dudd et al. 1999; Dumat & Staunton, 1999). Large concentrations of sorbed Pu were associated with smectite and Mn oxide fracture minerals. Sorption of Pu to Fe-rich regions was not observed. In a similar experiment in which Tuff was used, Pu was concentrated in the zones of altered orthopyroxenes. These zones contained Fe-rich amorphous materials (Vaniman et al., 1996). Sanchez et al. (1985) found that adsorption Pu onto goethite is related to different hydrolytic character of Pu (IV) and Pu(V) in the solution and occurs for Pu (IV) at pH 3 to 5 and for Pu(V) at pH 5 to 7. It was determined also that an increase in ionic strength did not affect the adsorption of Pu on goethite (Sanchez et al., 1986). It was shown that Pu(V) and Pu(IV) sorption on  $\gamma$ -alumina and goethite generally increases as a function of pH. Pu(IV) sorption on goethite occurs at pH values between 2 and 6, whereas Pu(V) sorption on goethite occurs at pH values between 4 and 8. Pu(V) sorption on  $\gamma$ -alumina also occurs at pH values between 6 and 10 (Turner, 1995). Pu sorption on amorphous silica or on quartz is expected to occur at much lower pH values because of the much lower pH ZPC (the pH point of zero charge), at about 2, in contrast to that of the iron and aluminium hydroxides, which generally occurs between 7 and 9.

The explanation of sorption behaviour of plutonium in complex heterogeneous system is rather difficult. We suppose that sorption on goethite is responsible for binding plutonium (reducible fraction, (Fig. 24). Plutonium associated with residual fraction most likely sorbet on the hema-

tite and aluminium oxide. Carbonate complexes can also affect plutonium behaviour; however, plutonium carbonate complexes under high pH are poorly understood. Direct measurements are required to support our suggestions. The studies related to the identification of minerals are in the progress.

Rather different behaviour of Am was observed, up to 40% of Am was found in exchangeable and carbonate bound fractions. We suppose that sorption to carbonate minerals; co-precipitation and incorporation into calcite are responsible for higher Am  $K_d$  values in comparison with that of Pu  $K_d$ .

## **7. Nordic inter-comparison for speciation analysis of radionuclides in soil and sediment**

Over the last 25 years, sequential extraction has proved a useful technique for studying the binding of radionuclides in soils and sediments ( Desideri et al. 2002; Lucey et al. 2007; Oughton et al. 1992; Riise et al. 1990; Skipperud et al. 2000a; Skipperud et al. 2000b; Skipperud et al. 2005; Tessier et al. 1979). Many of the applications are based on a method proposed by Tessier et al. (1979), for the study of heavy metal speciation in sediments. The techniques are particularly valuable when used in studies designed to compare spatial or temporal variation of radionuclide speciation in an ecosystem, to investigate differences in speciation as a function of source or environmental characteristics, or to compare the behaviour of different radionuclides in the same soil or sediment. To date, the application of these methods in radioecology has focused mainly on the study of Cs-137 and Sr-90, with less data available on the behaviour of plutonium (Lucey et al. 2004).

An inter-comparison exercise for the chemical speciation analysis of radionuclides including plutonium isotope, uranium, thorium,  $^{137}\text{Cs}$ , and  $^{129}\text{I}$  in soil and sediment was carried out under this project (NKS-B SPECIATION 2008-2009) within the partners' laboratories in Technical University of Denmark, Uppsala University, Helsinki University, Institute of Physics in Lithuania and Norwegian University of Life Sciences (UMB). The methods and the results are summarized in this report.

Two standard reference materials, IAEA-SRM-375 (soil) and NIST-SRM-4354 (sediment), were chosen. In addition, sediments from Lake Heimdalen was prepared by UMB and distributed to the participants.  $^{137}\text{Cs}$  was measured by gamma spectrometry in most of the laboratories,  $^{239,240}\text{Pu}$  was measured by alpha spectrometry,  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ ,  $^{238}\text{U}$  and  $^{232}\text{Th}$  were measured by ICP-MS (Thermal Scientific) at Risø National Laboratory for sustainable Energy, and  $^{129}\text{I}$  by accelerator mass spectrometry at Uppsala University using 3 MV Tandem accelerator.

### **7.1 Sequential extraction procedure**



A unified sequential fractionation procedure was used in all partner's labs. The detailed procedure is listed below. A sample/solution ratio of 1:10 was used for extraction for each step, and 10 g of samples was used for sequential extraction experiment; and in each lab, 2-3 sub-samples of each sample were processed. In addition, a blank sample was included in the analysis to identify any contamination due to the reagents or laboratory practices and, later on, to be subtracted from the real analyte signal. Between every fraction, the residue was rinsed with distilled water (water:sample = 5) by shaking the residue with water for 10 min., the wash of water was combined with leachate. The leachate and wash were separated from the residue by centrifugation, and the solutions were filtered through a membrane having a pore size of 0.45  $\mu\text{m}$ /0.2  $\mu\text{m}$  to ensure a "Clean" solution. Particles on the membrane were combined with the residue for the leaching of next step. All reagents used in this study were analytical reagent grade. Deionised water (18 M $\Omega$  cm<sup>-1</sup>) was used in all procedure. In most labs the fractions were first analyzed for <sup>137</sup>Cs by gamma spectrometry, and then fractions 1-4 were divided into two; for the determination of Pu, Th and U using ICP-MS (using 80% of the fraction by weight) and for the determination of <sup>129</sup>I by AMS (using 20% of the fraction by weight). As show below fractions 5a and 6a went to AMS measurement of <sup>129</sup>I, and Fractions 5b, 6b and 7 to ICP-MS and alpha spectrometry for Pu, Th, and U determination. For AMS measurement of <sup>129</sup>I, the separated fractions in solution and/or residue (the last step) were sent to Risø, where <sup>129</sup>I was separated using a procedure reported (Englund et al.,2007) for target preparation. The prepared AgI targets were sent to Uppsala University for AMS measurement.

### ***Fractionation procedure***

Fraction-1: Water (Milli Q), shaking for one hr, Centrifugation.

Fraction 2: 1M NH<sub>4</sub>Ac-HAc (pH7), 20°C, shaking, 2hr, centrifugation and removal of liquid phase.

Fraction-3: 1M NH<sub>4</sub>Ac-HAc (pH5), 20°C, shaking, 2 hr, centrifugation.

Fraction-4: 0.04M NH<sub>2</sub>OH HCl, (pH 2) in 25 % (v/v) HAc, 80°C, 6hr, centrifugation.

Fraction-5a(<sup>129</sup>I). NaOH, 3 M, 85°C, shaking, 3 hr, after separation of leachate by centrifuge, add 5% NaOCl to residue, 85 °C shaking 2 hr. (using 20 % of residue from step 4 by weight)

Fraction-5b (other nuclides): 30 % H<sub>2</sub>O<sub>2</sub>, pH2 (HNO<sub>3</sub>), 80°C, shaking 5.5 hr, then add 3.2 M CH<sub>3</sub>COONH<sub>4</sub>(NH<sub>4</sub>Ac) in 20 % (v/v) HNO<sub>3</sub>, 20°C (solution/sample = 2.5), shaking 0.5 hr (using 80% residue from step 4 ).

Fraction-6a: Residue (for <sup>129</sup>I, the residue is dried at 60-70 °C)

Fraction-6b: 7 M HNO<sub>3</sub>, 80°C, 6 hr (using the residue from 5b) for Pu, Th, U, Cs

Fraction 7: Residue (Pu, Th, U, Cs), *Aqua regia* digestion (HCl:HNO<sub>3</sub>, 3:1) liquid solid ratio = 10, heating under reflux (100°C) for 2 hr or more, or other digestion methods available at the different labs.

Table 6. Rationale behind the selected reagents included in sequential extraction

Processes	Model	Agents	Reagents
Physical sorption	Consecutive layers, reversible reaction	Indifferent (inert) electrolyte	H <sub>2</sub> O NH <sub>4</sub> OAc, soil/ sediment pH
Electrostatic sorption	Monolayer, Reversible reactions	Ion-exchangeable species, increased acidity (pH)	pH < soil/sediment NH <sub>4</sub> OAc, pH <sub>5</sub>
Chemisorption	Monolayer, Irreversible reaction	Red/ox agents, increase in temperature	Weak reducing: NH <sub>2</sub> OH•HCl Weak oxidizing: H <sub>2</sub> O <sub>2</sub> , pH 2, 80°C Strong oxidizing: 7 M HNO <sub>3</sub> , 80°C

**Fraction 1:** This fraction is included to define the solid:solution distribution of species using centrifugation. 100 ml of deionised water was added to the solid samples and the samples were shaken for 1 hour at room temperature. After extraction the samples were centrifuged. The leachates were separated from the solid residue very carefully by decantation. The leachates were filtered through a membrane.

**Fraction 2:** This fraction should reflect species associated to solids via physical sorption mechanisms (Table 25). 100 ml of 1 M NH<sub>4</sub>Ac-HAc (pH 7) was added to the residues from previous step and the samples were shaken for 2 hours at room temperature. After extraction the samples were centrifuged. The leachates were separated from the solid residue by decantation. 50 ml of deionised water were added into residues and the samples were shaken for ten minutes. The wash water was separated from the residues by centrifugation and decantation and combined with the original leachates. The leachates were filtered to ensure clean solution.

**Fraction 3:** This fraction should reflect species associated to solids via electrostatic sorption mechanisms (Table 25). 100 ml of 1 M NH<sub>4</sub>Ac-HAc (pH 5) was added to the residues from step 2 and the samples were shaken for 2 hours at room temperature. The samples were centrifuged and the leachates were separated by decantation. Residues were washed for ten minutes with 50 ml of deionised water. The wash water was separated from the residues by centrifugation and decantation. The wash water was combined with the original leachates which were filtered.

**Fraction 4:** This fraction should reflect species associated to solids via chemisorption mechanisms using a weak reducing agent. 100 ml of 0.04 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25 % (v/v) HAc (pH 2) was added to the residues from step 3 and agitated in hot water bath at 80 °C with stirring for 6 hours. The samples were centrifuged and the leachates were separated from the solid residues by very careful decantation. Solid residues were shaken with 50 ml of deionised water for ten minutes at room temperature. The wash water was separated from the residues by centrifugation and decantation and combined with the original leachates.

The leachates 1 through 4 was divided into two, 80 % and 20 % by weight to go forward for the determination of  $^{137}\text{Cs}$ ,  $^{238,239,240}\text{Pu}$  and for isotopes of U and Th with alpha spectrometry and ICP-MS and for the analysis of  $^{129}\text{I}$  by AMS, respectively. All leachates (not for iodine determination) were acidified immediately after filtering with concentrated HCl until pH 2 to prevent the adsorption of radionuclides onto the walls of the sample containers.

After fraction 4 the solid residues were divided into two sub-samples, A and B, approximately 20 % and 80 % by weight, respectively, taking the approximate liquid content of the sample into account. Fractions 5A and 6A including with the 20 % of the fractions 1-4 were sent to Risø for the preparation of the AMS –samples for the analysis of  $^{129}\text{I}$ . The extraction conditions used in fractions 5A and 6A were:

**Fraction 5A:** 60 ml (NIST-SRM-4354) and 30 ml (IAEA-375) of 3 M NaOH was added to the residues A and the samples were agitated at 85 °C with stirring for 3 hours. The leachates were separated from the solid residues by centrifugation and decantation. 60 ml (NIST-SRM-4354) and 30 ml (IAEA-375) of 5 % NaOCl were added to the residues and the samples were agitated in 85 °C for 2 hours. After extraction the samples were centrifuged and leachates were separated from the solid residue by decantation. Residues were washed with deionised water with water to sample ratio of 1:5. The water were added into the residue in question and shaken for ten minutes. The wash water was separated from the residues by centrifugation and decantation and combined with the original leachates. The leachates were filtered to ensure clean solution.

**Fraction 6A:** Residues from previous step were dried in the oven at 65 °C in the original centrifuge tubes. The dried samples were sent to Risø-DTU for  $^{129}\text{I}$  determination.

**Fraction 5B:** This fraction should reflect species associated to solids via chemisorption mechanisms using a weak oxidizing agent. 80 ml of 30 %  $\text{H}_2\text{O}_2$  were gradually added to the residues B and the samples were agitated at 80 °C for 5.5 hours. Then 20 ml of 3.2 M  $\text{NH}_4\text{Ac}$  in 20 %  $\text{HNO}_3$  (v/v) were added and the extraction were continued for 30 minutes in room temperature with shaking. After extraction the samples were centrifuged. The leachates were separated from the solid residue by decantation. Residues were washed with deionised water with water to sample ratio of 1:5. The water were added into the residue in question and shaken for ten minutes. The wash water

was separated from the residues by centrifugation and decantation and combined with the original leachates. The leachates were filtered and the pHs were checked. If necessary concentrated HCl were added to reach pH of 2.

**Fraction 6B:** This fraction should reflect species associated to solids via chemisorption mechanisms using a strong oxidizing agent (Table 25). 80 ml of 7 M HNO<sub>3</sub> were added to the residues from step 5B and heated at 80 °C with stirring for 6 hours. After extraction the samples were centrifuged. The leachates were separated from the solid residue by decantation. Residues were washed with deionised water with water to sample ratio of 1:5. The water was added to the residue in question and shaken for ten minutes. The wash water was separated from the residues by centrifugation and decantation and combined with the original leachates and finally filtered.

**Fraction 7:** This fraction should reflect species associated to mineral lattices. Residues from previous step were transferred to 400 ml beakers and refluxed in 80 ml of *aqua regia* on a hotplate approximately 2-4 hours. The leachates were separated by filtration through a glass fibre filter. The residues were washed with 40 ml of deionised water. The wash water was separated from the residues by decantation and combined with the original leachates and filtered.

## 7.2 Determination of radionuclides

<sup>137</sup>Cs were directly measured from 50 or 100 ml aliquots taken from the separated leachates with gamma spectrometry in the partners' laboratories. The samples were measured approximately 24 h to gain enough counts in the <sup>137</sup>Cs –peaks. Due to very low concentration of <sup>137</sup>Cs activity in sediment sample (NIST-SRM-4354), the <sup>137</sup>Cs is lower than the detection limit in most of fractions under the measurement condition, it is therefore not mentioned in this report.

Due to low concentration and high interference, <sup>239,240</sup>Pu in the fractions was first separated from the matrix and other elements and radionuclides before measurement. The individual radiochemical procedure, which is routinely used in the partners' laboratories, was used in this work for the separation of plutonium. <sup>242</sup>Pu was used as yield tracer in all laboratories. In two laboratories, the separated plutonium was electrodeposited on disk and <sup>239,240</sup>Pu was measured using alpha spectrometry. While in another laboratories, ICP-MS was used to measure <sup>239</sup>Pu and <sup>240</sup>Pu, the sum of activity of these two isotopes was reported as <sup>239,240</sup>Pu in the result for easy comparison.

About 2 millilitres of sequential extracted fractions, which were obtained from all partners' lab were sent to Risø-DTU. The solution was diluted in 0.5M HNO<sub>3</sub> solution, and <sup>232</sup>Th and <sup>238</sup>U were measured by ICP-MS at Risø-DTU.

For the fractionation analysis of <sup>127</sup>I and <sup>129</sup>I in two samples, 20% of solution from steps 1-4 and fraction 5a and 6a were collected in the partners' laboratories and sent to Risø-DTU for the determination. Of these solution, one millilitres of solution was used first taken out, which was directly

diluted in 1% NH<sub>4</sub>OH solution, and measured using ICP-MS for <sup>127</sup>I after addition of Cs<sup>+</sup> as internal standard. To the remained solution, <sup>125</sup>I was added as yield tracer and stable <sup>127</sup>I (Woodward company, US) and iodine in the fractions was then separated. For the solutions from step 1-4, iodine was separated by solvent extraction using CCl<sub>4</sub> and converting iodine to molecular iodine. For fraction 6b (residue), the remained residue sample was put in a combustion furnace (Hou, et al. 2008, NKS report 2008), and iodine is separated from the residue by combustion at 800 °C under oxygen flow, the released iodine was trapped in a NaOH solution, which is then separated by CCl<sub>4</sub> extraction. The separated iodine as iodide was precipitated as AgI, and sent to Uppsala University for AMS measurement in Tandem Accelerator.

### 7.3 Intercomparison: Sequential extraction of radionuclides in two standard reference standard materials

Four laboratories reported analytical results, of which the Lab-1 reported the results as the average of two samples, Lab-2 reported two sets of results measured in two sub-samples, and Lab-3 reported the results measured in one sub-sample, and Lab-4 only reported the results of Pu isotopes in one sup-sample.

#### Results of <sup>137</sup>Cs:

The analytical results of <sup>137</sup>Cs fractionation in IAEA-375 from three laboratories are shown in Fig. 26. <sup>137</sup>Cs fraction in the residue was not determined except by Lab-1. Due to low concentration of <sup>137</sup>Cs in sediment sample (NIST-4354), no result was reported. The results in 7 fractions agree well in three laboratories, the highest <sup>137</sup>Cs was observed in the fraction treated with 8 M HNO<sub>3</sub>, followed by the fraction treated with *aqua regia*, and the concentrations of <sup>137</sup>Cs in other fractions are relative low, especially for the first fraction treated with water.

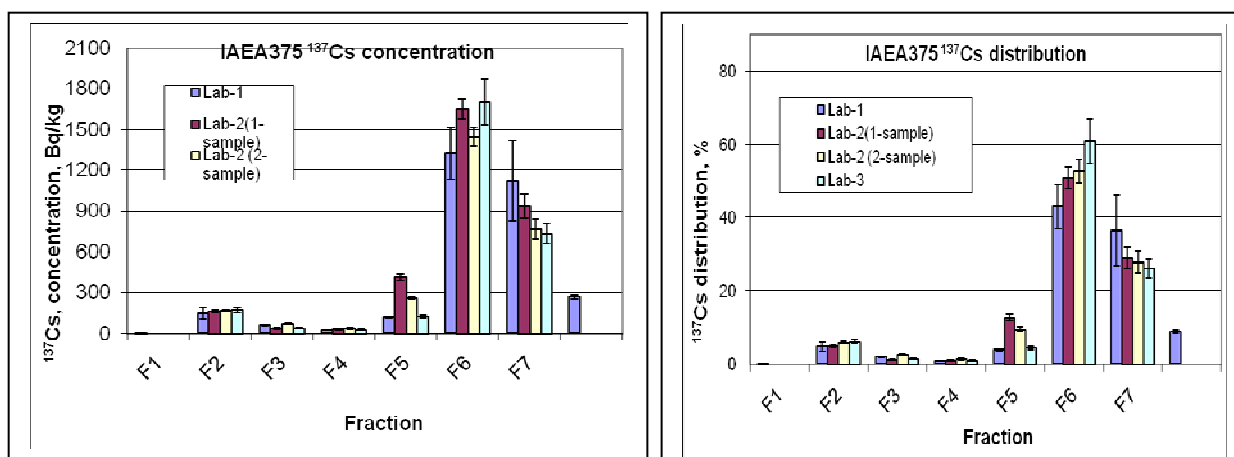


Figure 26 Inter-comparison results of <sup>137</sup>Cs fractionation in soil (IAEA-375)

## Results of Pu isotopes

Four laboratories provided data for  $^{239,240}\text{Pu}$  (Fig. 27, 28). In the fractionation analysis of soil (IAEA-375), some fractions were lost during the sample preparation and separation in Lab-2, which resulted in missing data for some fractions from Lab-2.

Based on many years of experience, the uncertainties should have been within 10 % to account for man-man and lab-lab variations. However, large variations are seen for all fractions obtained, mainly due to results provided by lab2 and lab3. The variations are especially large for F2 (extraction with 1M  $\text{NH}_4\text{Ac-HAc}$  (pH of sediment/soil) and F5 (30 %  $\text{H}_2\text{O}_2$ , pH2 ( $\text{HNO}_3$ ), which reflect variations in the performance of the laboratories. Methodological effects due to differences in centrifugation speed, temperature, use of filters etc can partly explain the variations. The results call for training and renewing intercomparison exercise.

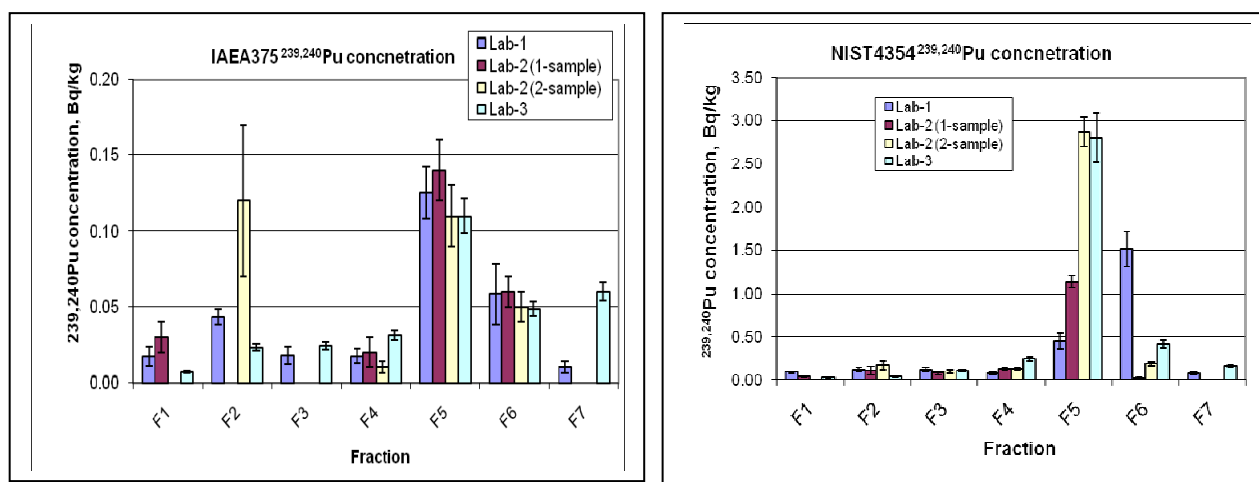


Figure 27 Intercomparison of  $^{239,240}\text{Pu}$  concentration in extracted fractions of soil and sediment standard reference materials

## Results of $^{238}\text{U}$

Three labs reported  $^{238}\text{U}$  values in both soil and sediment standard reference materials (Fig. 29). Uranium mainly distributes in Fraction 3,4, 5 and 6 in soil (IAEA-375) and in Fraction 3, 4, and 5 in sediment (NIST-SRM-4354). The analytical results of  $^{238}\text{U}$  in each fraction are not in good agreement in three laboratories for both samples. Unlike Pu, no chemical separation is applied for the leached solution, and the disagreement may only be attributed to the sequential extraction steps.

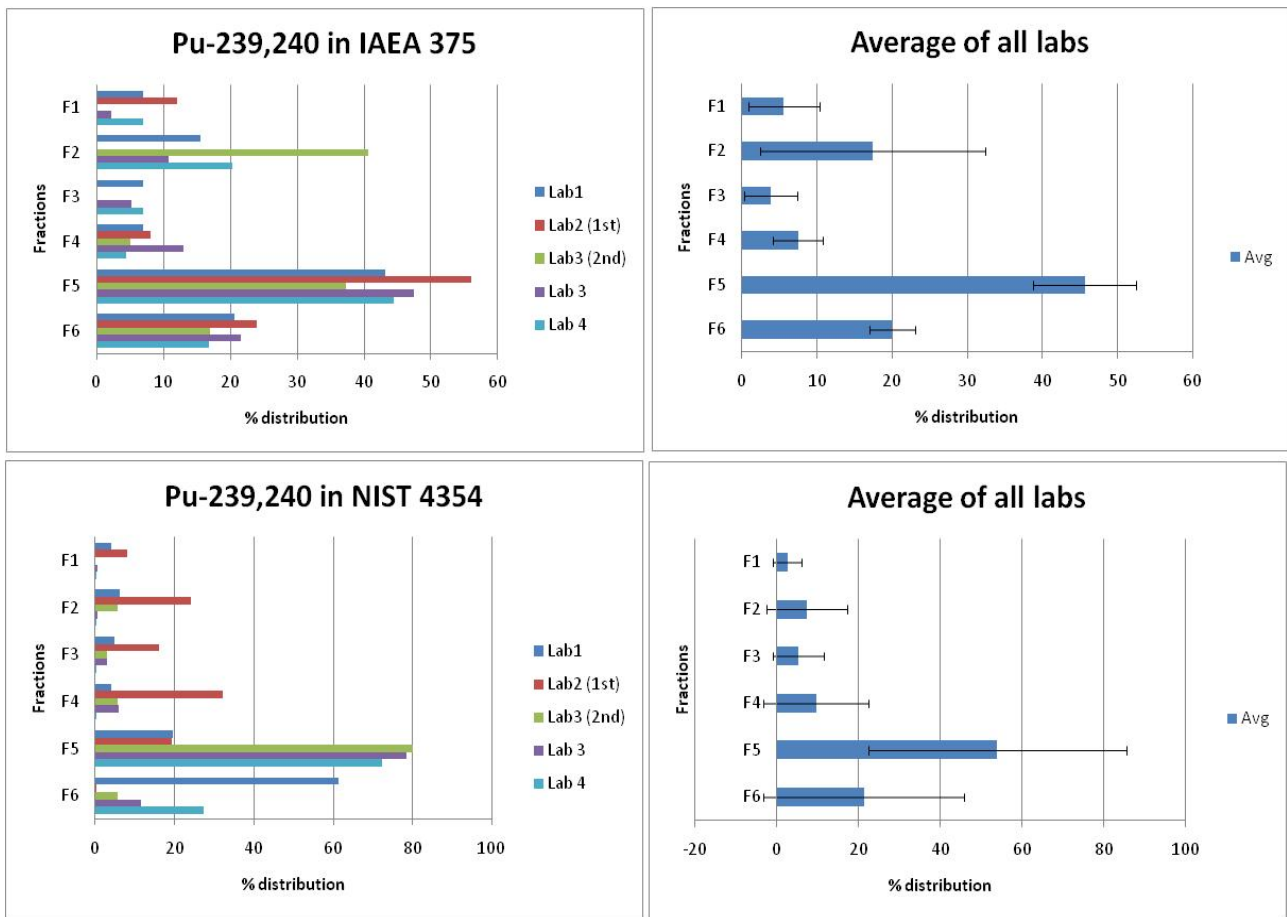


Figure 28 Inter-comparison results of  $^{239,240}\text{Pu}$  distribution in fractions from sequential extraction of standard reference material of soil (IAEA-375) and of sediments (NIST 4354)

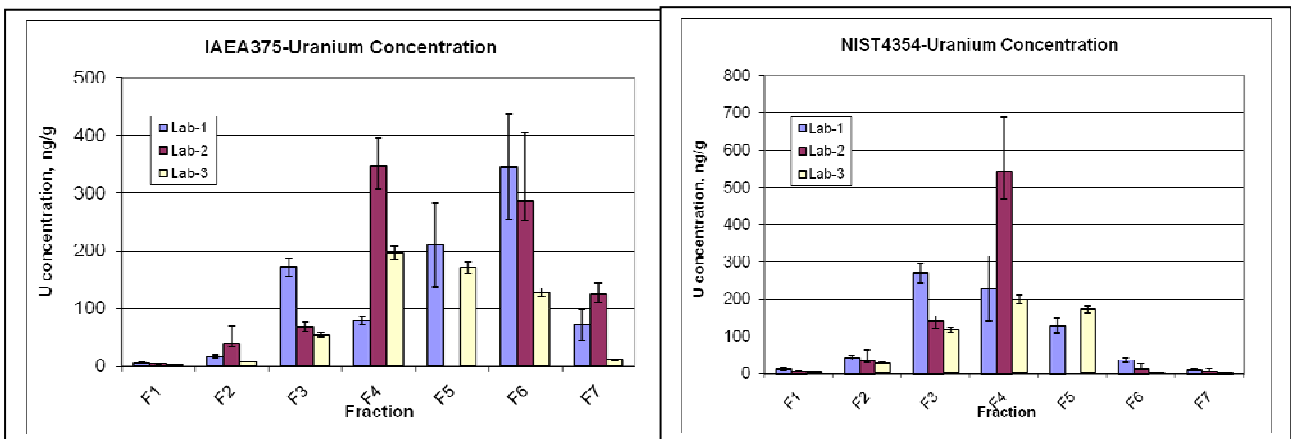


Figure 29 Intercomparison results of  $^{238}\text{U}$  fractionations in soil (IAEA-375) and sediment (NIST-SRM-4354)

### Results of $^{232}\text{Th}$

In two samples, thorium mainly distributed in fraction 6, i.e. leached by 8M  $\text{HNO}_3$ , the fractionation results of Th from three laboratories agree well for soil samples (IAEA-375), and for most

of fractions in sediment sample (NIST-SRM-4354), and the sum of the Th concentration in all fractions is corresponding to 80-95% of the certified value (Fig. 30). For sediment sample, low Th concentrations in fraction 6 were reported by Lab-2 and Lab-3, which caused a low sum of Th concentration in all fraction reported by Lab-2 and Lab-3 (only <30% of the certified value in the samples, 6590 ng/g), comparing with the value from Lab-1 (70% of the certified value).

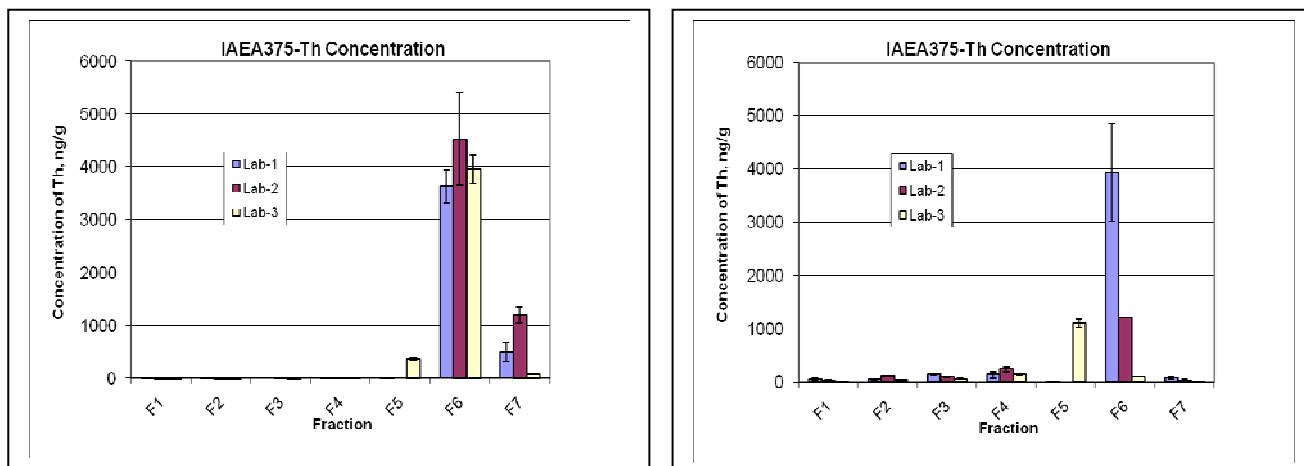


Figure 30 Intercomparison results of  $^{232}\text{Th}$  fractionations in soil (IAEA-375) and sediment (IAEA-SRM-4354)

### Results of $^{129}\text{I}$ and $^{127}\text{I}$

The analytical results of fractionation of  $^{129}\text{I}$  in three laboratories (Fig. 31) show that for most of fractions, the analytical results from the three laboratories are in a good agreement for both  $^{129}\text{I}$  and  $^{127}\text{I}$  in two samples, except fraction 5 in sediment and fraction 6 in soil sample. The extremely high  $^{129}\text{I}$  concentration in fraction 5 (sediment) or 6 (soil) reported by Lab-3 might be attributed to the contamination of the sample fractions during the chemical separation.

The analytical results of  $^{127}\text{I}$  fractionation in two samples (Fig. 32) also show a good agreement among three laboratories for most of fractions except the fractionation 5 from Lab-2, where a lower  $^{127}\text{I}$  concentration was measured.

To our best knowledge, this is the first inter-comparison on the fractionation of radionuclides in environmental samples, the results obtained in this work shows that the unified sequential procedure is applicable for most of radionuclides used in the comparison exercise. However, for uranium and some fractions, the results are not in a good agreement, this may be attributed to many reasons, including some steps of extraction and separation procedure, i.e. the separation of the residue from the solution by centrifuge with different speed, filtration using different pore size of membrane, the method for the mixing of the leaching solution with sample, such as stirring, shaking in vertical or



horizontal, etc. A further work is therefore needed to draw a clear conclusion on the sequential extraction method for the radionuclides.

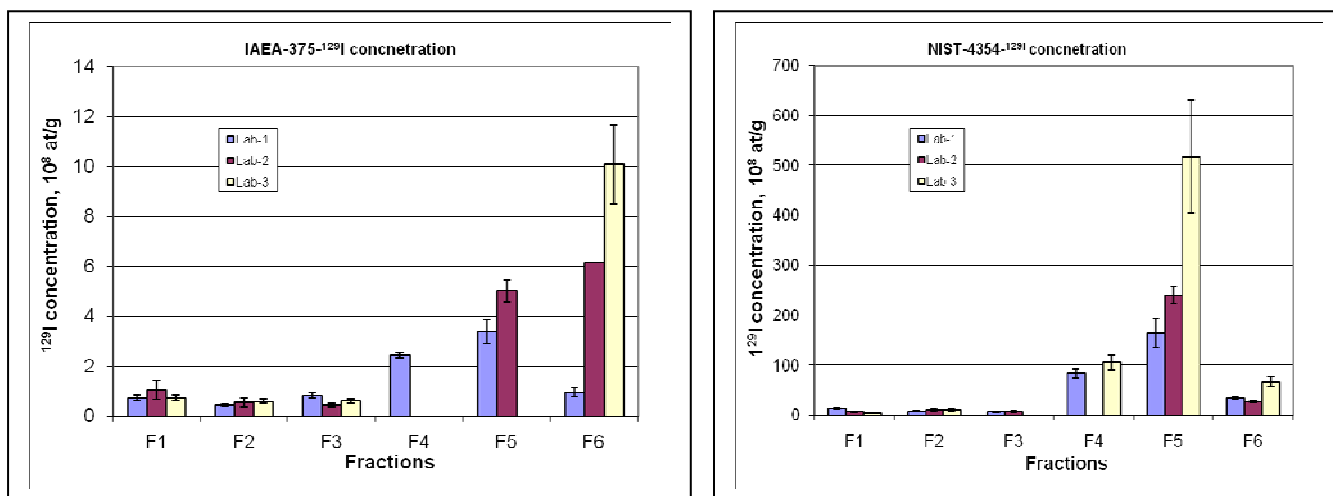


Figure 31 Intercomparison results of  $^{129}\text{I}$  fractionations in soil (IAEA-375) and sediment (IAEA-SRM-4354)

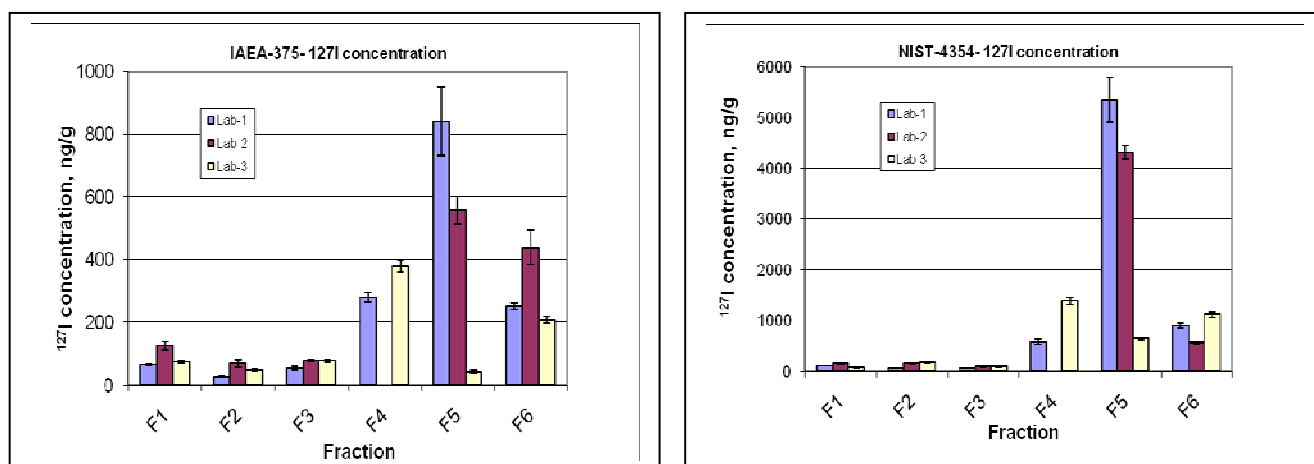


Figure 32 Intercomparison results of  $^{127}\text{I}$  fractionations in soil (IAEA-375) and sediment (IAEA-SRM-4354)

#### 7.4 Intercomparison: Sequential extraction of Pu in sediment from Lake Heimdalen, Norway

Sediment samples were collected in Lake Heimdalen and transported to UMB. The fresh samples were distributed to participating laboratories.

Only 2 labs reported results for Pu ( $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{239,240}\text{Pu}$ ) in extracts from sequential extraction of the sediments (Fig. 33). Pu in the extracts was determined by the same lab using the same ICP-MS. Thus, differences in results obtained can only be attributed to the performance of the sequential extraction procedure.

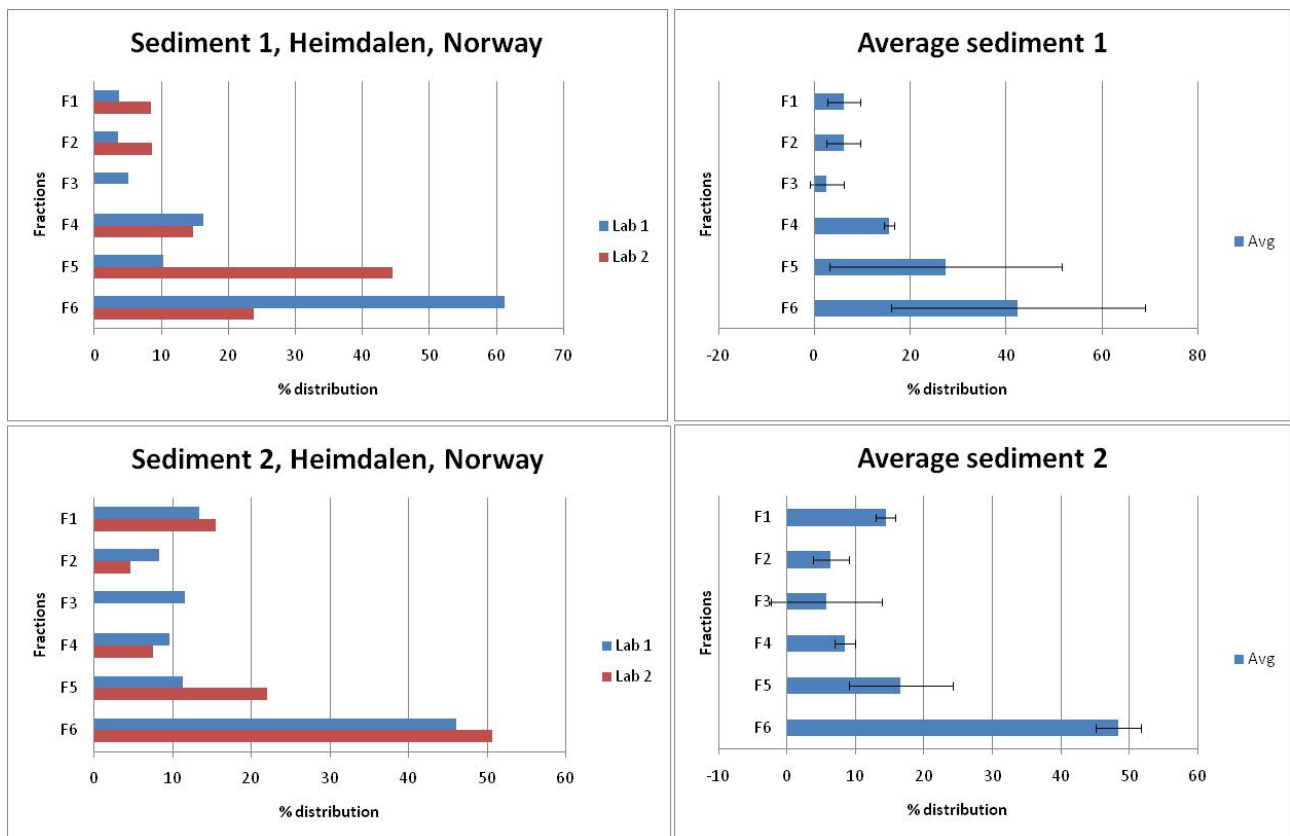


Figure 33. Intercomparison results of  $^{239,240}\text{Pu}$  in extracts from sequential extraction of 2 Heimdalen sediments.

As observed with two standard reference materials, the largest variations are observed for the F2 and F5 fractions, although most of the data is within 10 %. Variations observed in F1 and F2 can be attributed to differences in centrifugation speed (sedimentation coefficients) where colloidal fraction can distribute different between solid and solutions. Variations in F5 can be attributed to differences in oxidizing conditions. These results call also for training and renewing intercomparison exercise.

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## 9. Two review articles published by collaboration among participants of this project.

### 9.1 Speciation of Iodine ( $^{129}\text{I}$ ) in the Environment

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#### Review

### A review on speciation of iodine-129 in the environmental and biological samples

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#### ABSTRACT

As a long-lived beta-emitting radioisotope of iodine,  $^{129}\text{I}$  is produced both naturally and as a result of human nuclear activities. At present time, the main part of  $^{129}\text{I}$  in the environment originates from the human nuclear activity, especially the releases from the spent nuclear fuel reprocessing plants, the  $^{129}\text{I}/^{127}\text{I}$  ratios have been reached to values of  $10^{-10}$  to  $10^{-4}$  in the environment from  $10^{-12}$  in the pre-nuclear era. In this article, we review the occurrence, sources, inventory, and concentration level of  $^{129}\text{I}$  in environment and the method for speciation analysis of  $^{129}\text{I}$  in the environment. Measurement techniques for the determination of  $^{129}\text{I}$  are presented and compared. An overview of applications of  $^{129}\text{I}$  speciation in various scientific disciplines such as radiation protection, waste depository, and environmental sciences is given. In addition, the bioavailability and radiation toxicity (dose to thyroid) of  $^{129}\text{I}$  are discussed.

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*Abbreviations:* AMS, accelerator mass spectrometry; AmAD, activity median aerodynamic diameter; DIT, diiodotyrosine; DRC, dynamic collision/reaction cell; EXAFS, extended X-ray absorption fine structure spectra; HpGe, high purity germanium; HPLC, high performance liquid chromatography; ICP-MS, inductively coupled plasma mass spectrometry; LSC, liquid scintillation counter; MIT, monoiodotyrosine; NAA, neutron activation analysis; SIMS, secondary ion mass spectrometry;  $\text{T}_3$ , triiodothyronine;  $\text{rT}_3$ , reverse-triiodothyronine;  $\text{T}_4$ , thyroxine; TBAH, tetrabutylammoniumhydroxide; TEDA, triethylenediamine; TBP/OK, tri-*n*-butyl phosphate in odourless kerosene; XANES, X-ray absorption near-edge structure.

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## 1. Introduction

Iodine occurs as a trace element in the Earth's crust, with an average abundance of  $0.45 \text{ mg kg}^{-1}$ . Most of iodine (>70%) in the Earth's surface environment exists in the oceans with a concentration range between 45 and  $60 \text{ ng mL}^{-1}$  [1,2]. The only stable isotope of iodine is  $^{127}\text{I}$  and the most long-lived radioisotope (15.7 My) is  $^{129}\text{I}$ , which is also the only naturally occurring radioisotope of iodine (Table 1). Human nuclear activity has produced and released a large amount of  $^{129}\text{I}$  to the environment thus elevating the  $^{129}\text{I}/^{127}\text{I}$  ratio by at least 2 orders of magnitude compared with the natural values. Due to the long half-life and high mobility with its near conservative behavior in stored radioactive waste,  $^{129}\text{I}$  is an important radionuclide in the waste management.

In order to assess short- and long-term consequences of radioactive contamination in the environment, information on the distribution of radionuclide species influencing mobility and biological uptake is needed [3]. Such information can be obtained by means of radionuclide speciation analysis, which can be defined as the identification and quantification of a radionuclide species in a sample. Information on total concentration (without speciation) alone is not sufficient to evaluate the potential impact of radioactive pollutants in the environment and consequently their bioavailability. Speciation analysis thus provides realistic picture about the radionuclide transport mechanisms in the environment and to the human body, as well as accurate risk assessments. Despite the significance of elemental speciation analysis, there are many difficulties associated with achieving universally accepted analytical methods as well as problems related to sampling and storage.

$^{129}\text{I}$  is one of key radionuclides in the nuclear waste depository,  $^{129}\text{I}$  has also been shown a very useful isotope for the age dating [4,5], a suitable oceanographic tracer for studying transport and exchange of water mass [6–15], as well as a useful environmental tracer for investigating geochemical cycle of stable iodine [16–19]. Knowledge on the speciation of  $^{129}\text{I}$  is a key issue for safety assessment of radioactive waste repositories, for estimation of human exposure through multiple pathways, as well as its application as an environmental and oceanographic tracer. In this article, we present a review on the state-of-the-art speciation analysis methods available for  $^{129}\text{I}$ .

Empirical data have shown different ratios of  $^{129}\text{I}/^{127}\text{I}$  for the different chemical species of iodine in water, soil, sediment [20–23], implying that the speciation of anthropogenic  $^{129}\text{I}$  in the environment is different compared with the speciation of stable iodine. The concentration of  $^{129}\text{I}$  in the environmental samples is normally 4–12 orders of magnitude lower than that of stable iodine, for this reason the analytical methods, including the species separation and analytical techniques for the stable iodine ( $^{127}\text{I}$ ) cannot be directly used for  $^{129}\text{I}$ . The speciation of stable  $^{127}\text{I}$  has been widely investigated in the environmental and biological samples; a few review articles related to the speciation of stable iodine are available [1,24–30]. However, the investigation of  $^{129}\text{I}$  speciation in the environmental, especially biological samples is still very limited. To our best knowledge, a comprehensive review article on speciation of  $^{129}\text{I}$  has not been published. This article aims to review the

occurrence, sources, environmental inventory, distribution, analytical method and speciation analysis of  $^{129}\text{I}$  in environmental and biological samples. The bioavailability of  $^{129}\text{I}$  and its radiation toxicity are also discussed.

## 2. Iodine in the nature and its speciation

Iodine is widespread trace element in the hydrosphere, lithosphere, atmosphere and biosphere. Oceans are considered the main source of iodine (concentration at  $45\text{--}60 \text{ ng mL}^{-1}$ ) to the continental environments, which is back ventilated to the oceans by runoff at concentration of about  $1\text{--}3 \text{ ng mL}^{-1}$  in fresh water. The lowest iodine concentration was observed in atmosphere ( $1\text{--}100 \text{ ng m}^{-3}$  total concentration) [20,31], while the iodine concentration in precipitation ( $1\text{--}6 \text{ ng mL}^{-1}$ ), which is removed from the atmosphere, is relatively higher [16,31]. In the continental environments, the oceanic iodine is commonly trapped by soils, sediments and biota, whereas another source of iodine is supplied by erosion of bedrock. Iodine concentration in soil ranges from  $0.5$  to  $40 \mu\text{g g}^{-1}$  with common concentration of  $1\text{--}3 \mu\text{g g}^{-1}$ , and the organic soils normally has a higher iodine concentration [32,33]. Generally, sedimentary rocks, especially surface sea sediments contain comparatively high concentrations of iodine ( $1\text{--}2000 \mu\text{g g}^{-1}$ ) compared to metamorphic and magmatic rocks ( $<0.1 \mu\text{g g}^{-1}$ ) [2]. In the biosphere, iodine concentrations depend on its availability and concentration in the surrounding environment. High concentration of iodine was observed in seaweeds ( $10\text{--}6000 \mu\text{g g}^{-1}$  dry weight), of which brown algae shows the highest values ( $100\text{--}6000 \mu\text{g g}^{-1}$ ) [34]. Terrestrial plants normally have lower iodine concentrations ( $<1 \mu\text{g g}^{-1}$ ) than the marine ones. In mammals, iodine is mainly concentrated to thyroid, with concentration of  $0.5\text{--}5 \text{ mg g}^{-1}$  dry weight [35,36], while iodine concentration in other tissues is normally much lower ( $<1 \mu\text{g g}^{-1}$  dry weight) [37].

Iodine is an electronegative element with oxidation states of  $-1, 0, +1, +3, +5,$  and  $+7$  and exists in multifarious in aqueous solution. Iodine is a redox sensitive element forming a wide variety of organic and inorganic compounds and the most common inorganic forms of iodine are  $\text{I}^-$  (iodide),  $\text{HOI}$  (hypoiodous acid),  $\text{I}_2$  (elemental iodine), and  $\text{IO}_3^-$  (iodate) in natural environmental Eh–pH conditions (Fig. 1) [38,39]. As a biophilic element, iodine occurs in many organic compounds in nature such as alkyl iodide and is incorporated in organic matters such as proteins, polyphenols and humic substances [40–43].

### 2.1. Speciation of iodine in water

Speciation of iodine in natural water depends on several parameters including water chemistry, pH, Eh, temperature and organic productivity. In seawater, iodine mainly exists as iodate, iodide and minor organic iodine [1]. Distribution of iodine species in seawater varies with depth and geographic location. In anoxic water, most of iodine exists as iodide, e.g. in the Baltic Sea and the Black Sea [23,44,45], while in oxygenated/oxic water, such as ocean water, the dominant species of iodine is iodate. The concentration in the ocean ranges at  $<1\text{--}25 \text{ ng mL}^{-1}$  for iodide and  $25\text{--}60 \text{ ng mL}^{-1}$  for iodate. Iodide maximum is often found in surface water while

## 9.2 Speciation of Plutonium in Environmental Samples (structure)

A draft of re-view article on this topic is being prepared, and all partners make contribution to this paper. This paper is planned to be submitted to Anal. Chim. Acta for publication in year 2009.

1. Introduction (LS/BS)
  - 1.1. Definitions
  - 1.2. Relevance
  - 1.3. Input to impact and risk assessment models
2. Relevance for ecosystem transfer (BS/LS) Environmental aspects of Pu
  - 2.1. Past, existing and potential sources of Pu contamination
  - 2.2. Source Term Characteristics Including Physicochemical Forms
    - 2.2.1. Release conditions and transport pathways Atmospheric etc
  - 2.3. Environmental Pu chemistry in waters
  - 2.4. Mobility in soils and sediments
  - 2.5. Biological uptake and effects
3. Separation techniques (LS/BS/OCL)
  - 3.1 Aquatic phases
    - 3.1.1. Size fractionation
      - 3.1.1.1. Filtration
    - 3.1.2. Ultrafiltration
      - 3.1.2.1. Hollow fibre
      - 3.1.2.2. Tangential Flow Filtration
    - 3.1.3. Redox Techniques/Oxidation state distribution
  - 3.2. Solid phases
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  - 4.1 Radiometric
    - 4.1.1  $\alpha$ -spectrometry
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  - 4.2 Mass spectrometry
    - 4.2.1 ICP-MS
    - 4.2.2 AMS
5. Characterization of Pu in particles
  - 5.1 Autoradiography Identification/isolation
    - 5.1.1 Digital autoradiography: Palomares, Thule, Semipalatinsk
    - 5.1.2 Fission track
  - 5.2 Microanalytical techniques
    - 5.2.1 Electron microscopy
      - 5.2.2 SEM and ESEM with X-ray microanalysis
      - 5.2.3 TEM with X-ray microanalysis
        - 5.2.3.1 EELS
        - 5.2.3.2 Electron diffraction
    - 5.3 Synchrotron radiation based micro beam techniques
      - 5.3.1  $\mu$ -XRF:

- 5.3.2  $\mu$ -XAS
- 5.3.3  $\mu$ -XRD
- 5.3.4  $\mu$ -PIXE TAB left
- 5.4 Laser-induced Spectroscopic Methods
- 5.5 SIMS
- 5.6  $\mu$ -RAMAN
- 6. Discussion
  - 6.1 Perspective
  - 6.2 Future developments
- 7. Conclusions (LS)

## 10. List of publications in the partners lab related to this project

### 10.1 Publications in peer-reviewed scientific journals

1. Hou X.L., Aldahan A., Possnert G., Lujanienė G., Lehto J., Salbu B., Speciation analysis of radionuclides in the environment, NKS-B speciation project report 2007, NKS-176, 2008.
2. Hou X.L., Hansen V., Aldahan A., Possnert G., Lind O.C., Lujanienė G., Speciation of Iodine-129 in the Environment, *Anal. Chim. Acta*, 632(2008)181-196
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7. Xiaolin Hou, Ala Aldahan, S.P. Nielsen, Göran Possnert, (2008). Time Series of  $^{129}\text{I}$  and  $^{127}\text{I}$  speciation in Precipitation from Denmark, *Environ. Sci. Technol.* 43(2009)6522-6528.
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9. Englund E., Aldahan A., Hou X.L., Petersen R., Possnert G., Speciation of iodine ( $^{127}\text{I}$  and  $^{129}\text{I}$ ) in lake sediments, *Nucl. Instr. Methods, B*. 2009, Accepted.



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15. Lehto J., Americium in the Finnish environment, Boreal Environ. Res., 2009, 14, 427-437.
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## 10.1 Papers presented in conferences and meetings

1. *Aldahan, A.; Possnert, G.; Hou, X.*, Iodine (I-127 and I-129) in aerosols. In: Book of abstracts. 11. International conference on accelerator mass spectrometry, Rome (IT), 14-19 Sep 2008. (University of Salento, Lecce, 2008) p. 115
2. *Englund, E.; Hou, X.; Petersen, R.; Aldahan, A.; Possnert, G.*, Sequential extraction of I-127 and I-129 in sediment. In: Book of abstracts. 11. International conference on accelerator mass spectrometry, Rome (IT), 14-19 Sep 2008. (University of Salento, Lecce, 2008) p. 114-114
3. *Hou, X.; Hansen, V.; Aldahan, A.; Possnert, G.; Fievet, B.; Nies, H.*, Iodine-129 chemical forms in the surface water of the English Channel. In: Book of abstracts. 11. International conference on accelerator mass spectrometry, Rome (IT), 14-19 Sep 2008. (University of Salento, Lecce, 2008) p. 133-133
4. *Hou, X.; Hansen, V.; Aldahan, A.; Possnert, G.*, A simple method for the speciation analysis of  $^{129}\text{I}$  in seawater. In: Book of abstracts. 11. International conference on accelerator mass spectrometry, Rome (IT), 14-19 Sep 2008. (University of Salento, Lecce, 2008) p. 18-18
5. *Hou, X.*, Radiochemical analysis in decommissioning of nuclear facilities. In: Book of abstracts. 7. International conference on nuclear and radiochemistry, Budapest (HU), 24-29 Aug 2008. (Committee on Radiochemistry of the Hungarian Academy of Sciences, Budapest, 2008) p. 91-91
6. *Hou, X.*, Critical comparison of radiometric and mass spectrometric methods for the determination of radionuclides. In: Program. Abstract book. 2. International nuclear chemistry congress, Cancun (MX), 13-18 Apr 2008. Navarrete, M. (ed.), (National University of Mexico, Cancun, 2008) p. 63-63
7. *Hou, X.; Aldahan, A.; Nielsen, S.P.; Possnert, G.; Nies, H.*, Speciation of  $^{129}\text{I}$  and  $^{127}\text{I}$  in seawater. In: Proceedings. Oral and oral poster presentations. Part 2. International conference on radiowcology and environmental radioactivity, Bergen (NO), 15-20 Jun 2008. Strand, P.; Brown, J.; Jølle, T. (eds.), (Norwegian Radiation Protection Authority, Østerås, 2008) p. 82-87
8. *Hou, X.; Aldahan, A.; Nielsen, S.P.; Possnert G.*, Speciation of  $^{129}\text{I}$  and  $^{127}\text{I}$  in Precipitation, 8<sup>th</sup> International conference on Methods and application of radioanalytical chemistry, 5-10 April, 2009

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Abstract	<p>The second stage of the NKS-B project SPECIATION was complemented in 2008-2009, which mainly focus on three aspects: (1) Further improvement and development of methods for speciation analysis of radionuclides; (2) Investigation of speciation of some radionuclides in the environment (water, sediments, particles); and (3) Intercomparison exercise for speciation analysis of radionuclides in soil and sediment. This report summarizes the work completed in the project partners' laboratories, Method developments include: Development of an rapid and in-suit separation method for the speciation analysis of <sup>129</sup>I in seawater samples; Development of a simple method for the speciation analysis of <sup>129</sup>I in fresh water and seawater samples; Development of an on-line HPLC-ICP-MS method for the direct speciation analysis of <sup>127</sup>I in water and leachate samples; Speciation of radionuclides in water includes: Speciation of <sup>129</sup>I and <sup>127</sup>I in time-series precipitation samples collected in Denmark 2001-2006 and its application for the investigation of geochemistry and atmospheric chemistry of iodine, Speciation of radionuclides in Ob and Yenisey Rivers, and Speciation of <sup>129</sup>I and <sup>127</sup>I in Lake Heimdalen water. Speciation of radionuclides in soils and sediments includes: Sequential extraction of radionuclides in sediments and of trace elements in soil samples. Sequential extraction of radionuclides in aerosols and particles has also been performed. Further-more, sorption experiments have been performed to investigate the association of Pu, Am and Cs with different geological materials. The intercomparison exercises included sequential extraction of Pu, <sup>137</sup>Cs, U, Th, and <sup>129</sup>I in one soil and one sediment standard reference materials (NIST-4354, IAEA-375) and Pu in sediment collected from the Lake Heimdalen, Norway.</p>
Key words	Speciation, radionuclides, radioecology, radioanalytical chemistry, Iodine-129, plutonium, fractionation, intercomparison, water, sediment, soil, aerosol, precipitation