

Edited by Peter Warwick

Environmental Radiochemical Analysis IV



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Preface

Environmental Radiochemical Analysis IV is a collection of refereed papers presented at the 11th International Symposium on Environmental Radiochemical Analysis, held in Chester, UK in September 2010. This is the fourth of the Symposia to have its proceedings published as a book by the RSC.

The Symposium is run by the Radiochemistry Group of the RSC and is held every four years. Its scope has changed gradually over the years and, from an initial focus on analytical methods for environmental samples, it has now expanded to include studies of environmental source terms, transport pathways and impacts. The papers were presented as oral or poster presentations by delegates from many different countries.

I am particularly grateful to all the members of the organising committee: Peter Warwick (Loughborough), Margaret Graham (Edinburgh), Terry Gingell (Dstl), Miranda Keith-Roach (Plymouth), Kath Morris (Manchester), Ian Croudace (Southampton), Kinson Leonard (CEFAS) and Tony Ware. The last two made a massive contribution in raising sponsorship and controlling the finances respectively. A special thank you also to Claire Lowe (Loughborough), Secretary to the Organising Committee, for her patience and organisational skills.

Professor Francis Livens,
Chair of the Organising and Technical Committee,
ERA11.

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A SEARCH FOR LONG LIVED ^{242m}Am ISOTOPE IN FOREST LITTER SAMPLES FROM POLAND

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1 INTRODUCTION

The ^{242m}Am is a long lived ($T_{1/2}=143$ years) transuranic isotope which is produced in nuclear reactors mainly as a result of a neutron capture of ^{241}Am . It can be also produced in this way by high neutron fluxes during nuclear explosion.¹ For many particular environmental sources, as for example global fallout, one can expect the ^{242m}Am activity on the level of about 1% of that of ^{241}Am .² ^{242m}Am decays by internal transition into ^{242}Am ($T_{1/2}=16$ h). The ground state ^{242}Am decays by beta minus (83%) or electron capture (16%) into an alpha emitter, ^{242}Cm ($T_{1/2}=163$ days), which then decays into another alpha emitter, ^{238}Pu ($T_{1/2}=88$ years). As discussed elsewhere² the direct detection of ^{242m}Am at environmental levels is not technically possible and only indirect methods are suitable. In our approach, the ingrowth of ^{238}Pu was determined on an old alpha source of americium. The original forest litter samples were collected in Poland in 1991 or 1987. Samples were subjected to typical radiochemical methods during 1991-1996. Americium was separated and alpha spectrometric sources were prepared (using NdF_3 method), measured and results were published.^{3,4} For the same set of samples, data on Pu activity (including ^{241}Pu) are also available.^{5,6} In the present paper original codes are kept to enable any further comparisons. Some of the litter samples showed clear dominant Chernobyl influence (for example traces of ^{244}Cm , strongly enhanced activity ratios ^{238}Pu to $^{239+240}\text{Pu}$ and ^{241}Pu to $^{239+240}\text{Pu}$), although for the majority global fallout was concluded to be the main origin of transuranic isotopes. In our laboratory 25 sources from this project were preserved and still available. After about 12 years (on average: 4065 days) which elapsed since the preparation of the Am alpha sources (plastic foil filters with several micrograms of NdF_3 crystals on it glued on to a metal plate) were taken for radiochemical separations in order to determine the ingrowth of plutonium alpha activity within them.

2 METHOD AND RESULTS

Prior to the radiochemical procedures all samples were re-measured by alpha spectrometry to ensure the self consistency between our past and present measurement techniques. The average ratio between past and present ^{241}Am results (decay corrected) was 0.95 with standard deviation of 0.12. Thus it was considered satisfactory. Radiochemical work

started with the dismantling of alpha sources. Filters were carefully removed from the metal discs and then dissolved in hot *aqua regia* with some boric acid added. A spike of ^{242}Pu was added (13.3 mBq) to each sample. After evaporation a few drops of perchloric acid was added to destroy any remains of filter material. Then the Pu oxidation state was adjusted to +4 using hydrazine and NaNO_2 followed later by a standard procedure used to separate Pu from 8 M HNO_3 on Dowex 1x8 anion-exchange resin.⁷ The NdF_3 sources were then prepared and measured by means of alpha spectrometry.

Table 1. Results of Pu measurements in Am sources and calculated $^{242\text{m}}\text{Am}$ activity.

Sample code*	$^{239+240}\text{Pu}$ [mBq/kg]	^{238}Pu [mBq/kg]	$^{242\text{m}}\text{Am}$ [mbq/kg]
1 A ₀ -23	11.0±2.1	4.1±1.9	51±24
2 A ₁ -23	13.7±3.2	<2	<25
3 A ₁ -142	16.2±4.2	15.4±4.6	191±58
4 A ₁ -224	7.7±1.8	<3	<35
5 A ₀ -90	46.2±4.6	19.3±3.2	241±40
6 A ₁ -90	20.3±2.7	3.7±1.1	47±13
7 A ₀ -161	2.5±0.7	<0.6	<8
8 A ₁ -161	50.8±4.5	5.9±1.4	74±18
9 A ₀ -186	8.6±1.3	<1.2	<15
10 A ₁ -186	18.7±2.5	7.9±2.0	99±25
11 A _{0L} -248	17.1±1.9	3.3±1.2	40±15
12 A _{0H} -248	3.0±0.8	<2	<24
13 A _{0L} -157	4.3±0.8	<0.6	<7
14 A _{0H} -157	2.7±0.7	<0.8	<11
15 A ₀ -30	3.3±0.4	<0.5	<7
16 A ₁ -30	17.9±2.0	<3.5	<43
17 A ₀ -204	47.4±9.9	22.2±9.6	277±120
18 A ₁ -204	8.4±1.5	2.6±1.6	33±20
19 A ₀ -13	5.8±1.2	<1.2	<15
20 A ₁ -13	5.6±1.0	<0.8	<10
21 A ₀ -258	4.1±0.8	<0.5	<6
22 A ₁ -258	22.3±6.9	<0.5	<7
23 H2	0.4±0.2	10.0±3.1	90±28
24 IAEA soil375	4.4±1.5	<1.2	<16
25 IAEA soil 6	11.2±3.8	<0.5	<5

* - more details on samples are described in: No 1-22^{3,5,6}, 23 in ⁴, 24 & 25 are the IAEA reference materials.

In the original study^{3,4} we used a relatively high activity of ^{243}Am tracer (usually 226 mBq per sample) and in some samples traces of $^{244+243}\text{Cm}$ were observed. These isotopes all result in the production of ^{239}Pu or ^{240}Pu , and the decay of americium tracer is the dominant source. Spectra therefore revealed traces of $^{239+240}\text{Pu}$ as well as ^{238}Pu . The results of Pu measurements in Am sources are presented in Table 1. The last column of this table shows the $^{242\text{m}}\text{Am}$ activity calculated from Beteman equation. In about half of our samples

an excess of $^{239+240}\text{Pu}$ activity above that expected from ^{243}Am decay is noticed, which suggests possible contamination of original Am fraction with tiny traces of Pu. This means that the observed ^{238}Pu activities are the upper limits of that ingrown from ^{242m}Am decay. The calculated ^{242m}Am activities do not correlate with measured ^{241}Am activity (see Fig. 1), which is of mixed Chernobyl and global fallout origin.

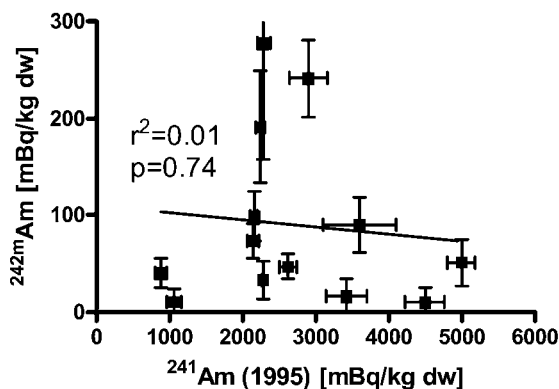


Figure 1 Lack of correlation between ^{241}Am and ^{242m}Am in forest litter samples

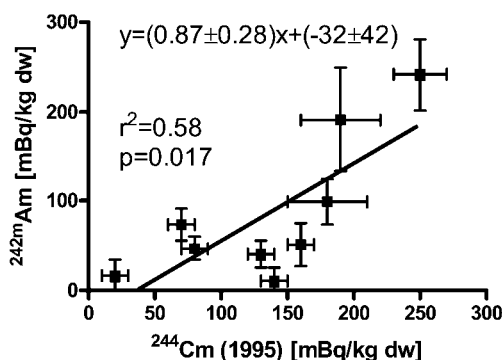


Figure 2 Correlation plot for ^{244}Cm and ^{242m}Am in forest litter samples

The mean value for $^{242m}\text{Am}/^{241}\text{Am}$ activity ratio is 0.023 with standard deviation of 0.033 so, in general, the ^{242m}Am to ^{241}Am ratio is on the level of a single percent. The high standard deviation reflects the mix of two sources (global fallout and Chernobyl) which differ in ^{242m}Am to ^{241}Am activity ratio. Moreover, ^{242m}Am activities (or rather upper limits) correlate with the ^{244}Cm activity measured in 1995 (see Fig. 2), which is of solely Chernobyl origin. This suggests that Chernobyl is the dominant source of ^{242m}Am in this area. The slope of the correlation line is 0.87 ± 0.28 ; after decay correction of activities back to 1986 this ratio equals 0.63 and this is an estimation of the upper limit of ^{242m}Am to ^{244}Cm activity ratio for fresh Chernobyl fallout. This is about order of magnitude higher than reported in the past⁸. Taking into account the estimated released 6.2 TBq of ^{244}Cm gives an upper limit for release of ^{242m}Am from Chernobyl of 3.9 TBq. Available data

allows to estimate, that the ^{242m}Am to ^{241}Am ratio in Chernobyl fallout at present (including ^{241}Am ingrown from ^{241}Pu) may be even as high as 7%.

3 CONCLUSION

Analyses of ^{238}Pu traces present in americium sources obtained from forest litter samples was used to estimate the upper concentration limit of long lived ^{242m}Am . The phrase “upper limit for activity” instead of “activity concentration” reflect the potential for tiny traces of plutonium to be present in the original americium sources. The current results confirm a previous estimation² that ^{242m}Am activity is on level of single percent of ^{241}Am . Moreover, a correlation between the ^{242m}Am upper limit and the ^{244}Cm activity concentration (as measured in 1995) was found, which allowed the ^{242m}Am to ^{244}Cm upper limit ratio in fresh Chernobyl fallout to be 0.63 (in 1986). This leads to a maximum release of ^{242m}Am from Chernobyl, of 3.9 TBq. Thus, the ^{242m}Am to ^{241}Am activity ratio for Chernobyl fallout at present is estimated to be equal up to 7%.

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THE FATE OF TECHNETIUM-99 (^{99}Tc) IN THE NORTH AND NORDIC SEAS AFTER REDUCTION IN THE DISCHARGES FROM SELLAFIELD

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1 INTRODUCTION

Technetium-99 (^{99}Tc) is a long-lived, pure β -emitting ($E_{\text{max}} = 292 \text{ keV}$) radionuclide with a half-life of 2.13×10^5 years. During the period 1994-2004, large amounts of ^{99}Tc were discharged into the Irish Sea from the nuclear reprocessing plant Sellafield (UK)^{1,2,3,4} (Figure 1). In oxygenated seawater, ^{99}Tc is transported over long distances as the highly soluble pertechnetate ion, TcO_4^- . As a result of the increased discharges, the concentrations of ^{99}Tc increased in seawater and marine organisms in Norwegian and adjacent waters during the late 1990s.⁵ This caused serious concerns in Norwegian fisheries and seafood industries although there was no known health or environmental impact from the measured concentrations.^{4,5} The issue also attracted strong criticism from Norwegian Ministers, media, NGOs and community groups at the beginning of the new millennium.⁶ In 2004, the implementation of a new treatment process for spent nuclear fuel led to a reduction in the discharges of 90%.⁶

The Institute of Marine Research (IMR) participates in the Norwegian national monitoring programme RAME (Radioactivity in the Marine Environment), coordinated by the Norwegian Radiation Protection Authority (NRPA), where concentrations of ^{99}Tc in Norwegian waters have been monitored.⁷ The aim of the present study was threefold: to present IMR's monitoring data on ^{99}Tc in Norwegian waters from the period 2003-2010; to follow and document the decrease in concentrations of ^{99}Tc in Norwegian waters after the reduction in the discharges from Sellafield; and to extend already existing datasets which can be used to model developments and validation.

2 MATERIALS AND METHODS

2.1 Sample collection

Sample collection took place during cruises conducted by IMR in the North and Nordic Seas and by local fishermen along the Norwegian coast in the period 2003-2010. Surface seawater (50-100 L from a depth of 0-5m) was collected in 25 L polyethylene carboys using a shipboard pump or by lowering the carboy into the seawater. Since the samples

were collected in open sea areas with low concentrations of suspended materials, filtering prior to analysis was not necessary.

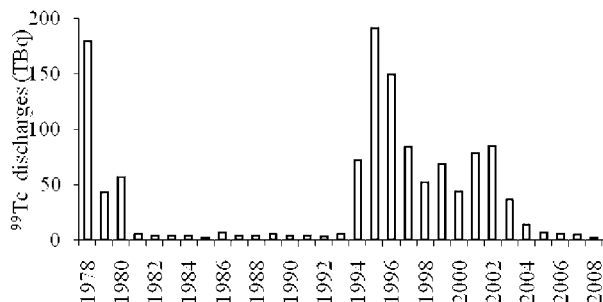


Figure 1 Discharges of technetium-99 from Sellafield in the period 1978-2009. A total of 879 TBq was discharged in the period 1994-2004.

In July 2010, 20 samples from the North Sea, Skagerrak and the Norwegian Coastal Current (NwCC) were collected during a cruise aboard R/V *Johan Hjort*. The sampling stations are shown in Figure 2.

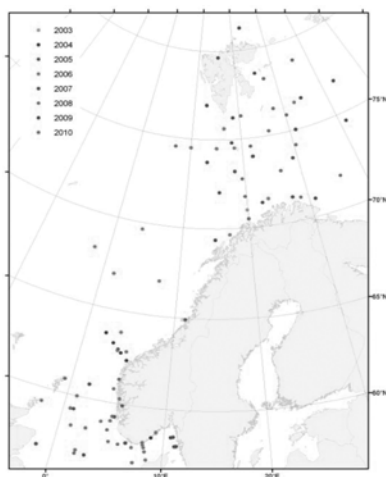


Figure 2 Sampling stations for collection of surface water during the years 2003-2010. Map provided by K. Bakkeplass, IMR.

2.2 Analytical Method

Radiochemical separation of ^{99}Tc from the sample matrix removes interference from other β -emitting radionuclides, and is necessary for quantitative analysis. The analytical method for determination of ^{99}Tc in seawater used at IMR, is based upon Harvey *et al.*⁸ This method uses rhenium, in the form of KReO_4 , as a non-isotopic carrier and yield monitor. After adding rhenium, a preliminary extraction of ^{99}Tc (and Re) based on anion-exchange separation is performed. Iron hydroxide scavenging is thereafter performed to remove unwanted components such as alkaline and rare-earth elements and phosphates. ^{99}Tc and

Re are further extracted by a second anion-exchange separation and eluted with an alkaline sodium perchlorate solution. Next, two subsequent sulphide precipitations are performed in order to remove perchlorate ions. Finally, the tetraphenyl arsonium salts of ^{99}Tc and Re are isolated. Perchlorate ions will also form an insoluble tetraphenyl arsonium salt, and need therefore to be removed before the final precipitation. The yield of the rhenium tetraphenyl arsonium salt is determined gravimetrically. ^{99}Tc is beta-counted using a RISØ low-level beta GM multicounter system. Count times were of the order of 48 hours and all counts were corrected for background (typically 0.0025 cps). The theoretical detection limit for 100 L seawater is 0.05 Bq m^{-3} .

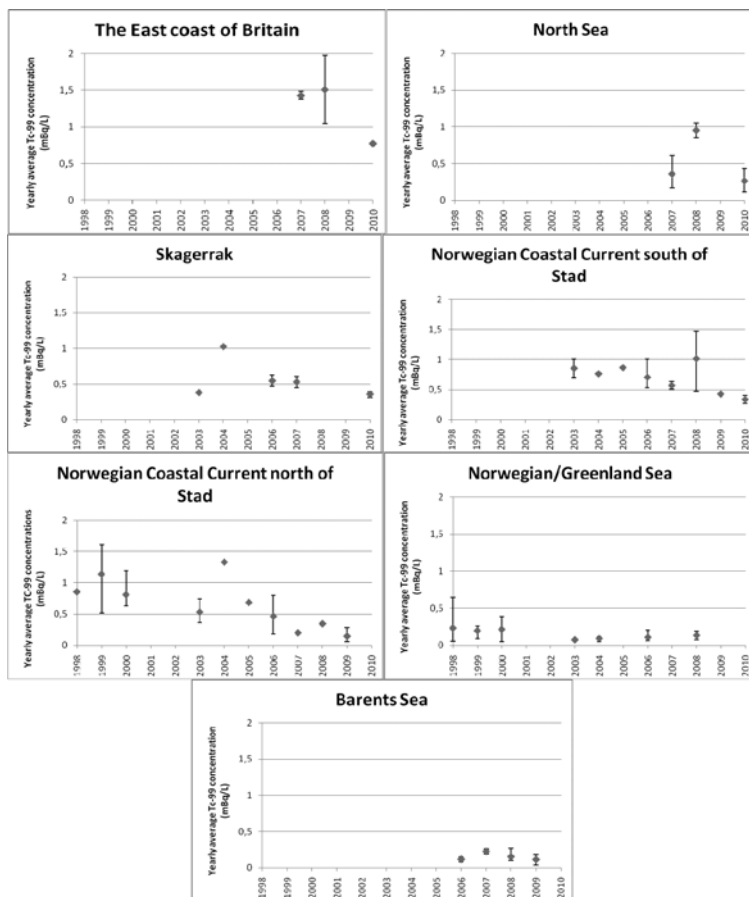


Figure 3 Technetium-99 (Bq m^{-3}) in surface waters in the North and Nordic Seas. Diamonds show average concentrations for each year. Bars show minimum and maximum concentrations. Note that some of the averages are based on few measurements, and may not represent good averages. A few samples from the Norwegian/Greenland Sea had concentrations below the detection limit. These are not included in the calculation of average concentrations.

3 RESULTS AND DISCUSSION

Time-series of ^{99}Tc activity concentrations in the North and Nordic Seas are shown in Figure 3, also including data from an IMR/CEFAS (Centre for Environment, Fisheries and Aquaculture Science) study conducted during the years 1998-2000.⁴

The highest concentrations are measured in samples from the east coast of Britain, the North Sea, Skagerrak and the NwCC, reflecting the closeness to Sellafield and the general circulation pattern of surface water in this area. The concentrations in the Norwegian, Greenland and Barents Seas have been generally low (below 1 Bq m^{-3}) during the whole period. The time-series show that the ^{99}Tc concentrations in the North and Nordic Seas are generally decreasing. However, measurements from the North Sea and the NwCC in 2008 showed somewhat higher concentrations than anticipated ($0.72\text{--}2.0 \text{ Bq m}^{-3}$). The reason for this is not clear.

In 2010, the concentrations of ^{99}Tc in the North Sea and the Skagerrak ranged from $0.12\text{--}0.77 \text{ Bq m}^{-3}$. The highest concentration was observed off the Scottish coast. The average concentrations in the North Sea, Skagerrak and the NwCC south of Stad were 0.26 , 0.35 and 0.34 Bq m^{-3} , respectively. These results are similar to the levels reported by Herrmann *et al.*⁹ of 0.4 and 0.3 Bq m^{-3} in the NwCC and the Skagerrak, respectively, in July 1991. However, the source of the ^{99}Tc contamination observed by Herrmann *et al.*⁹ was mainly elevated discharges from the French reprocessing plant La Hague during the 1980s.

Although the ^{99}Tc concentrations in the North and Nordic Seas has decreased after the reduction in the discharges from Sellafield, the levels in the North Sea off the Scottish coast are still significantly higher today than before 1994 ($0.1\text{--}0.2 \text{ Bq m}^{-3}$ in 1992 and 1993).¹ Further, the present levels are much higher than the 'fallout background level' of 0.005 Bq m^{-3} reported for oceanic Atlantic water.¹⁰

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FURTHER DEVELOPMENT OF A FAST METHOD FOR DETERMINING PLUTONIUM AND AMERICIUM IN SOILS IN GERMANY

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1 INTRODUCTION

The ubiquity of the plutonium nuclides Pu-238 ($t_{1/2} = 88$ a), Pu-239 ($t_{1/2} = 24\,000$ a), Pu-240 ($t_{1/2} = 6\,500$ a) and Pu-241 ($t_{1/2} = 14$ a) in soil today results mainly from the fallout after the atmospheric testing of nuclear weapons in the period 1950 to 1963.¹⁻⁴ Additional amounts of Pu-238 were globally dispersed after a satellite burned out in the upper atmosphere in 1964. Local increases in plutonium contamination of soil have been caused by emissions during the early years of nuclear technology and by accidents at nuclear installations. Am-241 ($t_{1/2} = 430$ a) occurs in soil as a result of Pu-241 decay. Thus the activity of Am-241 has been increasing since the nuclear weapons tests. Owing to their relative half-lives, almost equal activities of Pu-241 and Am-241 are to be expected in the environment today.

The activities in soil and other environmental samples are usually much less than 1 Bq/kg dry mass. The analysis of such small activities of these radionuclides in soil samples for environmental surveillance purposes requires specific separation from large amounts of sample, typically about 100 g soil ash. Conventional analysis methods are very difficult, laborious with analysis times of 4 to 5 days frequently providing only small nuclide yields. There is urgent need for a fast method of efficiently and reproducibly separating Pu and Am from a wide range of soils.

At ERA 10 in 2006, Horwitz et al.⁵ described an alternative method for the analysis of “non-refractory” Pu and Am in large (100 g) soil samples. The method is based on the sequential and specific separation of Pu and Am from an acid extract of the soil ash with the aid of pre-packed ion-exchange columns of DGA and TEVA from Triskem International. Am and Pu are collected separately on ResolveTM filters after micro-precipitation prior to α -spectrometry.

With the aim of establishing an improved method for the official surveillance and monitoring of these nuclides in Germany, the method was used to analyze tilled soils from all the sampling locations for routine radioactivity surveillance. To test the more general applicability, some samples of undisturbed soils from pastures and moors were also analyzed.

Initially a selection of the soils was used to test the method for the conditions in Germany. In these tests several problems occurred that seemed to depend on soil type. Therefore the method was appropriately further developed, modified and validated.

This study describes the initial problems along with the modifications to the method, the results of the validation experiments as well as of the subsequent survey on tilled soils from almost all of the German federal states. The activities of Pu-239/240 determined in this survey are compared to those found in Germany in 1996 with a different and more difficult method. As Horwitz et al. intended the method for the analysis of “non-refractory” Pu and Am, work was carried out to determine how much of the nuclides not accounted for (i.e. not acid extractable). The results of this work are also described.

2 EXPERIMENTAL

2.1 Sampling, Preparation and Ashing of the Soils

Soil samples from moor and pasture were taken to a depth of 10 cm at the research farm of the MRI in Schaedtbek. The samples were air dried, sieved to particle size less than 2 mm with the aid of a special mill (Firma Jemlich, Nossen) that automatically separates stones, roots and plant residues from the soil while milling and sieving. The soil was then distributed to a maximum depth of 1 cm in ceramic trays (height 55 mm, width 145 mm, length 205 mm, wall thickness 4 – 5 mm; Firma Haldenwanger, Waldkraiburg). In initial experiments the soils were ashed at a temperature of 600°C. The results of initial experiments (see 3 RESULTS) showed that more intensive ashing was needed. Therefore in all other experiments the samples were ashed at 700 °C for at least 18 hours.

The tilled soils were taken by the official monitoring laboratories of the German states (Länder) according to the sampling plan of the federal routine monitoring program. This stipulates a sampling depth of 30 cm for such samples. The samples were dried and ashed by the monitoring laboratories prior to despatch to the MRI with details such as soil description and sampling location. The locations were in all cases those used year for year for annual radioactivity monitoring purposes.

2.2 Microwave oven supported extraction and radiochemical separation

The acid leaching of the ash described by Horwitz et al (Reference 5, Figure 2) is replaced here by microwave supported acid extraction of the ash at a maximum pressure of 10 bar. The laboratory microwave oven system was an Ethos 2 or Ethos plus from MLS (Leutkirch, Germany) fitted with 1 litre sample containers and pressure release valves that open automatically at pressure greater than 10 bar. Following this treatment the separated acid phase was filtered through 3 glass fibre filters and a fine membrane filter in series. This procedure is essential to prevent blockage of the DGA column subsequently used for Pu and Am binding from the acid extract (see 3 RESULTS). The procedure details are given in Appendix 1.

2.3 Special Reagents and Materials

DGA and TEVA resins (respectively N,N,N',N'-tetra-n-octyl-3-oxopentadiamid and Aliquat 336 – a trialkylmethylamin on carrier resin) in the form of 2 ml pre-packed columns (particle diameter 50 – 100 µm), Resolve™ filter (diameter 25 mm, pore diameter 0.1 µm) and the Vakuum Box AC-12 were purchased from Triskem International, Brux France. Schleicher und Schüll (Düren, Germany) supplied the fibre glass filters (diameter 100 mm, type GF6) and Sartorius the Cellulose Nitrate Membrane filters (diameter 47 mm,

pore diameter 0.45 μm). TiCl_3 in hydrochloric acid solution was obtained from Sigma. All other reagent were of analytical quality from VWR, Germany.

2.4 Alpha Spectrometry

2.4.1 Counting. Pu-238, -239, -240 and Am-241 are α -emitters and were measured by alpha spectrometry with the Alpha Analyst System (Canberra-Eurisys, Dreieich) with 12 low-level, evacuated α -measurement chambers fitted with PIPS semiconductor detectors (17 keV FWHM). Pu-241 decays by β -emission and was not measured in this study. Prior to measurement the ResolveTM filters with the Pu or Am precipitates were glued on stainless steel plates and placed directly beneath the PIPS detectors. The resolution of the α -spectra of such preparations were similar to those of spectra obtained by electrodeposition (5–50 mBq nuclide, counting time 7 days).

The Pu and the Am α -spectra were measured separately for each sample in the energy range 3.6–8.0 MeV with counting times of at least 7 days. The nuclides of interest were counted in their respective, characteristic energy “regions of interest” (ROI). As expected the detectors did not resolve the α -peaks of Pu-239 and Pu-240. Therefore the sum of the count rates of these two nuclides (Pu-239/240) at 5.1 MeV was counted. Pu-238 was counted at 5.4 MeV. In the Am spectrum Am-241 was counted at 5.5 MeV. All nuclear data (alpha energies, emission probabilities and half-lives) were taken from references 6 (for Pu) and 7 (other nuclides).

2.4.2 Internal Standards/Tracers. Pu-242 ($t_{1/2} = 3.7 \times 10^5$ years) and Am-243 ($t_{1/2} = 7.4 \times 10^3$ years) were used as yield tracers for Pu and Am, respectively. To allow quantitative evaluation of the nuclides of interest the tracers were purchased as standard solutions (Eckert and Ziegler Nuclitec GmbH, Braunschweig). The analysis certificates (from the National Physical Laboratory, UK) stated the following impurity levels for the Pu-242 standard: Pu-241 less than 7 % and Am-241 less than 0.3 % of total activity at the reference date 01.08.2005. For the Am-243 standard the stated impurity levels were: Am-241 less than 0.03 % of total activity on 30.04.1997. The Am-243 is of course in radioactive equilibrium with the daughter Np-239 ($t_{1/2} = 2.36$ days). Np-239 is however a β -emitter and does not interfere with the α -spectrometric measurements carried out here. The emissions of Pu-242 and Am-243 were counted at 4.9 and 5.5 MeV, respectively. In the respective Pu and Am α -spectra, these peaks are well resolved and interfere insignificantly with the other peaks of interest.

2.4.3 Determination of Net Count Rates. Contributions from background, reagents and tracers (Pu-242 or Am-243) were subtracted from the observed count rates. The reagent blank count rates were obtained by carrying out all steps of the analysis without the sample material (i.e. reagent only). The contributions from the tracers were determined by applying the usual amount of tracer solution (0.5 to 1.0 ml) dropwise to a ResolveTM filter and drying in air prior to α -spectrometry. (Background and reagent blank count rates were determined with counting times of about 1×10^6 seconds). Sample results were calculated from the net count rates.

Table 1 summarizes typical count rates for background, reagent blanks and tracers in the relevant α -energy regions and shows the importance of such studies prior to evaluating sample spectra. Clearly, the Am-241 impurity of the Pu-242 tracer significantly increases the blank value for this nuclide in the Am spectrum. All Am sample spectra were therefore corrected for this contribution. On the other hand the Pu-241 and Np-239 impurities described in the tracer certificates are pure β -emitters and do not interfere with the α -spectrometry.

Table 1 Typical count rates in the alpha spectra of Pu and Am tracers and of reagent blanks with and without tracer addition

Description	Alpha spectrum	$t_m^{1)}$ (10^3 s)	Impulses / 10^5 s at energy (MeV)		
			(4,8 - 4,9)	(5,1 - 5,2)	(5,4 - 5,5)
Reagent blank (no tracer) ²⁾	Pu	9,4	1,6	0,5	1,2
	Am	6,2	--	2,3	2,6
Filter + ca. 100 mBq Pu-242 ³⁾		16,2	2004	1,7	9,1
Filter + ca. 50 mBq Am-243 ³⁾		3,6	2,6	971	0,9
Reagent blank and 100 mBq Pu-242 + 50 mBq Am-243)	Pu	9,5	2055	3,4	0,6
	Am	9,3	16,4	997	11,8

¹⁾ real counting time of the sample. ²⁾ Analysis procedure as described in the appendix but without sample and tracers. ³⁾ 0.5 bis 1.0 ml wässrige Tracerlösung added dropwise to the ResolveTM filter then dried.

2.5 Validation

As reference materials for validation of the modified procedure back samples from previous ring experiments were used. For Pu soil samples (sandy clay, 95 % ash) from a ring experiment on tilled soil in Germany in the year 1995/1996 was used.⁸ Am-241 was checked with the aid of river sediment from a ring test in Germany in the year 2006.⁹

3 RESULTS

In initial studies the separation columns of DGA frequently blocked during elution of the acid extract of the soil ash. Filtering the extract through a fine membrane filter prior to application on the DGA column did not prevent this. The effect occurred most frequently with soils of somewhat larger organic content (more than about 8 %). Microscope studies of the soil ashes and of the acid extracts showed the presence of minute black or brown-coloured fibrous particles – presumably incompletely ashed or undigested organic material. The appearance of this material in the acid extract could finally be prevented by a combination of measures: 1) intensifying the ashing procedure (to 18 hours at 700°C, 2) carrying out the acid extraction with the aid of a laboratory microwave oven at increased pressure (up to 10 bar), 3) filtering the acid extract of the ash through 3 fibre glass filters in series. The combined procedures strongly improved the nuclide yields of the separation method, and blockages were no longer observed.

The initial investigations of the Pu and Am alpha spectra of the soil samples often indicated the presence of a peak at about 3.95 MeV in several spectra. This is characteristic of the α -emission of natural Thorium (Th-232). Soils in Germany may contain between 5 to 700 Bq Th-232/kg soil dry mass i.e. three to four orders magnitude greater than the expected activities of Pu and Am nuclides. The presence of even a small fraction of the total thorium activity may interfere in the analysis of Pu and Am nuclides owing to emissions from Th-232 daughters like Th-228 ($t_{1/2} = 1,9$ years) and Ra-224 ($t_{1/2} = 3,66$ days). The α -particle energies of Th-228 are 5.34 and 5.42 MeV while those of daughter Ra-224 are 5.45 and 5.66 MeV. These alpha particles interfere strongly with the measurement of those of Pu-238 and Am-241 (5.5 MeV in both cases) and of the tracer Am-243 (5.20 MeV). These effects were considerably stronger in the Am than in the Pu spectra.

According to Horwitz et al Thorium is initially bound (with Pu) on the TEVA column (see figure 3 of reference 5). Th is then eluted from the TEVA and removed from the system with a wash of 20 ml 9 mol/L hydrochloric acid. Washing with greater acid volume did not eliminate the 3.95 MeV signal in the α -spectra. Presumably this procedure is inadequate for soils containing large amounts of Th. However, placing an additional TEVA column between the TEVA and DGA columns shown in Figure 3 of reference 5 decreased the Th contamination to an insignificant level in the Am spectra. This procedure was then applied to all subsequent analyses i.e. at the stage described in figure 3 of reference 5, two TEVA columns are placed in series followed by a DGA column. After elution the additional (second) TEVA column is discarded. The remaining weak interference with Pu-238 to be expected in some of the Pu spectra was accepted because in general the net count rate in this region was below the limit of detection and the peak was not evaluated.

In all subsequent analyses the modified procedure as described in appendix 1 was used. Table 2 compares the results obtained by analysis of the ring test back samples with this procedure and the results of the original ring tests on these materials.

Table 2 Results of analyses of back samples of ring test materials: Pu in soils and Am-241 in river sediment

Nuclide	Modified method of Horwitz et al.	Bq / kg dm		n ²⁾
		PTB reference value ¹⁾	Mean of laboratory means	
Pu-238 ³⁾	18,6 $\pm$ 1	19,6 (s = 1,3)	20 (s = 1,4)	12
Pu-239/240 ³⁾	1,3 $\pm$ 1	1,1 (s = 0,1)	1,2 (s = 0,3)	20
Am-241 ⁴⁾	134 $\pm$ 5	154 (s = 5)	133 (s = 12)	24

¹⁾ determined by the Physikalisch-Technische Bundesanstalt, Braunschweig.²⁾ number of values in ring test free of outliers.³⁾ In soil^(8), 4) In river sediment⁽⁹⁾. dm is dried mass.

The procedure was also carried out on soils from moor pasture and moor with a much greater organic content (ash fractions only 65 and 70% respectively) than in the ring test soil. The means of the Pu-242 tracer yields in 10 analyses of the moor pasture and 4 of the moor the Pu yields were 69% (standard deviation, s = 14%) and 66% (s = 11%). The means for Am-243 tracer in both cases were 69% (s = 8, respectively 14%).

The results of the analyses of the tilled soil samples from the different federal states are shown in the form of a map of Germany in Figure 1. The means with one standard deviation as well as the number of sampling locations are given at about the mid position of each state. (Hessia and Saarland did not provide samples and are shown blank). Most sample analyses were carried out in duplicate and a few were repeated several times. The maps show only values for Pu-239/240 and for Am-241. The values for Pu-238 were less than the detection limit of about 12 mBq/kg for all of the tilled soils.

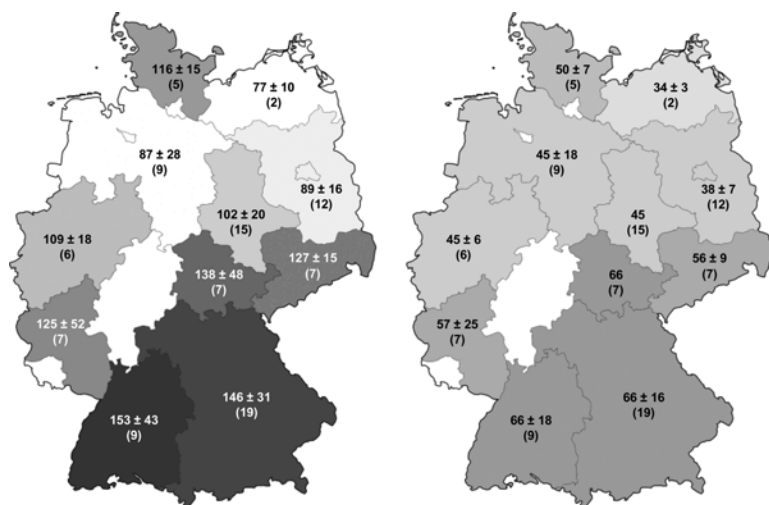


Figure 1 Political maps of the Federal Republic of Germany with activities of *Pu-239/240* (left) and *Am-241* (right) in Bq / kg soil dry mass in each of the federal states (apart from Hesse and Saarland).

Some of the sampling locations are similar to those sampled in the year 1996 in a previous study on Pu nuclides in German tilled soils.^{10, 11} In that study Am was not determined and Pu was extracted by a conventional radiochemical procedure after acid leaching of the soil ash. The Pu-239/240 activities determined in the present study and in 1996 are compared in table 4.

It is possible that under the conditions used here a fraction of the nuclides is not extractable. Therefore, following the microwave assisted acid extraction and prior to the radiochemical separation procedure, some samples were treated with concentrated and evaporated to dryness. The hydrofluoric acid treatment removes silicates from the system, making the nuclides more acid soluble, and was repeated several times until no weight loss of the sample occurred. The Pu and Am were then separated from the residue as for all other samples. The details of the procedure are given in the appendix 2.

The results in Table 4 imply that for the soil types studied microwave assisted acid extraction is least efficient for clay soils. In this case about 13% ($1/[A1 + 1] \cdot 100$) of the total amount of Pu-239 measured ($A1 + A2$) was contributed by the repeated hydrofluoric acid treatment of the ash residue after the microwave assisted acid extraction. Or 87% of the total amount of Pu-239/240 extracted by both procedures was extracted by the microwave assisted process.

Table 3 Comparison Pu-239/240 activity concentrations of tilled soils sampled in the years 1996 und 2008 at the same same locations.

Land	Sampling location	mBq Pu-239/240 / kg soil	
		1996	2008
BAY	Abensberg	116 ± 5	106 ± 5
	Alersheim	175 ± 8	166 ± 7
	Elsenfeld	126 ± 7	125 ± 1
	Geiselwind	141 ± 26	131 ± 1
	Haldewang	104 ± 6	128 ± 1
	Hemau-Wollman.....	153 ± 4	155 ± 6
	Pfolfeld-Gundelsheim...	131 ± 13	125 ± 1
	Plech	142 ± 3	169 ± 14
	Poppenhausen	105 ± 9	100 ± 11
	Schillingsfürst	141 ± 18	161 ± 1
	Schleßlitz-Wiesen...	128 ± 10	161 ± 11
	Schondra-Schöne....	113 ± 8	134 ± 5
	Schwandorf-Neul.....	101 ± 9	135 ± 1
	Sulzemoos	140 ± 1	155 ± 9
	Traunitz-Söllitz	153 ± 9	196 ± 22
	Weißdorf-Beuk..	183 ± 4	185 ± 16
BRA	Alt Lüdersdorf	57 ± 2	101 ± 4
	Karstädt	92 ± 2	78 ± 1
NDS	Ganderkesee	98 ± 4	113 ± 3
	Hornburg	120 ± 2	91 ± 1
	Mariental	83 ± 10	92 ± 2
	Salzgitter, Drütte	76 ± 3	111 ± 2
RLP	Dellfeld	132 ± 4	124 ± 1
	Fürfeld	71 ± 4	75 ± 2
	Holzhausen	131 ± 4	125 ± 1
	Neustadt a. W.	86 ± 1	95 ± 1
	Reinsfeld	67 ± 15	252 ± 13
	Schifferstadt	91 ± 3	86 ± 1
SAS	Klipphausen	112 ± 1	108 ± 4
	Markersdorf	114 ± 2	141 ± 22
	Neuensalz	155 ± 6	136 ± 9
SAH	Kakerbeck	99 ± 1	83 ± 5
SLH	Brunsbek	69 ± 5	107 ± 4
	Kükels	108 ± 3	119 ± 10
	Leck	76 ± 3	140 ± 1
THÜ	Haufeld-Teichröd....	235 ± 10	248 ± 9
	Guthmannshausen	98 ± 1	119 ± 3

Abbreviations: BAY, Bavaria; BRA, Brandenburg; NDS, Lower Saxony; RLP, SAS, Saxony; SAH, Saxony Anhalt; SHL, Schleswig Holstein; THÜ, Thuringia.

Table 4 Efficiency of microwave assisted acid extraction: Activity extracted from ashes of different soils by microwave assisted acid extraction (A1) relative to that extracted from the residue of this extraction after repeated hydrofluoric acid treatment (A2).

Sampling location	Soil description	A1 / A2	
		Pu-239/240	Am-241
Hauchfeld (THÜ)	clay	7	10
Hüde (NDS)	moor (peat)	16	17
Bornheim (NRW)	sandy silt	16	>12
Karstädt (BRA)	sand	21	>14
Hemau-Wol (BAY)	Silty loam	10	>52

4 DISCUSSION

The results on the back samples of the ring experiments on Pu in soil and Am-241 in river sediment confirm the study of Horwitz et al.⁵ and indicate that the modifications in this work do not decrease the accuracy of the results.

All α -spectra of Am were free of natural thorium interferences. This confirms the effectiveness of the additional TEVA column (see reference1, figure 3). However some of the Pu α -spectra showed small count rates at 3.95 MeV, implying the presence of Th-232. In these cases the contributions of the Th daughters in the region of the Pu-238 peak around 5.5 MeV must be considered. After correction for such contributions the remaining net count rate did not exceed the limit of detection. This corresponds to about 12 mBq Pu-238 / kg soil (dm) for all tilled soil samples.

The Pu-239/240 activities in Germany vary only slightly with a mean value of 125 mBq/kg soil (dm) and standard deviation of 40 mBq/kg. This mean value agrees well with the study carried out on 87 tilled soils in 1996 (mean 123, standard deviation 66 mBq/kg dm). Table 3 shows that for most locations sampled in 1996 and in 2008 the Pu-239/240 values agree well. The largest discrepancy is at the location Reinsfeld. In this case, however, the residue after ashing was greater than 95 % in 1996 but only 87 % in 2008. This value does not correspond with the description “sandy soil” given by the sampler in both cases and may indicate that the samples are not from the same location.

The values for Am-241 in Germany 3 also show only small variations: the mean is 54 mBq/kg (dm) and standard deviation 19 mBq/kg. The maps of Pu-239/240 and of Am-241 activity concentration in the different federal states may indicate that there is a general increase in activity over the approximately 1000 km from north to south. The mean of the relative activities of Pu-239/240 and Am-241 in the whole of Germany is 2.3 with a standard deviation of 0.3. This applies to all states, implying the source of the nuclides is the same. This ratio is consistent with that expected for these nuclides when the source is “fallout” from atmospheric nuclear weapons testing.

The chemical yields for Pu and Am are reproducible and large for all the soils analyzed in this study. The mean values for the yields of all analyses of the tilled soils are for Pu 87% (standard deviation 11%) and for Am 72% (standard deviation 14%).

Repeated treatment with hydrofluoric acid following the microwave assisted acid extraction may increase the total activity of extractable Pu and Am for some soil types (clay) up to 13% in the case of Pu and about 9% in the case of Am. This effect was much

weaker for the other soil types tested (see Table 4). This implies that the method without additional hydrofluoric acid treatment estimates with acceptable accuracy the potentially available Pu and Am in all German soils routinely sampled for environmental radioactivity surveillance purposes. The times required for the different stages of the analysis are as follows: sample preparation (drying, sieving and ashing) 24 to 48 hours, radiochemical separation from the ash about 8 hours, α -spectrometry at least 5 days for current routine (low-level) samples. The radiochemical separation is much faster than conventional methods which take 4 to 5 days. The additional measures introduced to the original method of Horwitz et al. (ashing at greater temperature – 700°C, microwave assisted acid extraction at 10 bar pressure, filtration of the acid extract through 3 glass fibre filters and the use of a second TEVA column in series with the first) provide a procedure that gives consistently large yields with a wide range of soil types.

Furthermore the good agreement of the results obtained in the present study with those of the 1996 study (see Table 3) determined by the conventional extraction may imply that migration of these nuclides to deeper soil layers is insignificant in this time period and support the method's validity.

Work is continuing to improve the Pu spectra by more efficient Th removal, as well as to determine the Pu-241 activities in the soil samples by ultra-low-level liquid scintillation counting. Preliminary work shows also that the modified method functions well in the analysis of ash samples of hay, maize, sediments and dried sewage sludge.

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Appendix 1: Radiochemical Separation of Pu and Am from Soil Ash - Procedure

1 Microwave assisted acid extraction

1.1 Place 100 g of soil ash, 450 ml of about 8 mol/l hydrochloric acid (150 ml deionised water and 300 ml 36 – 38% hydrochloric acid) and a teflon coated magnetic stirring bar in the microwave oven sample container (volume 1 Liter). Add carriers and radiotracers: 400 µg samarium as SmCl_3 , 4.5 g $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$, Pu-242 (100 mBq) and Am-243 (50 Bq).

1.2 Place the sealed container in the microwave oven and irradiate to attain the temperature 100°C in 20 minutes. Maintain this temperature for 30 minutes. The pressure within the vessel increases to a maximum of 10 bar above which the vessel automatically ventilates. Cease irradiation. Allow the contents of the vessel to cool to a temperature less than 60°C (1 hour). Open the vessel carefully.

2 Collection and pre-filtration of the acid extract

2.1 Transfer the contents of the vessel in 1.2 to a 1 litre centrifuge flask and centrifuge. Decant the clear liquid into a 1 litre beaker. Slurry the residue in the centrifuge flask with 60 ml 6 mol/l hydrochloric acid then centrifuge. Combine the clear liquid with the initial sample solution in the 1 litre beaker. Repeat this procedure

2.2 Filter the combined sample solution and washings in 2.1 under suction through the 3 glass fibre filters layered on top of each other. Finally, filter the filtrate through a cellulose nitrate membrane filter. Keep the filtrate and discard the filters.

3 Separation of Pu and Am from the acid extract

3.1 Place the contents of a pre-packed 2 ml DGA-column in a glass column (diameter 10 mm) fitted with a reservoir, glass frit (P2) and stop-cock. Condition the DGA with 5 ml of 4 mol/l hydrochloric acid. Finally discard the hydrochloric acid.

3.2 Allow the sample solution in 2.2 to elute through the conditioned DGA column in 30 to 40 minutes. Wash the DGA with two 5 ml portions of 4 mol/l hydrochloric acid then with two 2.5 ml portions of 3 mol/l nitric acid. Discard all eluates. (Pu and Am remain on the DGA).

3.3 Elute Pu and Am from the DGA column with 20 ml 0.03 mol/l oxalic acid in 0.25 mol/l hydrochloric acid at a flow rate of 1 to 2 ml/minute.

4 Separation of Am from Pu

4.1 To the eluate in 3.3 add 4.7 ml 65% nitric acid and 0.5 g sodium nitrite (NaNO_2). (The nitric acid concentration in the eluate is now about 3 mol/l).

4.2 Connect two pre-packed TEVA columns (columns 1 and 2) and one pre-packed DGA column (column 3) in series so that the DGA is at the bottom. Condition all three columns

with 15 ml 3 mol/l nitric acid. Discard the nitric acid. (The vacuum box AC-12 from Triskem facilitates the elution of the columns under suction).

4.3 Pass the eluate in 4.1 through all 3 columns under suction with the vacuum box AC-12 at a flow rate of 1 ml/minute. Finally wash the columns with 10 ml 3 mol/l nitric acid. Discard the eluate, the washings and the 2nd TEVA column (i.e. column 2). Column 1 (TEVA) binds Pu while column 3 (DGA) binds Am. Keep these two columns.

5 Elution, purification and microprecipitation of Pu.

5.1 Wash column 1 (TEVA) in 4.3 with 10 ml 3 mol/l nitric acid then with 20 ml 9 mol/l hydrochloric acid. Discard the washings.

5.2 Elute Pu from the column with 20 ml of a solution containing 0.03 mol/l titanium chloride (TiCl_3), 0.05 mol/l hydrofluoric acid and 0.1 mol/l hydrochloric acid at flow rate of 1 ml/minute.

5.3 To the eluate add 50 μg cerium(III) nitrate ($\text{Ce}(\text{NO}_3)_3$), 0.5 ml 30% hydrogen peroxide and 5 ml concentrated (40%) hydrofluoric acid. Store the mixture for 30 minutes.

5.4 Activate a ResolveTM filter by washing with a few ml of a solution containing 80% ethanol in water followed by 0.5 ml deionised water.

5.5 Collect the invisible precipitate of Pu- and CeF_3 by filtering the mixture in 5.3 under suction through the ResolveTM filter.

5.6 Wash and dry the filter and the precipitate by passing 5 ml of the 80% ethanol in water solution through it under suction. Prior to α -spectrometry of Pu, the dried filter is glued to a small stainless steel disc.

6 Elution, purification and microprecipitation of Am

6.1 Wash column 3 (DGA) in 4.3 with 5 ml of 3 mol/l nitric acid followed by 20 ml of 0.1 mol/l nitric acid. Discard the washes.

6.2 Elute Am from this column with 20 ml of 0.1 mol/l hydrochloric acid. Collect the eluate, evaporate it to dryness then dissolve the residue in 10 ml of 4 mol/l ammonium thiocyanate (NH_4SCN) in 0.1 mol/l formic acid.

6.3 Condition a fresh (unused), pre-packed TEVA column with 5 ml of 4 mol/l ammonium thiocyanate (NH_4SCN) in 0.1 mol/l formic acid.

6.4 Pass the solution obtained in 6.2 through the TEVA column at a flow rate of 1 ml/minute. Wash the column with 10 ml of 1.5 mol/l NH_4SCN in 0.1 mol/l formic acid. Discard the eluate and the washings.

6.5 Elute Am from the TEVA column with 25 ml of 0.25 mol/l hydrochloric acid at a flow rate of 1 ml/minute. Add 50 μg ceric nitrate ($\text{Ce}(\text{NO}_3)_3$), followed by 5 ml of concentrated (40 %) hydrofluoric acid. Store the mixture for 30 minutes.

6.6 Activate a ResolveTM filter by washing with a few ml of a solution containing 80% ethanol in water followed by 0.5 ml deionised water.

6.7 Collect the invisible precipitate of Am- and CeF_3 by filtering the mixture in 6.5 under suction through the ResolveTM filter.

6.8 Wash and dry the filter and the precipitate by passing 5 ml of the 80% ethanol in water solution through it under suction. Prior to α -spectrometry of Am, the dried filter is glued to a small stainless steel disc.

Appendix 2: Treatment of the Residue after Microwave Assisted Acid Extraction with Hydrofluoric Acid

The dry mass of the residue obtained after microwave assisted acid extraction of the tilled soil ashes is about 80 to 90% of that of the initial ash. To dissolve Pu or Am fractions that were not extractable by the microwave assisted acid extraction these residues were further treated with concentrated hydrofluoric acid. To facilitate sample handling the dried residue was divided into 4 approximately 20 g portions each of which were then treated according to the following protocol:

- 1** Carefully (effervescence) add 30 ml of concentrated (65%) nitric acid and 5 to 15 ml of concentrated hydrofluoric acid to the 20 g sample portion in the Pt-crucible and evaporate to dryness.
- 2** Add 5 to 10 ml of the concentrated hydrofluoric acid and evaporate again to dryness.
- 3** Repeat step 2 with 15 ml additions of hydrofluoric acid at least 5 times and until constant weight of the residue.
- 4** Dissolve the residue in 6 mol/l hydrochloric acid and add solid SmCl_3 and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ proportionately corresponding to stage 1.1 in the method described in appendix 1.
- 5** Combine all sample portions and filter through a cellulose nitrate filter (diameter 47 mm, pore diameter 0.45 μm).
- 6** Treat the filtrate as in the method described in appendix 1 from step 2.2 onwards and measure Pu-239/240 and Am-241 by α -spectrometry.

ACCELERATOR MASS SPECTROMETRY MEASUREMENT OF ^{129}I IN SOLID SAMPLES BY A MICROWAVE BASED PROCEDURE

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1 INTRODUCTION

The presence of ^{129}I in the environment has been strongly elevated since the mid 20th century, due to contributions from nuclear weapon tests, nuclear plant operation and nuclear fuel reprocessing plants. Two of these plants (placed at Sellafield, England, and La Hague, France) are mainly responsible for the ^{129}I present in the Biosphere nowadays. A detailed compilation of releases can be found¹.

^{129}I has a strong potential as a tracer of environmental processes. To take advantage of this, radiochemical methods for ^{129}I extraction from different kinds of environmental samples have to be developed or optimized. The actual iodine extraction procedures, like combustion² and alkaline leaching³, although have proved its high extraction yield, have the main disadvantages of the long time and quantity of sample needed for the total extraction. To beat these limitations, we have developed a new microwave based method to extract the iodine from solid samples, looking for shorter preparation times, small sample sizes and higher automation.

In this work, we present the results for the ^{129}I concentration in several solid samples that have been obtained with this new radiochemical method.

2 MATERIALS

Although we have already prepared and measured successfully more than 250 solid environmental samples (lichens, algae, peat bogs, soils, atmospheric filters, etc.) and nuclear residues following this radiochemical procedure, we present in this report materials that have international relevance with respect to the interlaboratory comparison. The samples that have been included are: (1) the IAEA standard soil #375⁴ and the certified reference material of fish flesh IAEA-414⁵, (2) “sample 7” (pine needles) and “sample 10” (soil) from ^{129}I interlaboratory comparison I⁶ and (3) “sample 8” (maple leaves) from ^{129}I interlaboratory comparison I⁶ and II⁷. Besides, surface soil from Uppsala (Central Sweden) was included².

All chemicals used in the extraction procedure were analytical or suprapure grade. The carrier solution was prepared by diluting Woodward iodine (with a published⁶ $^{129}\text{I}/^{127}\text{I}$ ratio of 5×10^{-14}) with water ($>18 \text{ V cm}^{-1}$) produced in a Milli-Q apparatus (Millipore Co.,

Bedford, MA, USA) at a concentration of 1 mg I⁻/ml. To improve this dilution, 200 µl of NaHSO₃ and 0.09g of NaOH were added. These two compounds reduce I₂ to I⁻, retaining iodide in the aqueous phase and avoiding its evaporation.¹⁶ Nitric acid 60% (v/v), suprapure quality (Merck, Darmstadt, Germany), was used for the microwave digestions. Ba(NO₃)₂ analytical grade (Merck, Darmstadt, Germany) and AgNO₃ extrapure quality (Merck, Darmstadt, Germany), were used for AgI precipitation.

3 EXTRACTION PROCEDURE

Extraction of iodine from solid samples is usually carried out by leaching or combustion methods.^{2,3} These methods have proved to be reliable and have a high extraction yield. Their main disadvantage could be the long time needed for the total leaching or combustion. The microwave method presented here has been developed looking for shorter preparation times, small sample sizes and higher automation. The digestion procedure, shown in Figure 1, is based in other works that use it to obtain iodine concentration in environmental samples by different techniques to AMS.^{8,9}

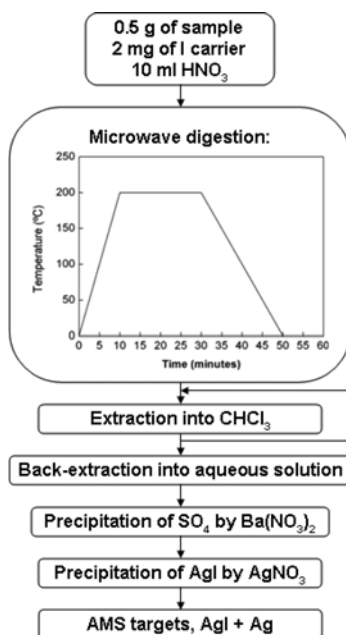


Figure 1 Flow chart summarizing the iodine extraction procedure.

3.1 Microwave Digestion

All samples were digested using a multiwave 3000 microwave sample preparation system (Anton Paar, Graz, Austria) with rotor HF100 and software version v1.52. The system was equipped with 16 high-pressure polyethylene vessels with an internal volume of 100 ml (maximum pressure and temperature of 40 bar and 240 °C, respectively). Typically, 0.5 g of sample, 2mg of I⁻ carrier and 10ml of 60% (v/v) HNO₃ were introduced into the vessels. The operational conditions and the heating program used were carried out according to

these conditions: 200°C for 10 min (ramp of 10 min), 200°C for 20 min and 0°C for 20 min (cooling). The known biophilic nature of iodine¹⁸ suggests that much of its concentration presented in soils and sediments will be associated to organic phase. Nitric acid is a strong oxidizing agent and is widely used for liberating trace elements from biological and botanical matrices.¹⁹ Nitric acid behaves ideally under microwave conditions. In the closed vessels, nitric acid reaches 200°C at about 20 min. This temperature is more than 50°C above its boiling point. At this elevated temperature, substantial increases in oxidation potential are achieved, avoiding use of other acids (HF, HCl, etc...).

The following chemical separation consists of an organic extraction followed by an aqueous solution extraction and is based in the fact that iodine has a strong tendency to be absorbed by organic compounds¹⁰.

3.2 Extraction with Organic Solvent

Extraction is the transfer of a solute from one phase to other. Common reasons to carry out an extraction in analytical chemistry are to isolate or concentrate the desired analyte or to separate it from species that would interfere in the analysis. The most common case is the extraction of an aqueous solution with an organic solvent denser than water, as chloroform, dichlorometane and carbon tetrachloride.

Suppose that solute S is partitioned between phases 1 and 2. The partition coefficient (K), is the equilibrium constant for the reaction: S (in phase 1) $\leftrightarrow$ S (in phase 1), following Equation 1, where $[S]_i$ is the concentration of solute in phase i.

$$K = \frac{[S]_2}{[S]_1} \quad (1)$$

Suppose that solute S in V_1 ml of solvent 1 (liquid phase extracted from microwave) is extracted with V_2 ml of solvent 2 (chloroform). Let m be the moles of S in the system and let q be the fraction of S remaining in phase 1 at equilibrium. The molarity in phase 1 is therefore qm/V_1 . The fraction of total solute transferred to phase 2 is $(1-q)$, and the molarity in phase 2 is $(1-q)m/V_2$. Therefore (Equation 2), from which we can solve for q (fraction remaining in phase 1 after 1 extraction), obtaining Equation 3.

$$K = \frac{[S]_2}{[S]_1} = \frac{(1-q)m/V_2}{qm/V_1} \quad (2)$$

$$q = \frac{V_1}{V_1 + KV_2} \quad (3)$$

Equation 3 says that the fraction of solute remaining in the liquid phase extracted from microwave (phase 1) depends on the partition coefficient and the volumes. If the phases are separated and fresh chloroform (solvent) is added, after n extractions with volume V_2 , the fraction of solute remaining in the liquid extracted from the microwave is (Equation 4):

$$q^n = \left(\frac{V_1}{V_1 + KV_2} \right)^n \quad (4)$$

It is demonstrated^{11,15} that iodine solubilities in chloroform and aqueous solution are, respectively, 0.0228 mol-fraction (4.846g I₂ per 100 g CHCl₃) and 0.0295g I₂ per 100 ml aqueous solution, both at 25°C. So, in terms of solubilities, the partition coefficient between chloroform and aqueous solution is given by Equation 5. In each microwave vessel there is a volume of 12 ml so, if the same volume of chloroform is used (V₁=V₂=12 ml) and the extraction is realized three times (as shown in Equation 4), almost 100% of present iodine will be extracted to the organic solvent.

$$K = \frac{[S]_{\text{CHCl}_3}^{\text{iodine}}}{[S]_{\text{aq. solution}}^{\text{iodine}}} = \frac{0.04846 \text{ g I}_2 \text{ g CHCl}_3}{0.000295 \text{ g I}_2 \text{ ml aq. solution}} \times \rho_{\text{CHCl}_3} = 242 \quad (5)$$

3.3 Back-extraction into Aqueous Solution

Once iodine is separated from other radionuclides with the organic solvent, is then back-extracted into aqueous solution using NaHSO₃. This compound reduces I₂ to I⁻, retaining iodide in the aqueous phase and avoiding its evaporation.¹⁶ Volume and molarity of this compound is adjusted considering that one probable reaction could be the following:



3.4 Precipitation of Sulphate by Addition of Ba(NO₃)₂

If an excessive volume of NaHSO₃ is used in the previous step, chemical separation of sulfur from iodine has to be used in the sample preparation, which is achieved by precipitation of sulfur as BaSO₄. Remaining sulfur normally exists as sulfate, which can be co-precipitated together with the AgI as Ag₂SO₄. To avoid this, Ba(NO₃)₂ is added to force this ions to precipitate as BaSO₄, following this reaction:



3.5 Precipitation of AgI by Addition of AgNO₃

Then the solution is filtered to remove these ions and, finally, AgI is precipitated by addition of AgNO₃ in excess. The precipitate is washed two times with distilled water, isolated by centrifugation and dried at 50°C during 8 hours. Before AMS measurement, the AgI is mixed with Ag powder (*Alfa Aesar. Silver Powder Spherical, -635 mesh, 99.9 % metal basis*) at an AgI:Ag ratio of 1:2 and press into a copper cathode.

The extraction yield of the microwave digestion procedure has been tested by the application of the method to nine reference and certified materials. Extracted iodine amount has been measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with an Quadrupolar Inductively Coupled Plasma Mass Spectrometer (Thermo X7, Thermo, Madrid, Spain) equipped with a concentric quartz nebulizer (Meinhard Associates, Golden, USA), located at the Servicio de Investigación Agraria (University of Seville) laboratory. Various data quality tests were used during every instrumental running, such as replicate, matrix matching, memory effects, and both digestion analysis and laboratory reactive blanks checking. Overall chemical recoveries have an average value of 95% for all samples (paper in preparation).

4 AMS MEASUREMENTS

Determination of $^{129}\text{I}/^{127}\text{I}$ ratios in the samples was conducted at the 1 MV multielement compact AMS facility *SARA* (Spanish Accelerator for Radionuclides Analyses) at the Centro Nacional de Aceleradores (CNA) in Seville (Spain). Charge state 3+ after stripping was chosen to make the measurements. Background effects were evaluated through measurement of iodine blanks (Woodward Iodine, from Woodward Iodine Corporation, USA), with a measured ($^{129}\text{I}/^{127}\text{I}$) value of $3\text{--}4 \times 10^{-13}$. This is typically lower than 10% of the isotopic ratios measured for real samples. Background correction was carried out for all samples. A more detailed description of the system and the measurement details can be found.¹²

5 RESULTS AND DISCUSSION

The ^{129}I results of repeatedly digested samples used in this study show reproducible concentration levels within measuring accuracy (Figure 2). A good agreement between different measures demonstrates the reproducibility of the radiochemical method. Table 1 compares our results with results from other laboratories. Concentration of ^{129}I in IAEA standard soil #375 was compared to results from other laboratories (Table 1). Our results show an average concentration of $(1110 \pm 84) \times 10^6$ ^{129}I at./g, based on twelve separate digestions with error given in standard deviation. This result is in very good agreement with the certified value of $(1210 \pm 250) \times 10^6$ at./g given by IAEA⁴ (measured by AMS, Isotopic Dilution Mass Spectrometry and RNAA) and with values from other studies.^{2,7,13,14} Results of the fish flesh sample IAEA #414 (dry fish from the Irish Sea) from twelve different digestions indicate an average ^{129}I concentration of $(4900 \pm 231) \times 10^6$ at./g (Table 1), which is comparable to the reported average $(5700 \pm 700) \times 10^6$ at./g given², measured by AMS. In this case, iodine was extracted from the samples through a combustion method. Other ^{129}I concentrations reported⁵ were measured by ICP-MS but no information about the radiochemical method has been published.

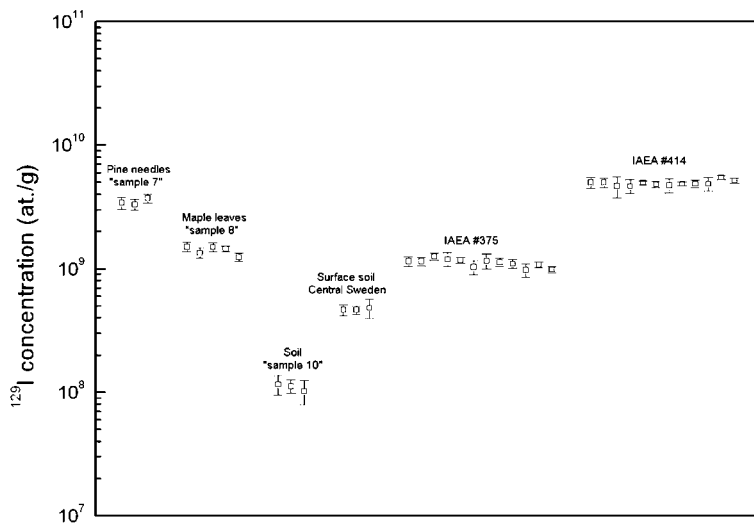


Figure 2 Summary of measured ^{129}I concentrations. Errors correspond with one standard deviation.

¹²⁹I concentration in pine needles “sample 7” was compared with results given by interlaboratory comparison I⁶ (Table 1). Our result, (3473±211)×10⁶ at./g, given as an average of three different digestions, is two orders for magnitude higher than reported⁶, although these results show a wide range of variability, depending on the laboratory which made the measurement.

Table 1 Average ¹²⁹I concentrations and standard deviations of samples analyzed in this study together with published and nominal values.

Sample	n	¹²⁹ I (×10 ⁶ at./g)
IAEA standard soil #375		
This study	12	1110 ± 84
[4] (certified)	10	1210 ± 250
[2]	5	1140 ± 40
[14]		1140 ± 250
[7]	23	936 ± 79
[13]	6	1400 ± 190
IAEA fish sample #414		
This study	12	4900 ± 231
[2]	2	5700 ± 700
[5]	3	6900 ± 70
Pine needles “sample 7”		
This study	3	3473 ± 211
[6]		
Lab. W		16.2 ± 2.4
Lab. M		680 ± 52
Maple leaves “sample 8”		
This study	5	1402 ± 112
[2]	3	49 ± 2
[6]		
Lab. Z		58.9 ± 4.7
Lab. W		31.0 ± 4.7
Lab. G		2000 ± 300
Lab. M		5210 ± 192
[7]		
Procedure 1	8	162 ± 131
Procedure 2	7	49.2 ± 22.7
Procedure 3	8	71.9 ± 74.7
Soil “sample 10”		
This study	3	109 ± 7
[2]	2	8.4 ± 0.7
[6]		
Lab. W		11.6 ± 3.5
Lab. G		250 ± 40
Lab. M		246 ± 14
Surface soil from Sweden		
This study	3	469 ± 9
[2]	5	244 ± 6

Maple leaves “sample 8” was another of the examined samples in interlaboratory comparison I⁶ and II⁷ that have been used in our radiochemical procedure. Through the digestion of five of these samples (Figure 2) an average ¹²⁹I concentration of (1402±112)×10⁶ at./g was found, thirty times higher than reported.² Other data^{6,7} show a wide range of variability (Table 1) without a nominal value, which indicates the difficulty to determine the real ¹²⁹I concentration of these samples. Our result is comparable with that given by Lab. G.⁶

Measurements of three soils “sample 10” provide us an average ^{129}I concentration of $(109 \pm 7) \times 10^6$ at./g (Table 1, Figure 2). This value is in the same order of magnitude than given by laboratories G and M⁶, but is one order of magnitude higher than given by Lab. W⁶. Unfortunately there is no nominal value reported for this sample and the wide spread of ^{129}I concentrations makes difficult to estimate its real concentration level.

Results of surface soil from Uppsala (Central Sweden) show an average ^{129}I concentration of $(469 \pm 9) \times 10^6$ at./g obtained by the measurement of three samples (Figure 2). These data are in the same order of magnitude that published² and can be compared with ^{129}I concentration of $(341 \pm 70) \times 10^6$ at./g published for a soil from Gävle (Sweden).¹⁷

The analytical reproducibility of the radiochemical procedure was verified (Table 2, Figure 3) by comparison of twelve measurements of IAEA #375 with certified value. The ^{129}I results of repeatedly digested IAEA #375 samples show reproducible concentration levels within measuring accuracy.

Table 2 Measured ^{129}I concentrations in twelve IAEA #375 samples with average value ($\pm$ one standard deviation) and nominal value⁴.

Sample	^{129}I ($\times 10^6$ at./g)
<i>IAEA standard soil #375</i>	
E1	1146 $\pm$ 107
E2	1145 $\pm$ 95
E3	1250 $\pm$ 83
E4	1190 $\pm$ 153
E5	1171 $\pm$ 64
E6	1027 $\pm$ 130
E7	1153 $\pm$ 161
E8	1122 $\pm$ 82
E9	1090 $\pm$ 89
E10	972 $\pm$ 127
E11	1074 $\pm$ 57
E12	982 $\pm$ 62
Average value	1110 $\pm$ 84
Certified value [4]	1210 $\pm$ 250

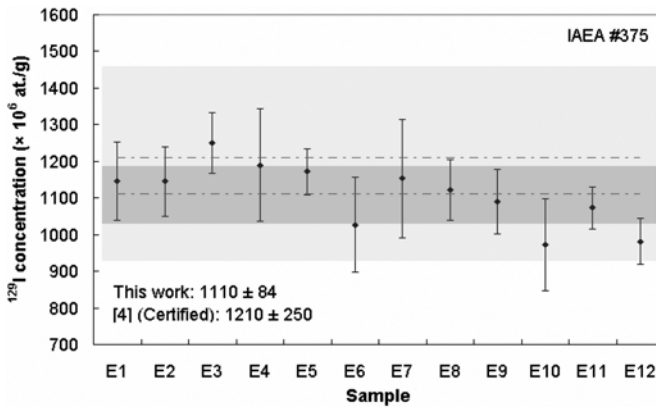


Figure 3 ^{129}I concentrations shown in Table 2. The lower dashed line and dark shaded area indicate average value with a confidence interval of one standard deviation. The upper dashed line and pale shaded areas indicate the nominal value with confidence interval⁴.

Besides, two samples from El Cabril, that is the Spanish low-activity nuclear waste storage place, were prepared two times by this radiochemical procedure and measured by AMS at the CNA. These samples were a wet ionic interchange resin from recirculation water of a nuclear reactor (code R-VD-9-01) and dried muds (code R-VD-9-02). Average concentration obtained for these two samples were, respectively, 1.20×10^9 at./g (6.67%) and 1.01×10^9 at./g (3.23%).

6 CONCLUSIONS

A radiochemical method for determination of ^{129}I concentrations in solid samples has been presented. As it is based on microwave digestion, its main advantages are the quickness and cleaning of the process, avoiding cross-talk contamination. At the same time, depending on the MW system, many samples can be digested at the same time. Closed vessels digestions can be made only with nitric acid because it behaves ideally under microwave conditions. In these vessels, nitric acid reaches 200°C. This temperature is more than 50°C above its boiling point. At this elevated temperature, substantial increases in oxidation potential are achieved, avoiding the use of other acids (HF, HCl, etc...).

This method has shown to be a reliable extraction procedure for iodine in solid materials and has been validated showing good accuracy and reproducibility. Different materials tested by other laboratories have been measured and, in most cases, the concentrations lie within the reported values. In particular, measurements of IAEA standard soil #375, the only solid reference material with certified ^{129}I concentration, shows satisfactory agreement of ^{129}I concentration with nominal value.⁴

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USING TIME RESOLVED LASER FLUORESCENCE SPECTROSCOPY AS AN INTERNAL PROBE FOR THE PHASE CHANGES IN ZIRCONIUM OXIDE

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1 INTRODUCTION

The importance of zirconium oxide in various technical applications makes this compound the topic of numerous studies. Much has been previously published on the mechanical, electrical, thermal, and optical properties of numerous forms of zirconium oxide.¹ The material is also investigated in nuclear applications as a waste form and advanced nuclear fuel²⁻⁴, and is relevant to the environmental performance of a nuclear waste repository as a mineral in both pure and mixed phases.⁵ Still little is known concerning the atomistic origins of the phase stability in these zirconium oxides, and even less is known about the process of accommodating dopants as environmental barriers to radionuclide migration and applications as nuclear waste forms. Most studies focus on the bulk structure or average dopant environment investigated by x-ray scattering or absorbance.^{6,7} More recently, time resolved laser fluorescence spectroscopy (TRLFS) has been used to investigate the specific local environment of a number of doping elements such as Eu⁸, Yb⁹, Pr¹⁰, and Nd¹¹ in an effort to achieve an atomistic level understanding of the local environment of atoms substituted in a zirconium oxide lattice. Still, a systematic study by TRLFS of the various phases of zirconium oxide has not been conducted since 1984.¹² Although this was an excellent study, much progress has been made in the technique of TRLFS over the last 25 years. The study presented in this manuscript uses site-selective TRLFS to investigate Eu doped zirconium oxide in amorphous, monoclinic, tetragonal, and cubic morphologies in an effort to illustrate trends and point out advantages of this technique in assessing the atomic scale local environment of incorporated atoms. In addition, the current study expands the dopant element to actinides, namely Cm, which proves the applicability of lanthanides as homologs to actual nuclear waste applications. Cm also has a detection limit of 10^{-12} by TRLFS allowing for the detection of trace concentrations relevant to the environmental conditions of a nuclear waste repository.

2 METHOD

2.1 Synthesis

All chemical used in the synthesis were reagent grade purchased from Alpha Aesar with the exception of curium. For these experiments ^{248}Cm was used ($t_{1/2} = 3.4 \times 10^5$ years). The isotopic composition of the Cm stock solution stored in 2M HCl was 89.7% ^{248}Cm , 9.4% ^{246}Cm , and less than 1% other Cm isotopes. Samples were synthesized using a coprecipitation method. Concentrated nitrate salt solutions were made using zirconium ($\text{ZrO}(\text{NO}_3)_2$), yttrium ($\text{Y}(\text{NO}_3)_3$), and europium ($\text{Eu}(\text{NO}_3)_3$). These solutions were mixed in desired proportions and the metals were coprecipitated with ammonium hydroxide. The oxy-hydroxide precipitate was then filtered and washed with purified water before drying in an oven at 100°C overnight. The dried solid was then heat treated in a tube furnace under synthetic air for 24 hours at the desired temperature. A list of sample compositions and temperatures can be seen in Table 1.

Table 1 Concentrations and temperatures used to synthesize zirconium oxide phases

Phase	ZrO ₂ (at. %)	YO _{1.5} (at. %)	EuO _{1.5} (ppm)	CmO _{1.5} (ppm)	Temp. ($^\circ\text{C}$)
Amorphous	100	0	400	0	400
Monoclinic	100	0	400	0	700
Tetragonal	96.8	3.2	400	0	1000
Cubic	98.2	1.8	400	0	1600
Monoclinic (Cm)	100	0	0	30	700

2.2 X-ray Diffraction and Scanning Electron Microscopy Characterization

Powder samples were prepared for x-ray diffraction by being spread on a low background sample holder (single crystal silicon wafer) with the aid of methanol. Analysis was performed with a Bruker D8 Advance diffractometer using a Cu anode with monochromator $\text{K}\alpha_1 = 0.1540598$ nm. Patterns were taken using 40 mV and 40 mA from 10° to 90° 2θ with a step size of 0.01° 2θ and 10 s per step. Phases were identified using Bruker DIFFRAC plus EVA software.

Powder samples were prepared for scanning electron microscopy (SEM) by adhering to double stick carbon tape and carbon coated to eliminate charging. Analysis was performed on a CamScan FE44 microscope equipped with energy dispersive x-ray analyzer.

2.3 Time Resolved Laser Fluorescence Spectroscopy

The time resolved laser fluorescence spectroscopy (TRLFS) measurements were performed by probing either Eu or Cm. Samples were cooled to < 20 K in a helium refrigerated cryostat under a vacuum of $10^{-5} - 10^{-6}$ mbar for improved spectral resolution and enhanced fluorescence. A XeCl excimer pumped dye laser (20 Hz) was used for excitation. The dye QUI, with an emission maximum at $\lambda = 380$ nm was used for the indirect excitation of Cm (396.6 nm) and Eu (394.0 nm). The direct excitation of Cm was performed with Rodamin B (maximum emission $\lambda = 620$ nm), and the direct excitation of Eu was achieved with the dye Rodamin 6G (maximum emission $\lambda = 580$ nm). The luminescence emission signal was recorded time resolved by a fiber coupled optical multi-channel system consisting of a polychromator with 300, 600 and 1200 lines/mm gratings and a gated, intensified diode array.

The information obtained from TRLS measurements was used to assess the extent of the covalent interactions with ligands through the chemical shift in the emission spectra. The lifetime of the fluorescence emission in absence of other quenching processes (e.g. metal-to-ligand transfer) can be directly correlated to the number of water ligands in the inner coordination sphere of the Eu or Cm ion.^{13,14} The uncertainty in these measurements is typically ± 0.5 waters corresponding to errors in lifetime of around 10%. This is used to distinguish between outer and inner sphere sorption and incorporation species. The degenerate splitting of the F_1 and F_2 transitions were used to gain information on the symmetry of the Eu center. Lower symmetry environments increase the splitting and the point group can be determined through the splitting patterns in these two transitions with polarized filters. Lastly, the intensity of the F_0 , F_1 , and F_2 transitions are compared as an indication of local symmetry and J-state mixing. Lower symmetry and a higher amount of J-state mixing between the Eu center and ligand field lead to a promotion in the intensity of the F_2 magnetic transition as compared to the F_1 electronic transition.

3 RESULTS AND DISCUSSION

3.1 X-ray Diffraction and Scanning Electron Microscopy

All samples were analyzed by powder x-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS) after synthesis. Phase purity of greater than 99 wt. % was confirmed for all samples by XRD. It should be noted that cubic zirconium oxide and tetragonal zirconium oxide share the same major reflections. The distinguishing factor between these two phases was the presence of minor reflections from the lower symmetry tetragonal phase. Because of this, a small amount of cubic zirconium oxide present in a predominantly tetragonal zirconium oxide sample is difficult to detect by powder XRD. The presence of zirconium, yttrium and erbium was confirmed by EDS in their respective samples. No other element was detected in any of the samples by EDS (detection limit approximately 0.1%). It was shown by SEM imaging that monoclinic, tetragonal and cubic materials were polycrystalline with particle sizes ranging from 1 to 100 μm . The amorphous sample appeared as round particles ranging from 5 to 100 μm by SEM imaging.

3.2 Fluorescence Lifetime Measurements

The lifetime of the fluorescence emission was measured for Eu in cubic, tetragonal, and amorphous zirconium oxide. The fluorescence emission from monoclinic zirconium oxide was too weak to accurately measure a lifetime for Eu so Cm was used as a doping ion, because of its higher fluorescence signal. Using an actinide such as Cm also expands the study to elements relevant to a nuclear waste repository. The lifetime of Cm in monoclinic zirconium oxide was bi-exponential over the entire range of excitation energies and lifetimes ranged from 65 to 300 μs . According to the equation by Kimura et. al.¹⁴, this corresponds to a range of 1 to 9 waters in the first coordination sphere. This would indicate that Cm adsorbed to the surface of monoclinic zirconium oxide, but does not incorporate into the bulk crystalline structure. The longer lived lifetimes corresponding to between 1 and 5 coordinating waters typical of an inner sphere surface complex in which the Cm ion has given up part of its hydration sphere and has complexed directly with the surface. The shorter lifetimes, which correspond to 8 or 9 waters in the immediate coordination environment of the Cm ion are evidence of outer sphere complexation. In

this case, the Cm retains its hydration sphere, which is then complexed to the surface. This makes monoclinic zirconium oxide less effective at retaining trivalent actinides and lanthanides because the material is adsorbed at the surface without incorporation into the bulk.

The lifetime of Eu doped cubic zirconium oxide shows a single mono-exponential lifetime of 2.6 ms. The longer lifetime of Eu in cubic zirconium oxide corresponds to 0 waters by Horrocks¹³ equation and is clear evidence that Eu is incorporated into the bulk crystal structure. Tetragonal zirconium oxide doped with Eu was found to have a bi-exponential decay of the fluorescence. The shorter lifetime was measured to be 1.8 ms, while the longer lifetime approached that of Eu in a cubic environment (2.6 ms). Both lifetimes correspond to a complete loss of the hydration sphere and demonstrate that Eu is incorporated into the bulk. Amorphous zirconium oxide also shows a range of available species and corresponding Eu fluorescence lifetimes, similar to that of the monoclinic zirconium oxide. These lifetimes, however, were found to be much longer than in monoclinic zirconium oxide. The lifetimes of the amorphous zirconium oxide were 0.9 ms and 2.0 ms corresponding to 0.5 and 0 waters indicating that Eu is incorporated into the bulk crystal structure, which has some hydroxide contamination (0.5 waters). This indicates a clear difference from the results obtained of monoclinic zirconium oxide. A comparison of lifetime measurements for all systems investigated can be seen in Figure 1.

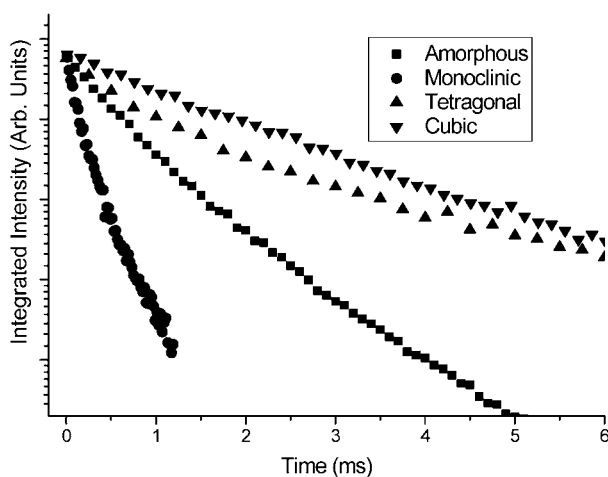


Figure 1 Fluorescence emission over time indicating a fast lifetime for monoclinic zirconium oxide due to coordinating waters and a trend towards longer lifetimes with increasing symmetry and sintering temperature

3.3 Cubic Zirconium Oxide

The Eu doped cubic zirconium oxide was analyzed by time resolved laser fluorescence spectroscopy (TRLFS). By directly exciting to the Eu $^3D_0$ and observing the fluorescence decay to the $^7F_{0,1,2}$ levels it was evident that three unique species exist at excitation wavelengths of 578.9, 579.6 and 580.5 nm (Figure 2).

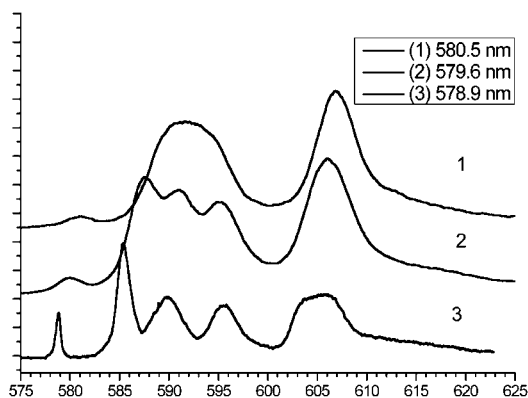


Figure 2 Europium emission spectra from cubic zirconium oxide showing isomorphic substitution with breaks in symmetry observed in the F_1 transition due to 1 and 2 oxygen vacancies at 579.6 and 578.9 nm respectively

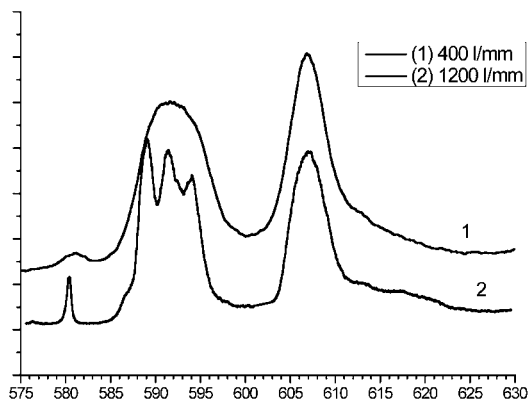


Figure 3 Europium emission spectra (excited at 580.5 nm) from cubic zirconium oxide at high resolution showing a disturbance in symmetry due to oxygen vacancies outside the first coordination shell

This was previously identified as Eu substituted on a zirconium site with two oxygen vacancies in the immediate coordination environment (578.9 nm), one oxygen vacancy (579.6 nm), and a complete nearest neighbor oxygen shell of eight (580.5 nm).¹² These three species had a similar single peak in the F_2 transition from 602 to 612 nm previously attributed to a high symmetry environment as expected from an isomorphic substitution of the zirconium site in cubic zirconium oxide by a europium atom. This high symmetry phase of cubic zirconium oxide is known to be stabilized by oxygen vacancies^{6,7}, which explains why three unique sites can be seen. With this explanation, the splitting of the F_1

transition is proportional to the disruption in the symmetry of the local environment by oxygen vacancies as can be seen in Figure 2. Upon further examination at higher resolution the species with no vacancies in the immediate environment was also found to have a small three-fold splitting in the F_1 transition as can be seen in Figure 3 with a high resolution grating of 1200 lines/mm. This is believed to be due to a small disturbance in the local symmetry due to next-nearest neighbor vacancies on oxygen sites outside of the first coordination shell.

3.4 Tetragonal Zirconium Oxide

An excitation spectra of Eu in tetragonal zirconium oxide was taken by direct excitation from 574 to 581 nm in steps of 0.1 nm and integrated over the F_0 transition and the entire emission spectra. This revealed two different excitation maxima at 577.5 and 579.3 nm (Figure 4) indicating two different groups of similar, multiple sites. The high-energy group of species at 577.5 nm was found to be a unique environment attributed to the Eu substituting for a Zr site in the tetragonal lattice. It was found to have three fold splitting of the F_1 transition and although poorly resolved, three or four fold splitting of the F_2 transition indicating C_{2v} or D_2 symmetry respectively (Figure 5 #1). The emission spectrum at 579.3 nm was collected at long delay times (2 ms) in an effort to isolate the longer-lived group of species that existed at lower energies. It was found that the emission spectrum was that of Eu in a cubic environment (Figure 5). This small amount of cubic phase zirconium oxide is difficult to identify with conventional XRD, but is readily apparent through the spectroscopy of the Eu species.

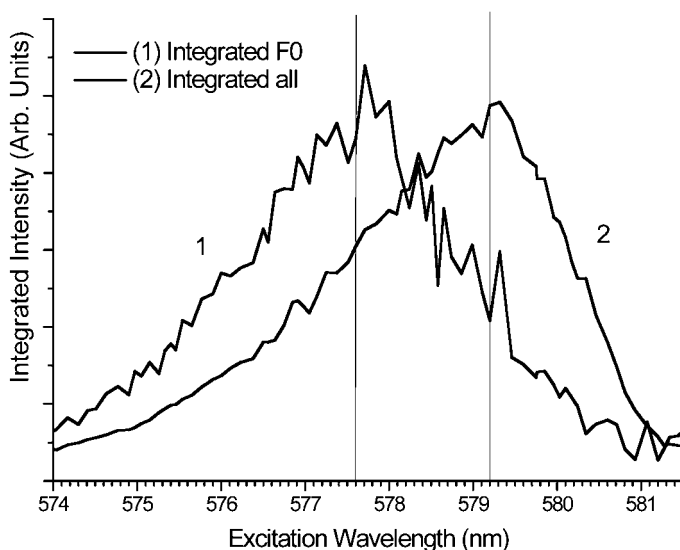


Figure 4 Excitation spectra integrated over F_0 and the entire emission spectra revealing two maxima excitation energies for two different local environments

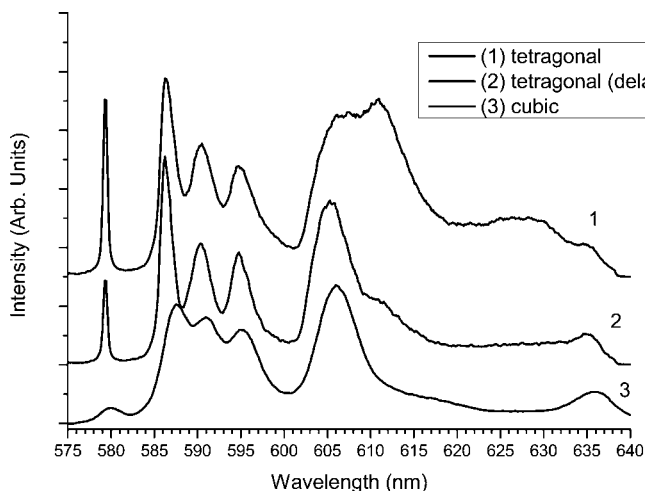


Figure 5 Emission spectra of Eu in tetragonal zirconium oxide at different delay times as compared to the emission spectrum of Eu in cubic zirconium oxide indicating that the long-lived species is in a cubic zirconium oxide environment

3.5 Monoclinic Zirconium Oxide

The amount of Eu in the monoclinic zirconium oxide sample was insufficient for direct excitation and therefore only UV excitation was performed on the sample. It was evident by UV excitation that a multitude of low symmetry sites were excited as the emission spectra had more than the maximum number of allowed peaks in the F_1 and F_2 transitions. Because Cm spectroscopy can be done by TRLFS at much lower concentrations, it was used as a probe to evaluate the behavior of trivalent lanthanides and actinides with monoclinic zirconium oxide. Excitation of Cm by UV shows an extremely broad emission from 610 to 650 nm (Figure 6). Direct excitation in this region indicates that this is made up of a continuum of closely related species as can be seen by the fluorescence line narrowing in the direct excitation emission spectra shown in Figure 6. This is expected for a surface adsorbed species as was shown in the fluorescence lifetime measurements. It was concluded that Eu and Cm are adsorbed to the surface but not incorporated into the structure leading to a range of local environments and hydration species.

3.6 Amorphous Zirconium Oxide

An excitation spectrum of europium in contact with amorphous zirconium oxide revealed a broad peak from 576 to 581 nm. Direct excitation within this range shows a continuum of discrete sites with similar emission spectra (Figure 7). This would be expected of an amorphous material in which the local environment is fixed but no order is present beyond the immediate coordination environment.

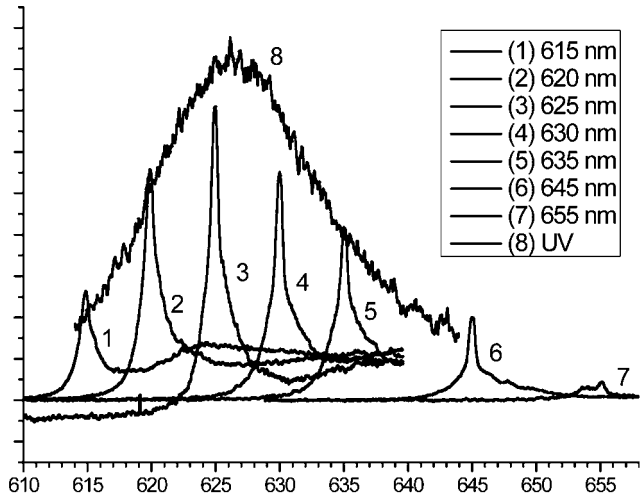


Figure 6 Emission spectra of Cm from UV and direct excitation in monoclinic zirconium oxide showing a range of related adsorption species

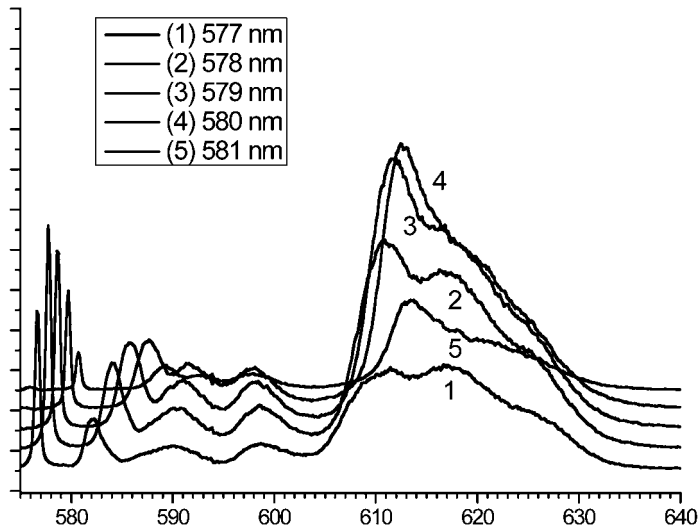


Figure 7 Emission spectra of Eu by direct excitation in amorphous zirconium oxide revealing a continuum of closely related species

The F_0 emission shows fluorescence line narrowing as was the case in the monoclinic environment and the signal has a maximum between 578 and 579 nm. The F_1 transition is similarly three-fold split over the excitation energy range in all emission spectra indicating only slight changes in the local coordination environment from one species to the next. The F_2 transition is poorly resolved, but at least three peaks can be seen at approximately 611, 619 and 626 nm in Figure 6. This would indicate an environment with symmetry of D_2 or lower. Although this is similar to the tetragonal zirconium oxide sample a clear difference in the shape of the F_2 transition can be seen (Figure 8). Through the systematic TRFLS study of trivalent lanthanide and actinide interaction with the available morphologies of zirconium oxide it was evident that the F_2/F_1 ratio is inversely proportional to the symmetry of the system (Figure 8). This might be expected since the F_2/F_1 ratio is an indication of the J-state mixing and local asymmetry of the system. It is interesting to note that this trend holds true even for the monoclinic zirconium oxide sample, which showed no incorporation and only surface adsorption was measured.

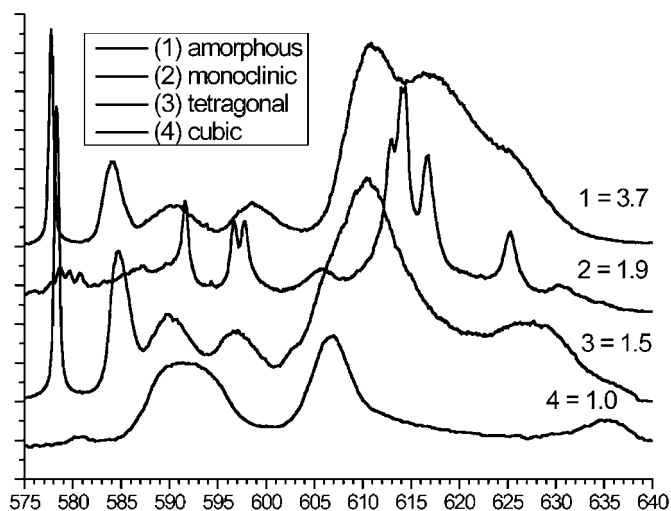


Figure 8 Emission spectra of Eu in four morphologies of zirconium oxide with F_2/F_1 ratio indicating a decrease in local symmetry and increase of J-state mixing with decreasing symmetry of the system

4 CONCLUSIONS

By systematically studying the various morphologies of zirconium oxide, it is possible to gain insight into the factors affecting sorption and incorporation processes. It was found that Eu readily incorporates into the zirconium site of all zirconium oxide morphologies in this study with the exception of monoclinic. This is attributed to a decrease in the size of the zirconium oxide site in the monoclinic structure as compared to tetragonal and cubic. It was possible to identify a minor cubic phase of zirconium oxide in a predominantly tetragonal matrix spectroscopically by site-selective TRFLS. The cubic phase is found to

have a distorted symmetry due to oxygen vacancies in the immediate environment and next-nearest neighbors causing a three fold splitting of the F_1 transition in all three species identified. The F_2/F_1 ratio of the doping ion trends with the symmetry of the sample, which could be used as an internal probe for the system. Time resolved laser fluorescence spectroscopy (TRLFS) of Eu and Cm doped zirconium oxide was a successful tool in accessing structural information at the atomic scale.

Acknowledgements

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DETERMINATION OF THORIUM AND URANIUM ISOTOPE RATIOS IN NORM AND NORM-POLLUTED SAMPLE LEACHATES USING ICP-QMS

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1 INTRODUCTION

Phosphoric acid production plants by the wet acid method are among the best-known NORM-industries.¹ From the radiological point of view, their most relevant characteristic is that the raw ore contains high activity concentrations of U-Series radionuclides (in the range of 1.5 kBq/kg, in the case of Morocco phosphate rock) under near secular equilibrium.² During the industrial process that equilibrium is broken, in such a way that uranium mainly follows the produced P₂O₅, while radium, thorium and lead isotopes follow phosphogypsum waste (CaSO₄·2H₂O) path. For example, in the case of the plants located at Huelva estuary (south-western Spain, at the confluence of Odiel and Tinto rivers) those proportions are at present day >99% for radium and lead and >85% for thorium.³

Until 1998, more than 15 millions tonnes of phosphogypsum were directly released to the Odiel River. Furthermore, more than 90 millions tonnes of phosphogypsum have been stored in a salt-marshes ground in the Tinto river. The effect of these practises has been reflected in the concentration levels of several of those radionuclides in waters, soils and sediments near the Huelva estuary, reaching values quite higher than natural background values. Besides, it is an ecosystem strongly affected by acid mine drainage (AMD), coming for the pyrite mines located upstream both Tinto and Odiel Rivers. This way, high concentrations of heavy metals, such as Fe, Cu, Zn y Mn, are transported downstream in dissolution, until mostly all precipitate due to several factors when they mixed with sea water in the Estuary.⁴⁻⁵ A recent study⁶ points to AMD as an additional source of uranium isotopes to this ecosystem. That uranium addition is being produced at the present time despite the direct phosphogypsum releases to the Odiel River ceased in 1998. In this way, the source of radioactivity pollution in sediments of this area couldn't be easily discriminated using activity concentrations.

Ketterer et al.⁷ proposed the use of ²³²Th/²³⁰Th isotope ratios to discriminate between the natural background and the effect due to NORM Industries discharges in riverine and estuarine sediments. Phosphogypsum is characterised by ²³²Th/²³⁰Th isotope ratios quite different from those typical of unpolluted soils and sediments⁸⁻⁹, hence the effect of phosphate factories pollution could also be identified using this indicator. ²³⁸U/²³⁴U isotope ratio could also be useful from that point of view as certain NORM samples are characterised by a value near unity³ while unpolluted estuarine sediments are slightly less

than one due to dissolved uranium precipitation.¹⁰ Therefore, uranium and thorium isotope ratios can provide information on the origin of pollution that single activity concentrations analyses cannot discriminate

The classical approach for the determination of U and Th isotope ratios is alpha spectrometry. Their detection using the ICP-MS technique is also attractive due to fast counting and high sensitivity. For environmental, low concentration samples, sector focusing instruments (mainly, MC-ICP-MS) are usually preferred due to their high sensitivity and precision and low background.¹¹ However, MC-ICP-MS instruments are not widely available due to their high cost. For example, at the present day there are more than 125 ICP-MS instruments working in public research facilities and private enterprises in Spain, but only three of them are sector focusing instruments (two single detector instruments and a MC-ICP-MS).

Sometimes, quadrupole instruments are the only available option. However, their limitations for the determination of isotope ratios have been already characterised.¹²⁻¹³ Mass scanning is sequentially performed, hence the external uncertainty will be limited by effects such as pumping-produced pulses, noise due to plasma power fluctuations and, in the case of our interest, the large range of isotope ratios (10^4 - 10^6), leading to (and caused by) the extremely low concentrations of the minor isotopes. Pumping-derived fluctuations can be minimised by the use of self-aspirating nebulisers. Plasma noise and power fluctuations can be partially mitigated by an adequate choice of dwell time and the number of sweeps, but that approach cannot completely remove this drawback. The use of a DRC system providing collisional damping as a way to reduce the magnitude of that uncertainty source was proposed by Bandura *et al.*¹⁴ Unfortunately, this technique is only efficient when the molecular mass of the gas used for damping is relatively large. The large difference in the isotope abundances cannot be negated, but the relatively low concentrations of the minor isotopes could be mitigated by an adequate use of radiochemistry, especially when the samples themselves show relatively large radionuclide concentrations. Bearing that in mind, it is clear that even the quadrupole instruments could be used for the analysis of stable lead, thorium and uranium isotope ratios in NORM and NORM-polluted environmental samples.^{7,15} However their use has not been very popular, especially in the case of thorium isotope ratios.

On the other hand, the accuracy of results is compromised by detector dead time, mass bias and the presence of spectrometric interferences. The first issue can be on-line corrected after an adequate calibration of detector dead time and the second one using either external or internal correction after the analysis of an adequate standard solution with certified isotope ratios. The third one must be handled, once again, by the use of radiochemistry in order to remove the elements producing the interference up to an acceptable level. The main interferences potentially overlapping the masses of our interest are Cd and In dimers and Os and Pt argides (at mass 230), Sn dimers and Os argides (232), Sn dimers, Pt and Hg argides and Th hydrides (234) and Sn dimers and Pt argides (238).

Like some other NORM wastes, phosphogypsum is also characterised by high concentrations of stable inorganic pollutants¹⁶, such as Cd which of course cannot be monitored using radiometric methods. ICP-QMS is the classical way of analysing this element in a wide variety of samples. The use of this kind of instruments for the monitoring of stable elements and lead, thorium and uranium isotope ratios could allow the researchers to avoid the use of different instruments (i.e., ICP-QMS and radiometric methods) and simplifying laboratory requirements and management.

The main aim of this work is to test the possibilities of the combination of a single radiochemical method and the use of ICP-QMS for the monitoring of, thorium and uranium isotope ratios in NORM samples and NORM-polluted environmental samples in

a way compatible with the use of the same sample aliquot for the determination of stable inorganic pollutants.

2 MATERIALS AND METHODS

The used samples comprising NORM matrices (phosphorite and phosphogypsum) and NORM-polluted sediment samples were collected in 2001 and stored in polyethylene sealed bottles. Before analysis, they were dried at 65°C to a constant weight and sieved by 10 µm mesh.

Suprapure grade HNO_3 , H_2O_2 and HCl (Merck) and 18.0 MΩ deionised water (Millipore) were used for samples leaching, chromatographic separations and solution matrix adaptation, when required. $\text{Al}(\text{NO}_3)_3$ and oxalic acid (Panreac) were analytical grade. 2 mL pre-packed minicolumns of Eichrom's UTEVA resin (TRISKEM, France) were used for the chromatographic separation and purification of Th and U.

Quantitative elemental analysis and isotope ratio determinations were carried out using an Agilent 7500c ICP-QMS provided with an Octupole Reaction System (ORS). Quantitative concentration analyses were performed using a Babington nebuliser being the ORS pressurised with H_2 (4.5 mL/min of flow rate) or He (2.5 mL/min) gases. Isotope ratio analyses were done using a PFA-100 micronebuliser working under self-aspiration regime being the ORS off. External calibrations for elements concentrations (Th, U and interfering elements), quality checks as explained below, recoveries/interfering elements decontamination monitoring and the calculation of dead time for count rates correction were carried out using a mix of single element standard solutions conveniently diluted until the required concentrations.

Mass bias correction for isotope ratio determinations were performed using certified reference materials: NIST-981, NIST, U.S.A. was used for lead. IRMM-035 and IRMM-056 were used for thorium and uranium, respectively (Institute for Reference Materials and Measurements, Geel, Belgium). It was performed by bracketing the samples between certified IR standard solutions and a blank solution using the linear approach. Each four samples, a certified reference material solution or a replicated sample was analysed as an unknown sample in order to test the accuracy, reproducibility and precision of the results.

The ICP-QMS was working under different conditions for element concentration determinations and isotope ratio calculations. For the first one, the instrumental conditions are summarised in Table 1. The instrumental conditions used for IR measurements were determined after an adequate specific instrumental setup. To do that, the instrument was first optimised in terms of response, oxides and doubly ionised ions in standard conditions (i.e., using the Babington nebuliser being the ORS off) by aspirating a Li/Y/Ba/Ce/Bi solution at the 10 ng/mL concentration level. Then, response, oxides and doubly ionised ions were monitored in the same solution using the PFA-100 micronebuliser with the same solution, and plasma conditions (i.e., RF-power, sampling depth, carrier gas flow rate and auxiliary gas flow rate) were readjusted.

After dead time calculation, conventional standard solutions (i.e., standard solutions having element' certified concentrations but not certified isotope ratios) of thorium and uranium solutions at the 10 ng/mL concentration level were self-aspirated using different dwell times in order to minimise the internal uncertainty.¹⁷⁻¹⁸ The reasons to work with these solutions were two: 1) the RSD level is not dependant of the accurate isotope ratio value within an order of magnitude, and 2) thorium and uranium isotope ratios were previously calculated for these solutions using ICP-MS and alpha particle spectrometry

respectively. The determined isotope ratios were even higher than expected values for NORM and environmental samples, hence that allowed us to optimise the instrument under the most exigent and pessimistic conditions that we could find in the samples of our interest.

After that, dwell time was fixed for every isotope to be considered in the isotope ratio calculations, and the RSD dependence with element concentration was studied.¹⁷⁻¹⁸ The selected conditions are also shown in Table 1.

Table 1 Operating conditions of the Agilent 7500c ICP-QMS used in this work

RF Power (W)	1550, torch shield
Sampling depth (mm)	5.9
<i>Quantitative analysis mode</i>	
Carrier gas (l/min, Babington nebuliser)	1.1
ORS	H ₂ (4.5 l/min), He (2.5 l/min)
Internal standard	⁶ Li, ¹⁰³ Rh, ²⁰⁹ Bi
Sample flow rate (l/min)	0.4
Replicates	3
<i>Isotope ratio mode</i>	
Carrier gas (l/min, PFA nebuliser)	0.5
Auxiliary gas (l/min)	0.4
ORS	Off
Sample flow rate (l/min)	0.05
Dwell time (ms)	230: 30, 232: 1; 234: 25; 238: 0.9
Replicates	7-10
M ¹⁶ O ⁺ /M ⁺ (%)	0.7-1.2
M ¹ H ⁺ /M ⁺ (%)	(1.0-1.4)·10 ⁻²
(M-1) ⁺ /M ⁺ (%)	<4·10 ⁻²
(SnSn) ⁺ /Sn ⁺ (%)	<4·10 ⁻⁴
Mass bias correction	External, linear

The radiochemical setup was based on the scheme proposed by Horwitz et al.¹⁹, designed to be coupled with alpha-spectrometry, although several modifications were tested (Figure 1). First, we choose the application of the E.P.A. 3050B leaching procedure as sample pretreatment. This method does not provide total sample dissolution but it offers a reasonable assessment of the worst case environmental scenarios where components of the sample become soluble and mobile.²⁰ Furthermore, more than 90% of radioisotopes are associated to the non refractory phase of the matrices of our interest.²¹ Avoiding the use of HF simplifies sample handling for ICP-QMS analyses, hence, an aliquot of the leachate can be extracted, diluted and analysed by ICP-QMS in order to measure the concentrations of the elements of our interest. That concentration will be used to study the fractionation of those elements through the radiochemical procedure.

The original method proposed starts with a sample dissolution (in our case, sample leaching by EPA 3050B and filtering). Then the solution is evaporated to dryness and redissolved using 3M HNO₃ (option I). Alternatively, it has been tested a previous sample concentration and purification step proposed by Carter et al.²² consisting in the co-precipitation of U and Th with Fe(III) after sample leaching and filtering and addition of NH₄OH (option II). The precipitates are then dissolved using 3M HNO₃.

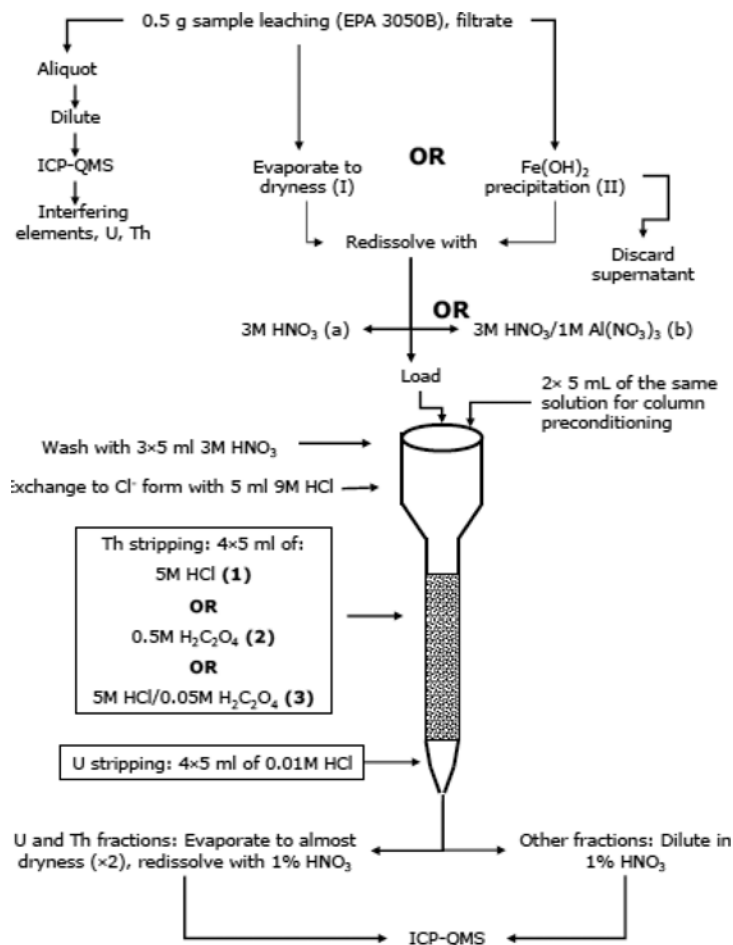


Figure 1 Radiochemical method used in this work

This solution is loaded onto a previously conditioned UTEVA minicolumn (option a), being U and Th concentrated in the resin. Option (b) consists in replacing that solution by 3M HNO₃/1M Al(NO₃)₃ in order to avoid radiochemical interferences due to the massive presence of phosphates.^{19, 23} The resin is washed using 3M HNO₃ and then changed to chloride form by adding 9M HCl. Th and U are sequentially stripped using 5M HCl (option 1) and 0.01M HCl respectively. The 5M HCl can be replaced by 0.5M H₂C₂O₄ (option 2²⁴), or 5M HCl/0.05M H₂C₂O₄ (option c²⁵).

We have tested the recoveries of U and Th and the decontamination of interfering elements comparing the concentrations obtained in the first aliquot with those found in the different column eluates. Every scheme was tested using 2-4 aliquots of the sample. For quantitative ICP-QMS analyses, the U.S. E.P.A. 200.8 methodology was used in order to check for calibration accurateness and precision and to test the presence of memory effects, sample matrix effects, etc. When Quality Checks were not passed, the sample dilution factor was increased until obtaining a successful Quality Checks result.

3 RESULTS AND DISCUSSION

3.1. Instrumental Setup

The behaviour of U and Th isotope ratio (on what follows, IR) RSDs with dwell time and concentration level are shown in Figures 2-5. Ten replicates per measurement were used during the instrumental setup. For uranium, a dwell time of 1.0 s was fixed for mass 238 at a concentration level of 0.62 mBq/mL and then different counting times were tested for mass 234. Both reproducibility and relative deviation were evaluated as a function of mass 234 dwell time (Figure 2). The mass bias-corrected isotope ratios were the same within the uncertainty intervals, and the relative uncertainties drastically decreased due to the higher net counting when increasing the dwell time for mass 234. Hence, 30 ms was selected as dwell time for ^{234}U .

Regarding Th, measured RSDs were higher (Figure 3) because the ^{230}Th concentration was close to the instrumental quantification limit (approximately 0.6 mBq/mL, i.e., about 0.08 pg/mL). Under these conditions, it is quite difficult to reduce the RSD below 10%. Two important conclusions could be extracted from this test: all the results are the same within the uncertainty intervals, and the ^{230}Th concentration should be raised in the analysed solutions in order to have net counting enough as to provide a reasonable statistics. As a commitment choice, 35 ms was selected as ^{230}Th dwell time, and the following experiment should provide a minimum concentration level as to provide reasonable RSD values.

Figure 4 shows the dependence of RSD and calculated IR value with the U-concentration. The calculated IR values were approximately the same for all the measurements, and the uncertainty decreases as U concentration increases due to higher count rates. It can be seen that when ^{234}U activity concentration is about 0.25 mBq/mL, the uncertainties are quite similar to those achieved by alpha spectrometry

A similar experiment was carried out using Th solutions at increasing levels (Figure 5) and it can be seen that RSD values better than those achieved in the previous Th experiment can be achieved when the concentration of ^{230}Th is over 0.5 mBq/mL. RSDs slightly increases when ^{230}Th activity concentration overpasses 800 $\mu\text{Bq/mL}$ due to higher than expected memory effects. That is reflected in unstable ^{232}Th count rates during the measurement of blanks. This finding highlights that washing time between samples should be increased when ^{232}Th concentrations are above ~ 500 ng/mL. On the other hand, a slight shift of the calculated IR appears above the 0.5 mBq/mL level, due to a high Th concentration difference between several of the solutions analysed in the experiment and the solution used for external mass bias correction. Hence on the determinations carried out with real samples, that concentration difference was reduced to a minimum.

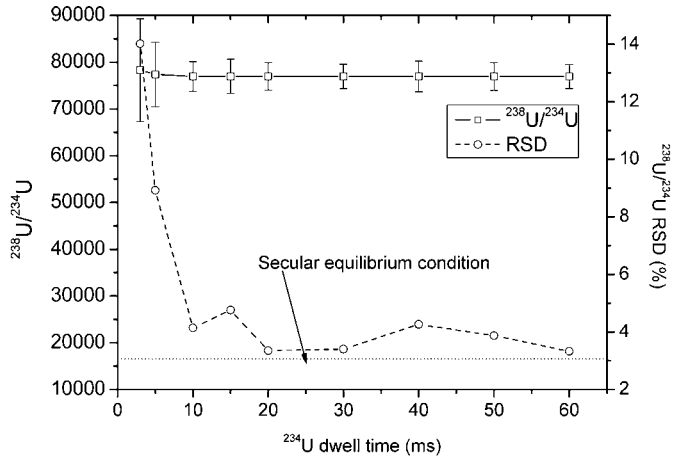


Figure 2 Dependence of $^{238}\text{U}/^{234}\text{U}$ isotope ratio value (expressed in terms of atom ratio) and RSD with ^{234}U dwell time

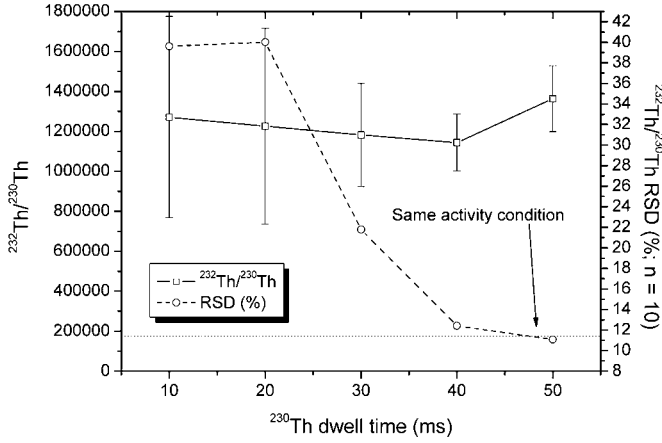


Figure 3 Dependence of $^{232}\text{Th}/^{230}\text{Th}$ isotope ratio value (expressed in terms of atom ratio) and RSD with ^{230}Th dwell time

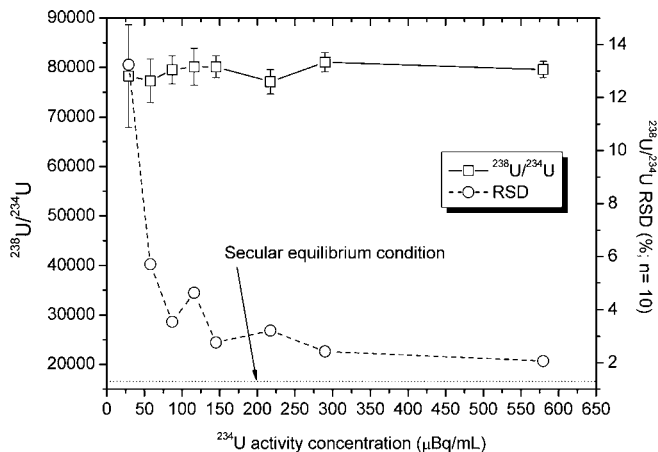


Figure 4 Dependence of $^{238}\text{U}/^{234}\text{U}$ isotope ratio value (expressed in terms of atom ratio) and RSD with ^{234}U concentration

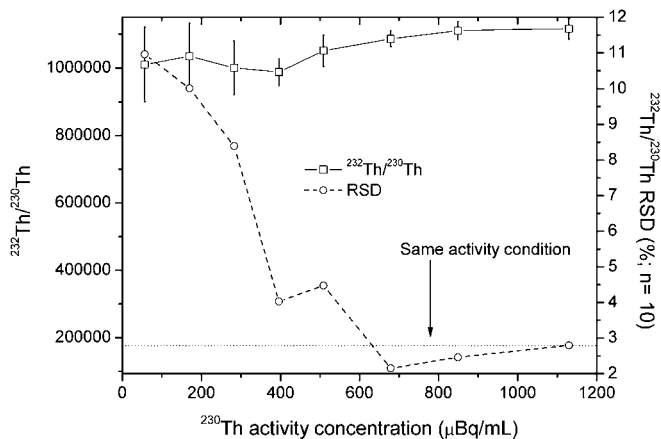


Figure 5 Dependence of $^{232}\text{Th}/^{230}\text{Th}$ isotope ratio value (expressed in terms of atom ratio) and RSD with ^{230}Th concentration

3.2 Chemical Fractionation of Th and U

Five setups were tested for U and Th recoveries and crosstalk: Setup A combines the options I+a+1 shown in Figure 1. Setup B combines II+b+1. Setup C combines options II+a+2. Setup D is for II+b+2. Setup E is for II+b+3. Setup F stands for I+b+3. The results for setups A-E are summarised in Table 2.

Setup A produced high recoveries for uranium but very low recoveries for thorium. Our results show that Th remained unstripped within the resin. This finding seems to be in disagreement with the results published by different authors^{22, 26}, who reach high recoveries for thorium using the same volume of 5M HCl than us. This result is not surprising, due to the different matrices used in both works. Those results were obtained on coral (mainly calcium carbonate), uranite and MOX samples. The main components of the sediments here used are silicates and phosphates, which could prevent the solubilization of Th.²⁷ No important differences were detected when the setup B was applied, a fact showing that most of U and Th precipitate with the iron hydroxide, furthermore this step does not introduce any difference in their performances of the resin.

The application of setups C and D produced higher recoveries in Th than setups A and B but a certain drop in U recoveries. However, none of these elements was fully extracted from the column. Th extraction is followed by U extraction, in order to prevent that the low Th Kd-values at low HCl concentration could lead to a high cross contamination of Th in the U fraction. However, it is easy to see that the application of this Th stripping procedure leads, in any case to a high crosstalk. First Th is incompletely extracted, but the application of H₂C₂O₄ allows a certain resin conditioning effect. The subsequent application of 0.01 M HCl allows the release of additional amounts of Th.

The main difference among the results obtained for setups C and D are due to the addition of the sample solution as 3M Al(NO₃)₃: that enhances the Th retention in the column. Thereafter, the addition of 0.5M H₂C₂O₄ improves its solubility, but the extension of such improvement is clearly dependent on the solution matrix used to load the Th in the resin. Hence, the Th mass available to be stripped with the U fraction is higher in setup D than in setup C.

Finally, the results were relatively satisfactory when the setup E was applied. The decreased H₂C₂O₄ concentration allows a convenient Th extraction from the resin. Cross contamination remains undetectable and recoveries of both U and Th are high enough as to provide adequate concentrations for the determination of isotope ratios.

Table 2 Results obtained for U and Th after application of setups A-E in aliquots of sediment sample T3

Phase / Setup	A (n=3)	B (n = 3)	C (n=2)	D (n=2)	E (n= 4)
U in U phase (%)	98.2±0.4	94.6±0.9	74.2±0.8	76±2	89±2
U in Th phase (%)	3.7±0.3	2.7±0.4	2.77±0.03	1.45±0.03	N.D.
Th in U phase (%)	N.D.	N.D.	26.2±0.3	42.0±0.5	N.D.
Th in Th phase (%)	6.59±0.15	2.3±0.6	44.4±0.9	23.7±0.4	74±2

In order to test the dependence of results on the sample matrix, we applied setups E and F to sediment samples and setup F to phosphogypsum samples. The results are shown in Figures 6 and 7.

U recoveries are high enough in the uranium fraction for both sample matrices. Recoveries were slightly higher (less than 10% higher) when no precipitation was applied to sediment samples, probably due to the application of higher volumes of U extractant, since this element was not detected in the supernatant phase. The results, however, were significantly worse when phosphogypsum was analysed. We don't have a clear explanation to this effect although it could be related with the massive presence of phosphates in phosphogypsum matrices acting as complexing agents of uranium nitrate that prevent their adsorption to DP[PP] extractant matrix in the UTEVA resin on spite the

Al(NO₃)₃ added. That hypothesis seems to be coherent with the detection of uranium in both load and conditioning solutions.

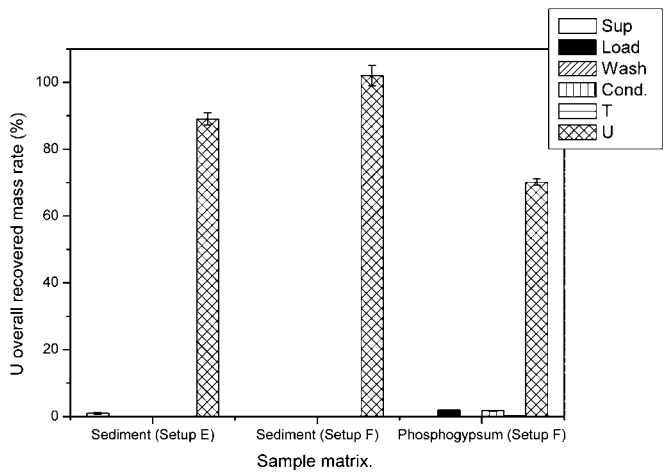


Figure 6 *U fractionation through the procedures described in the text as setups E and F*

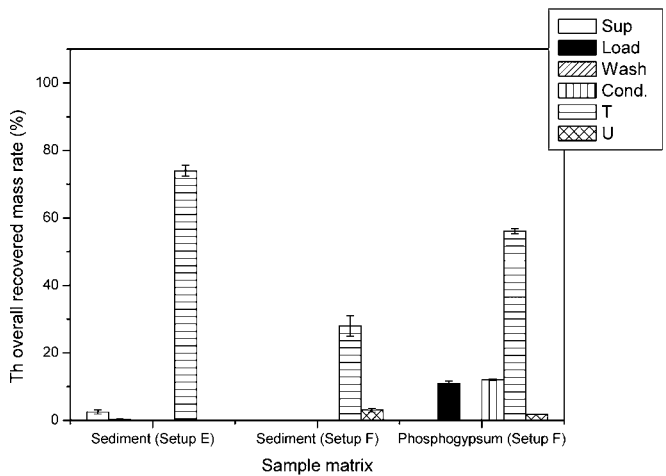


Figure 7 *Th fractionation through the procedures described in the text as setups E and F*

The results show more drastic differences for thorium. When no precipitation was applied to sediment samples, Th retention in the Th fraction was reduced by a factor approximately 2, and it was also detected in the uranium fraction. This effect was particularly drastic when phosphogypsum samples were analysed. In this case, Th was weakly adsorbed to resin leading to massive losses during the processes of sample load, resin washing and exchanging the resin form.

All these results show that results can be extremely dependent on the sample matrix, hence special care should be applied when a method previously established for a kind of environmental matrices is applied to another one. Accordingly, the fractionation of interferences was studied using setups E and F with sediment and phosphogypsum samples.

3.3 Chemical Fractionation of Interfering Elements

Os, Au and Hg were not detected in any of the analysed phases. This is due to the combination of a small concentration in the sediment sample²⁸ and the application of a high dilution factor for ICP-QMS measurement. Under these circumstances it is not possible to determine the fractionation of these elements in the radiochemical treatment. Those elements were also monitored in the U/Th fractions, and it was found that their count rates were below those achieved for ²³⁴U and ²³⁰Th isotopes by even more than one order of magnitude. According to the data provided in Table 1, the count rates due to these interferences should be negligible.

Cd, In, Sn and Pt were detected in both sediments and phosphogypsum samples in several phases produced along the radiochemical setup (Table 3). The complete mass balance can be established for the three first elements, as the analysed solutions contained 90-100% of masses introduced during the leaching. The unexplained fraction is associated to small (undetectable) concentrations in several phases and losses during the evaporations of phases concentrating U and Th. On the contrary, in the case of Pt a relatively large mass fraction remains unexplained, due to the very low concentrations in the starting samples.

Regarding Cd, the removal of a large fraction of its mass can be achieved through the previous precipitation step with iron hydroxide (set up E). On the contrary, In and Sn remain mainly in the precipitate. A great fraction of them follows the loading solution and the washing solution, being not adsorbed to the resin substrate. When no precipitation is applied, a certain fraction is also lost when the resin is changed to the chloride form.

In the specific case of indium, very tiny mass rates remain with the Th fractions when no actinide precipitation is applied. Considering that the In initial concentration present in the sample was already small, that will not be a problem for the analysis of Th IRs in phosphogypsum samples. It is possible to establish this conclusion because the expected counting rate associated to ²³⁰Th is several orders of magnitude higher than those due to In isotopes. Relatively large fractions (~20%) remain in the uranium phase. Although this is not a convenient situation, In dimers do not overlap uranium isotopes.

Finally, regarding Sn, the fraction lost during the loading onto the column is significantly higher when the precipitation is applied, and when no precipitation is applied a small but measurable amount remains in the uranium fraction. Hence, precipitation should be applied in order to minimise this possible interference and the setup E was applied in the rest of this work.

3.4 Internal Validation of the Technique

We checked the performances of the method (setup E) in terms of accuracy using sediment, phosphogypsum and phosphate rock samples that were previously analyzed by our research group using conventional, well-established, radiometric methods. The accuracy, precision and reproducibility of those methods have been tested through the participation in different national and international intercomparison exercises

Table 3 Summary of interfering elements fractionation for sediment and phosphogypsum samples. 3 replicates were performed per test. The results are shown as weighted averages $\pm$ weighted uncertainty

Phase	Supernatant	Load	Conditioning	Wash	Thorium	Uranium
Sediment (Setup E)						
Cd	66 $\pm$ 2	13.9 $\pm$ 0.7	2.44 $\pm$ 0.12	N.D.	N.D.	N.D.
In	0.22 $\pm$ 0.05	84 $\pm$ 2	11.1 $\pm$ 0.4	0.41 $\pm$ 0.10	N.D.	N.D.
Sn	3.2 $\pm$ 0.3	85 $\pm$ 4	11.3 $\pm$ 0.5	N.D.	N.D.	N.D.
Pt	N.D.	N.D.	N.D.	N.D.	4 $\pm$ 2	7 $\pm$ 5
Sediment (Setup F)						
Cd		88.2 $\pm$ 1.3	N.D.	N.D.	N.D.	N.D.
In		73 $\pm$ 7	12 $\pm$ 3	N.D.	1.4 $\pm$ 0.3	20.8 $\pm$ 2.3
Sn		52.0 $\pm$ 1.5	3.82 $\pm$ 0.16	N.D.	1.27 $\pm$ 0.06	2.2 $\pm$ 0.6
Pt		N.D.	N.D.	N.D.	N.D.	N.D.
Phosphogypsum (Setup F)						
Cd		50.3 $\pm$ 1.4	4.44 $\pm$ 0.12	N.D.	0.611 $\pm$ 0.014	1.71 $\pm$ 0.03
In		64 $\pm$ 7	N.D.	N.D.	1.7 $\pm$ 0.3	20 $\pm$ 3
Sn		48.9 $\pm$ 1.2	1.83 $\pm$ 0.09	15.3 $\pm$ 0.9	1.13 $\pm$ 0.11	2.2 $\pm$ 0.6
Pt		44 $\pm$ 18	0.06 $\pm$ 0.12	14 $\pm$ 4	4 $\pm$ 3	2.5 $\pm$ 0.8

The sample leaching procedure here applied and the absence of radiotracers mean that it is not possible to expect that the major isotope individual concentrations are in agreement among the application of alpha spectrometry-based methods and the coupling of EPA 3050B procedure with the analysis by ICP-MS. What we expect is that the corresponding isotope ratios are in agreement, and the major isotopes concentrations obtained by ICP-MS are minor than/equal than those obtained by alpha spectrometry. The results for validation samples are summarised in Table 4. It can be seen that the results for the major uranium and thorium isotopes are in very good agreement with the previous working hypothesis. The main difference appears for the phosphogypsum sample labeled as “CSN” for thorium, being almost half by ICP-MS than for alpha spectrometry. This finding is simply showing the limitations of the procedure here applied, and that certain uncontrolled losses occur during the procedure. On the other hand, isotope ratios are in good agreement within a 1- σ confidence interval. These results suggest the potential for the application of this methodology to samples of the area described in the section 1.

3.4 Application to Samples from the Huelva Estuary and nearby Industry

The results for additional phosphogypsum and sediment samples collected in that area are presented in Table 5. For uranium isotope ratios, the results are in good agreement with those found by Villa *et al.*⁶, while those of ²³⁸U concentration are in general good

agreement excepting a few samples, probably due to uncontrolled losses during the application of the radiochemical separation. As previously mentioned in the introductory section, the values of uranium isotope ratios are less than unit in a way statistically significant. These results are also in agreement with the results published by Bolivar *et al.*¹⁰ for samples collected at the OT1 and OT3 locations 5-10 years before than the samples here shown.

Table 4 Results obtained in the samples used for internal validation of the technique described in the text. N.M.: Not measured. Activity concentration is expressed in Bq/kg. Isotope ratios are expressed as activity ratios. F10: Phosphate rock. CSN: Phosphogypsum. T5-T6: Sediment

Sample	^{238}U (α)	^{238}U (ICP)	$^{238}\text{U}/^{234}\text{U}$ (α)	$^{238}\text{U}/^{234}\text{U}$ (ICP)	^{232}Th (α)	^{232}Th (ICP)	$^{232}\text{Th}/^{230}\text{Th}$ (α)	$^{232}\text{Th}/^{230}\text{Th}$ (ICP)
F10	694 $\pm$ 11	637 $\pm$ 9	0.999 $\pm$ 0.016	1.003 $\pm$ 0.011	11 $\pm$ 1	7.70 $\pm$ 0.24	0.0234 $\pm$ 0.0022 0.0184	0.0204 $\pm$ 0.0010 0.0192
CSN	55.0 $\pm$ 1.7	57.2 $\pm$ 1.0	0.98 $\pm$ 0.03	0.949 $\pm$ 0.004	6.1 $\pm$ 0.1	3.80 $\pm$ 0.06	$\pm$ 0.0005	$\pm$ 0.0006 0.130
T5	308 $\pm$ 7	297 $\pm$ 3	0.93 $\pm$ 0.03	0.919 $\pm$ 0.006	N.M.	24.3 $\pm$ 0.4	N.M.	$\pm$ 0.003 0.0642
T6	780 $\pm$ 15	476 $\pm$ 6	0.936 $\pm$ 0.025	0.941 $\pm$ 0.005	N.M.	31.2 $\pm$ 0.5	N.M.	$\pm$ 0.0009

Regarding thorium concentration, no external reference can be used, although the $^{232}\text{Th}/^{230}\text{Th}$ isotope ratios are above those found by Bolivar *et al.*¹⁰ by a factor ~ 2 . For this area, isotope ratios in the range of $\sim 0.7\pm 0.2$ could be considered as almost representative values of unpolluted sediments.⁸ This value is almost reached in samples T3, T4 and OT1. However, the remaining samples show thorium isotope ratios within a range of 0.06-0.13. The Th IR values in phosphogypsum are within a range 0.012-0.018. Hence those samples having low Th IR values are reflecting the mixing of two isotopic signals, that due to natural processes and that other associated to industrial and mining activities.

Table 5 Results obtained in the sediment and phosphogypsum (PG) samples used in this work. Isotope ratios are expressed as activity ratios

Sample	^{238}U (Bq/kg)	$^{238}\text{U}/^{234}\text{U}$	^{232}Th (Bq/kg)	$^{232}\text{Th}/^{230}\text{Th}$
O3	138.7±0.9	0.894±0.011	26.6±1.1	0.184±0.007
O5	320±5	0.934±0.006	36.0±0.9	0.0829±0.0011
O6	482±43	0.941±0.009	81±7	0.1260±0.0017
T3	129±2	0.919±0.021	15.75±0.16	0.486±0.016
T4	53.4±1.5	0.871±0.007	9.39±0.19	0.397±0.008
OT1	90.0±0.8	0.882±0.022	26.0±0.3	0.303±0.010
OT3	36.2±0.8	0.96±0.03	7.77±0.04	0.204±0.003
F06 (PG)	611±14	0.970±0.006	11.8±0.3	0.01152±0.00020
F17 (PG)	250±3	0.962±0.009	14.6±0.3	0.0212±0.0004
F18 (PG)	189±3	0.960±0.015	13.28±0.12	0.0186±0.0005

Acknowledgements

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FAST METHOD TO SEPARATE AM AND PU FROM SOIL MATRIX

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1 INTRODUCTION

In the context of the environmental monitoring of radioactivity and direct radiation in the vicinity of the Paul Scherrer Institut (PSI), Switzerland¹ the actinides ^{241}Am and $^{239,240}\text{Pu}$ have to be determined in soil samples. Figure 1 shows the original method of separating Pu and Am from soil matrices at PSI. There was no provision for fast analysis of emergency samples. Since the Eichrom® DGA resin of Triskem has proved to be suitable for Am preconcentration², the Ca-Oxalate step for preconcentration of Am and Pu, and the subsequent mineralisation were omitted (figure 1, grey steps) in the fast method. Furthermore, the Eichrom® TEVA – DGA and Eichrom® U/TEVA – DGA options were tested and compared to the original method (figure 1). The U/TEVA – DGA option was found to be the best method of separating Am from traces of thorium and uranium.

2 METHOD AND RESULTS

2.1 Method

2.1.1 Soil Preparation. As part of an environmental monitoring program, 6 soil samples are collected each year in the vicinity of the Paul Scherrer Institut in Switzerland. After the routine γ -measurement, the soil samples were sieved and milled with a steel ball mill (Mixer Mill, Retsch MM2000, Germany). For each analysis, 30 g of soil matrix were weighed into a 250 ml beaker and approximately 10 mBq of ^{243}Am and 20 mBq of ^{242}Pu tracer were added. In addition, 25 ml of conc. HNO_3 (65%) were added and the beaker was covered with a watch glass, then gently heated until nitrous gasses were no longer released (wet-ashing). Then, the sample was dried completely. The sample was placed in a preheated muffle furnace and ashed at 400°C for 15h (dry-ashing).

2.1.2 Leaching Process. 100 ml of 8 M HNO_3 were added to the ashed soil samples, followed by 2 ml conc. H_2O_2 (30%). The addition of hydrogen peroxide causes plutonium to stabilize into tetravalent state. The dissolved sample was covered with a watch glass and boiled for 1h. Another 2 ml of conc. H_2O_2 (30%) were added, the sample boiled for 10 min and then subsequently left to cool to room temperature. After the removal of the magnetic stirrer the sample was filtered (Whatman, GF/B) and rinsed thoroughly with 8 M HNO_3 . The residue was then discarded and the filtrate (approximately 100 ml) kept.

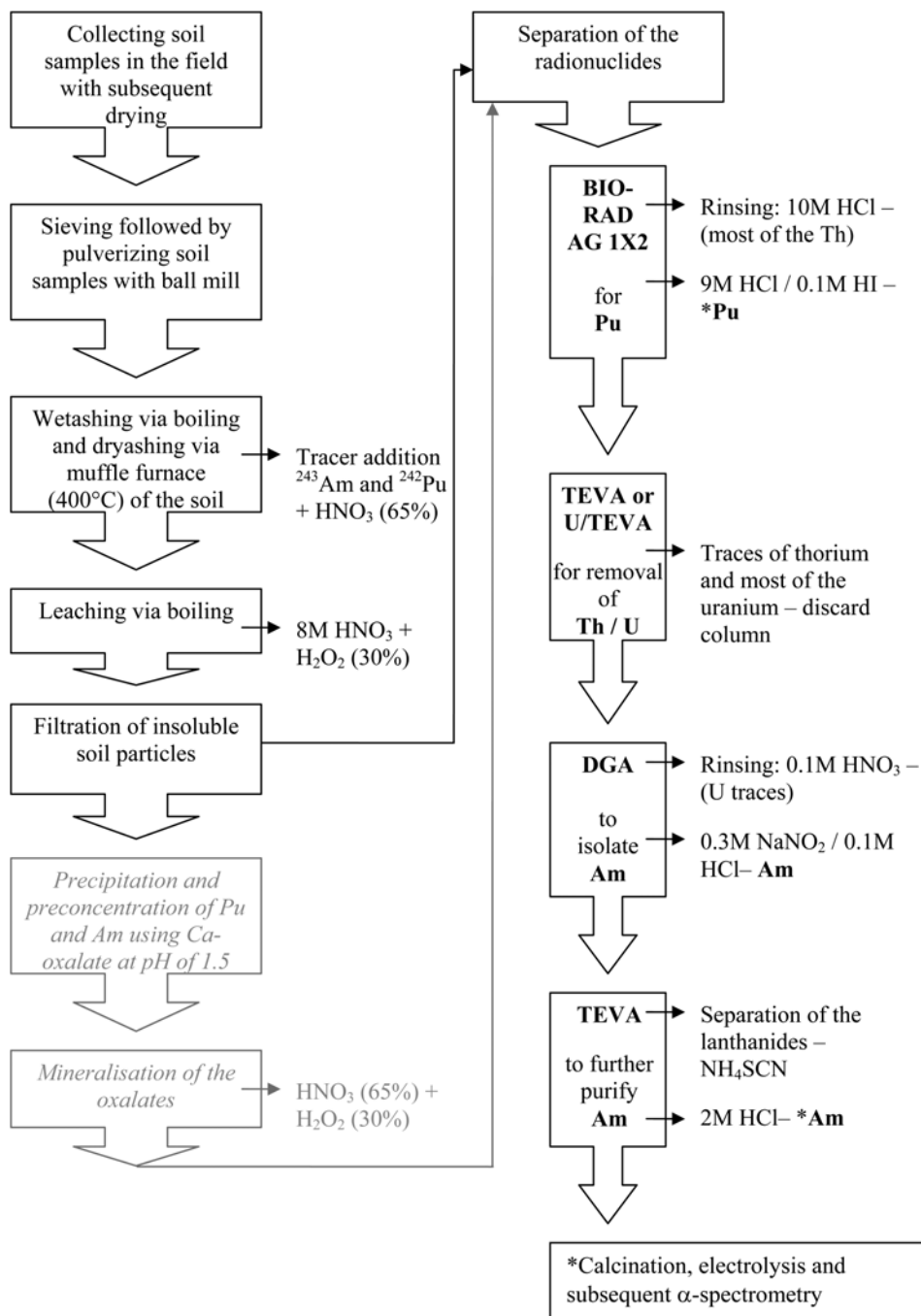


Figure 1 Method developed to separate Pu and Am from soil matrix at the Paul Scherrer Institut, Switzerland. Grey steps were omitted to obtain a fast method for emergency cases

2.1.3 BIO-RAD AG 1-X2: Plutonium Separation. 4 g of the anion exchanger BIO-RAD AG 1-X2 (chloride form, 100-200 mesh) were mixed with 2-3 ml of distilled water. The resin was then placed in a 1 cm diameter BIO-RAD Econo-column (20 cm long; glass and polypropylene) and the resin covered with a fiber filter disc (Whatman GF/B). To condition the column, 20 ml of 8 M HNO₃ were flushed through the tube.

The filtrate from the leaching process was then loaded onto the column step by step, with a 250 ml beaker placed underneath to collect the Am/U fraction for further processing. The column was then rinsed with 40 ml of 8 M HNO₃. Most of the thorium could be stripped off the column using 20 ml of 10 M HCl and were discarded. Finally, plutonium was eluted from the column with 20 ml of 9 M HCl / 0.1 M HI into a 25 ml glass beaker, containing 0.6 ml 1 M NaHSO₄ and 0.6 ml conc. H₂SO₄. The samples were calcinated and subsequently electrolysed³.

2.1.4 TEVA-DGA or U/TEVA-DGA: Americium Separation. For the Am separation, two possible methods were tested. Either an Eichrom® TEVA or a U-TEVA column was placed in series with the Eichrom® DGA column. The DGA column was connected to a Tygon tube (Tygon 2001, I.D. 2.06 mm, purple-purple, Ismatec SA), installed on a suction pump. As such, 4 samples were run in parallel and all future steps applied to both column combinations. The resins in series, were both conditioned with 20 ml 8 M HNO₃, using a slow suction speed to avoid air bubbles in the flow. Thereafter, the 100 ml Am/U solution was loaded on the columns in the same manner. The 8 M HNO₃ rinsing solution (derived from the BIO-RAD AG 1-X2) was then run through both columns. When the DGA column was still yellow (iron traces), it was rinsed further with 5-10 ml 8 M HNO₃ until the column was white. The TEVA or U/TEVA column was then discarded (traces of thorium and most of the uranium) and the DGA resin was rinsed with 15 ml 0.1 M HNO₃ (traces of uranium). In the last step, Am was eluted into a 50 ml glass beaker using 35 ml 0.1 M HCl / 0.03 M NaNO₂ and was subsequently evaporated. To remove traces of lanthanides, the Am-fraction was run through a TEVA column. 0.5 g TEVA was weighed into a BIO-RAD column (Poly-Prep, BIO-RAD Cat. Nr. 731-1550). Using a glass rod and about 2 ml of deionised water, the air bubbles were removed. The Am residue was dissolved with 5 ml 2 M NH₄SCN / 0.1 M HCOOH and the resin was conditioned with the same amount of solvent. The dissolved Am-fraction was then loaded on the TEVA column. In the next step, the resin was rinsed with 5 ml 2 M NH₄SCN and 10 ml 1 M NH₄SCN. Americium was then eluted with 15 ml 2 M HCl in a 25 ml glass beaker, containing 0.6 ml NaHSO₄ and 1 ml conc. H₂SO₄, and subsequently calcinated and electrolysed³.

2.1 Results

Figure 2 shows that the activity concentrations of ^{239,240}Pu and ²⁴¹Am between the different methods agree well. The ratio of ²⁴¹Am to ^{239,240}Pu, due to bomb testing in 1963, was 0.4 in Switzerland in 1999⁴ and 0.45 ± 0.14 for the area of the Paul Scherrer Institut in 2000.⁵ The values received were 0.42 ± 0.12 for the original method, 0.42 ± 0.09 for the fast method using TEVA and 0.48 ± 0.09 for the fast method using U/TEVA ($n = 6$; n is the number of samples tested). Regarding the value for the Paul Scherrer Institute in 2000, all ratios obtained are comparable to and confirmed by the original method. The percentage recovery for ^{239,240}Pu and ²⁴¹Am in the original method was $80\% \pm 16$ and $75\% \pm 14$, respectively ($n = 6$). The ^{239,240}Pu percentage recoveries for BIO-RAD AG 1-X2 in the TEVA method ($54\% \pm 4$) and the U/TEVA method ($61\% \pm 12$) were both lower than the original method, yet still acceptable to evaluate the activity concentration. Similarly, for ²⁴¹Am, both fast methods showed clearly lower percentage recoveries (TEVA-method:

71% $\pm$ 28; U/TEVA-method: 63% $\pm$ 26), yet the activity concentrations for both methods could be confirmed using the activity concentrations of ^{241}Am in the original method. The combination of anion-exchange resin and extraction chromatography works well and allows the treatment of large sample sizes.⁶

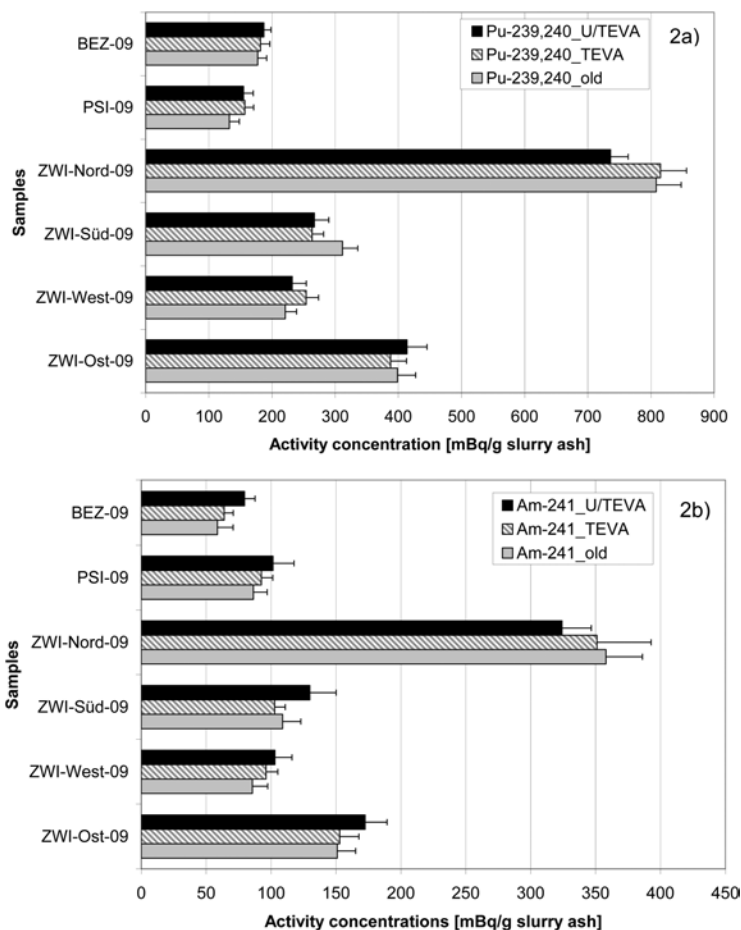


Figure 2 a) $^{239,240}\text{Pu}$, b) and ^{241}Am activity concentrations derived by the original method (light-grey bars), the fast method using TEVA (hatched bars) and the fast method using U/TEVA (black bars)

Using the TEVA-method, traces of ^{228}Th and its daughter products, the naturally occurring ^{232}Th and ^{230}Th deriving from the ^{238}U decay could occasionally be seen in the spectrum of ^{241}Am . Testing this method on the IAEA-300 sample, showed similar results in the ^{241}Am spectrum. However, when the BIO-RAD AG 1-X2 was followed by the U/TEVA – DGA columns in series, IAEA-300 and IAEA-384 samples showed that Th and U were effectively separated from the Am.

Table 1 Activity concentrations of the reference materials IAEA-300 and IAEA-384 and the results obtained, testing BIO-RAD AG 1-X2 for plutonium and the TEVA- and U/TEVA-method to test americium. The 95% confidence interval is shown in brackets for the reference values and the 2σ uncertainty for the measured values. The bold results belong to the finalised method

IAEA reference materials	IAEA-300 [Bq/kg] - % recovery	IAEA-384 [Bq/kg] - % recovery
$^{239,240}\text{Pu}$ – ref. material	3.55	107 (103-110)
$^{239,240}\text{Pu}$ – BIO-RAD AG 1-X2	3.34 ± 0.20 43	-- --
$^{239,240}\text{Pu}$ – BIO-RAD AG 1-X2	3.49 ± 0.26 46	112 ± 4.63 102
^{238}Pu – ref. material	0.15 (0.1-0.6)	39 (38.6-39.6)
^{238}Pu – BIO-RAD AG 1-X2	0.15 ± 0.02 43	-- --
^{238}Pu – BIO-RAD AG 1-X2	0.20 ± 0.03 46	37.4 ± 1.58 102
^{241}Am – ref. material	1.38 (1.2-1.5)	7.1 (6.7-7.4)
^{241}Am – TEVA-method	0.93 ± 0.10^a 103	-- --
^{241}Am – U/TEVA-method	1.44 ± 0.17^a 95	6.7 ± 0.41^b 98

^aCorrected for the ingrowth of ^{241}Am derived by the decay of ^{241}Pu since 01.01.1993.

^bCorrected for the ingrowth of ^{241}Am derived by the decay of ^{241}Pu since 01.08.1996.

Table 1 shows that the activity concentrations achieved, using BIO-RAD AG 1-X2 to elute ^{238}Pu and $^{239,240}\text{Pu}$, are in good agreement with the values of the reference material, despite the lower recoveries for IAEA-300. Since the ^{241}Am spectrum of the TEVA-method only, showed impurities of thorium and uranium, the U/TEVA-method was regarded to be the finalised method. This is further underlined, with the fact that the ^{241}Am activity concentration, derived with the TEVA-method, is below the 95% confidence interval of the reference value. Including the correction for ^{241}Am ingrowth derived by the decay of ^{241}Pu since the reference date, the achieved activity concentrations of ^{241}Am for the IAEA-300 and IAEA-384 samples (bold letters in table 1) agree well with the reference material and thus we regard our method to be validated.

3 CONCLUSION

The separation of plutonium and americium in soil matrix could be improved by one day, omitting the time-consuming preconcentration step, Ca-oxalate with adjacent mineralisation (Figure 1). The U/TEVA-method proved to be the finalised method, since no traces of Th or U could be seen on the ^{241}Am spectrum. Despite lower percentage recoveries for the activity concentrations, compared to the original method, the U/TEVA-method was validated by the IAEA-300 and IAEA-384 reference materials (Table 1). The original method could be successfully shortened and can be applied to emergency samples.

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BIOSORPTION OF URANIUM USING MODIFIED LEAF POWDER OF *PLATANUS ORIENTALIS*

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1 INTRODUCTION

Uranium which is one of the most important radionuclides, has special attention because of its chemical toxicity and radioactivity. Excess amounts of uranium released into the environment are increased by the activities of the nuclear industry, mining ore processing, agriculture and coal combustion.¹ In view of the extensive usage of uranium for various industrial purposes and its toxicity, removal of this metal in environmental, metallurgical, geological materials is of greatest importance prior to pollution control measures or its use as alloys or in understanding the correlation between diseases of animals and aquatic organisms and soil chemistry.² There are various separation techniques for the removal of uranium ions from wastewaters such as precipitation, membrane processes, ion exchange, solvent extraction and adsorption. However these technologies become expensive or inefficient for the treatment of effluents containing metal ions in the region of 100 mg/l.³

Biosorption is one of the popular separation methods, and is defined as the removal of metal or metalloid species, compounds and particulates from solution by biological material. It has many significant advantages in contrast to traditional methods such as rapid, reversible, economical, ecofriendly technology and convenient for lower concentration.⁴ Moreover, biosorbent materials often execute high metal-loading capacity and in some cases are highly specific for certain elements of particular interest.⁵ Different kinds of materials such as tree leaves, microorganisms, sawdust, bark, cone biomass, yeasts are used for biosorption processes.⁶ Biosorption can be a candidate for recovery of metals from dilute industrial aqueous solutions, the extraction of radionuclides and lanthanides from mine leachates, and metal recovery or water pollution control applications.⁷

Fallen tree leaves are dead biomasses, inexpensive and abundant. They contain various components such as polyphenolics, plant pigments and protein which would provide active sites for heavy metal binding.⁸ However, crude agricultural by-products has low adsorption capacity in general. In the heavy metal biosorption, there are two type pretreatment methods for increasing the uptake capacity of biomass. First is physical methods, such as; heating and autoclaving⁹, drying¹⁰⁻¹¹, freeze-drying and boiling.¹²⁻¹³ Secondly, previous studies has shown that chemical modification provides to enhance in improving the adsorption and the cation exchange capacity of agricultural by-products. Some extra acidic groups can be introduced to the material by forming an ester linkage and

improved their metal sorption capacity by poly acids (citric, tartaric, phosphoric i.e.) treatment.¹⁴ Especially, phosphoric acid is attracted much attention because polyphosphoric acid can react with various groups on the leaf, such as the glucose hydroxyl groups in cellulose, to form phosphate esters. These reactions usually occur most efficiently at temperatures above 150°C. The covalently bound phosphates increase the total charge on the leaf and therefore its ability to bind metals.¹⁵

There are many studies previously about biosorption of heavy metals on tree leaves from aqueous solutions. Removal and recovery of Pb(II), Cd(II), Cu(II) was tested on *Ulmus carpinifolia* and *Fraxinus excelsior* tree leaves and metal loading, model fitting, kinetics and effect of sorption parameters were investigated.¹⁶ The coniferous leaves and London plane leaves were used for the removal of Cr(VI).¹⁷⁻¹⁹ Lanthanum and cerium from rare earth elements were adsorbed on *Platanus Orientalis* and *Pinus Brutia* leaf powders without any chemical treatment and results show that *P. Orientalis* and *P. Brutia* leaf powders are available for biosorption of heavy metals.²⁰⁻²¹

In this study, the use of phosphoric acid modified *P. Orientalis* Leaf Powder was investigated for uranium biosorption. Central Composite Design Method was used in the experiments. The effects of initial pH, temperature, initial concentration of adsorbate and contact time on the biosorption were discussed. Freundlich, Langmuir and Dubinin-Radushkevich isotherms were studied related with the process were performed in order to explain adsorption characteristic.

2 EXPERIMENTAL

2.1 Materials and Methods

All chemicals used in this study were analytical grade. *P. Orientalis* leaves were collected from a number of trees at Ege University Campus area, Izmir, Turkey. The collected leaves were washed repeatedly with MilliQ water to remove dust and soluble impurities and dried in an oven at 80°C for 24 h, ground in a mortar to a fine powder and sieved through a 125 µm copper sieve and stored in a desiccator before use.

Uranium stock solutions (1000 ppm) were prepared from $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck) in deionized water. The working solutions were prepared by diluting the stock solutions to appropriate volumes. The pH values of these solutions were adjusted with 1 mol l^{-1} Na_2CO_3 and 1 mol l^{-1} HNO_3 solution by using Metrohm 654 pH meter with a combined pH electrode. The Phosphoric Acid (85 wt. % solution, Merck) was used for chemical modification of leaf powder. Ultrapure water (resistivity 18.2 MΩ-cm, TOC level 1–5 ppb) was prepared by the Milli-Q (Millipore, Milford, MA, USA) water purification system. 0.005 g of dry biomass were mixed with metal ion solution. Shaking experiments were done in a temperature controlled environment at 150 RPM using a GFL 1086 water bath shaker equipped with microprocessor thermostat.

After uranium loading, samples were filtered with blue ribbon filter paper, then clear liquid phases obtained were measured by Perkin Elmer Optima 2000DV ICP-OES.

2.2 Adsorbent Preparation

Powdered leaf of *P. Orientalis* was mixed with 0.6 M phosphoric acid (PA) at a ratio of 1.5 g powder to 50 ml PA. After stirring at 500 rpm for 30 min at ambient temperature, slurry was placed in a stainless steel tray and dried at 50°C for 24 h in an oven. The residual

amount of the solution which was 20 ml at the end of the drying process, was completed to 80 ml. The thermochemical reaction between acid and powder was proceeded by raising the oven temperature to 160°C for 90 min. After cooling, the reacted product washed with MilliQ water to remove any excess of PA. Following the washing thoroughly with MilliQ water, the PA-modified *P. Orientalis* wet powder was dried at 50°C until constant weight and preserved in a desiccator.

2.3 Adsorbent Characterization

Textural characteristics of the PA-modified *P. Orientalis* were determined by nitrogen adsorption using an automatic Micromeritics ASAP 2020 surface area analyzer. The Brunauer–Emmett–Teller (BET) surface area of the PA-modified *P. Orientalis* was determined using BET method, using the software available with the instrument. BET surface area was found as $1.34 \pm 0.03 \text{ m}^2/\text{g}$.

The spectrum of the PA-modified *P. Orientalis* showed a characteristic peak at 3600–3200 cm^{-1} region is due to the presence of $\gamma\text{O-H}$ of the hydroxyl groups. The absorption peaks at 2900–3000 cm^{-1} are ascribed to the asymmetric stretching of $\gamma\text{C-H}$ bond of the $-\text{CH}_2$ groups combined with that of the CH_3 groups. Visible broad absorption band at 1560 cm^{-1} could be correspond to the bending vibration of N-H group. The sharp peaks in between the 1400 and 1500 cm^{-1} are due to the presence of the carboxyl groups. The strong peaks at between 900 and 1200 cm^{-1} band are attributable to the presence of phosphate groups (Figure 1)^{5,22}.

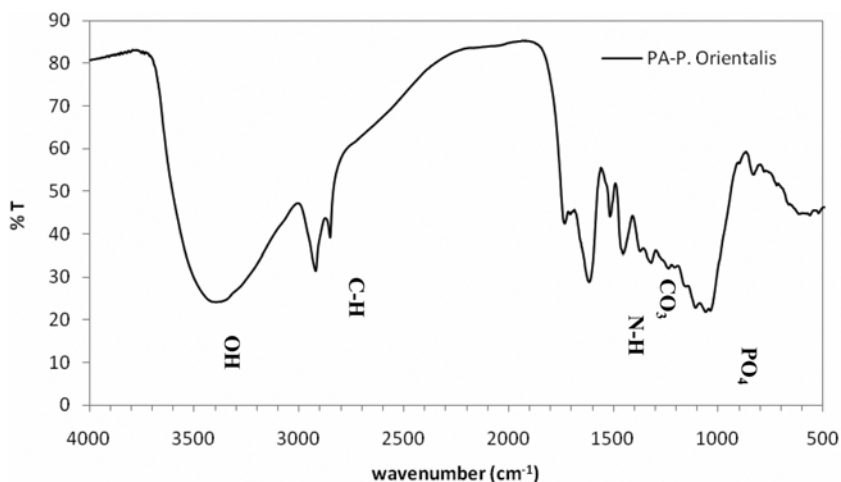


Figure 1 FTIR spectra of modified *P. Orientalis* leaf powder

2.4 Sorption Experiments

The experimental data in sorption can be expressed in terms of an uptake of metal, q , defined as the amount of uranium sorbed per unit mass of the biosorbent was evaluated by using the following equation:

$$q = (C_0 - C_e) \times \frac{V}{m} \quad (\text{mg g}^{-1}) \quad (1)$$

where q is the metal uptake (mg g^{-1}), C_o and C_e are the initial and equilibrium uranium concentrations in the solution (mg l^{-1}), respectively, V is the solution volume (l) and m is the mass of biosorbent (g). The distribution coefficient K_d (mg l^{-1}) of metal ions between the aqueous phase and the solid phase can be directly obtained using:

$$K_d = \frac{C_o - C_e}{C_e} \times \frac{V}{m} \quad (\text{ml g}^{-1}) \quad (2)$$

V/m is the ratio of the volume of metal solution (mL) to the amount of adsorbent (g) in a batch.

Batch tests are commonly used to determine q , K_d etc. values. The test is conducted by spiking a solution with the element of interest, mixing the spiked solution with a solid for a specified period of time, separating the solution from the solid, and measuring the concentration of the spiked element remaining in solution. The concentration of contaminant associated with the solid is determined by the difference between initial and final contaminant concentration. The primary advantage of the method is that such experiments can be completed quickly for a wide variety of elements and chemical environments²³.

2.5 Experimental Design

In assessing the effects of multiple parameters on sorption efficiency, the use of an adequate experimental design is particularly important. To study the interactions of two or more variables, Response Surface Methodology (RSM) has proved a useful tool.²⁴ It is a collection of mathematical and statistical techniques for designing experiments, building numerical models, evaluating the effects of variables and searching for the optimum combinations of factors. Experimental design methodology involves changing all variables from one experiment to the next. The reason for this is that variables can influence each other, and the ideal value for one of them can depend on the values of the others. This interaction between variables is a frequent phenomenon. RSM usually contains three stages: (i) design and experiment, (ii) response surface modeling through regression, (iii) optimization. The main advantage of RSM is the reduced number of experiments needed to describe the effects of multiple parameters and their interactions.²⁵

In this study in order to determine the optimum metal uptake conditions for biosorbent, Central Composite Design (CCD) has been used. The CCD is an effective design that is ideal for sequential experimentation and allows a reasonable amount of information for testing lack of fit while not involving an unusually large number of design points. CCD consists of 16 factorial points, 9 star points and 6 replicates. According to the CCD, the optimization of uranium removal was carried out by four chosen independent process variables (pH (X_1), temperature (X_2), initial uranium concentration (X_3) and contact time (X_4)) with seven replicates at centre points. The effects of independent variables on metal sorption of biosorbent were examined by batch tests. Batch sorption behavior of uranium ions on the PA-modified *P. Orientalis* biosorbent was conducted by immersing 0.005 g biosorbent in 10 ml of liquid phase. The ranges and the levels of the variables (high, low, centre and star points) investigated in the work are given in Table 1. Experiments were performed according to experimental design matrix given on Table 2.

Table 1 The ranges and the levels of the investigated parameters

Parameters	Code	- α	-1	0	+1	+ α
pH	X ₁	3	4	5	6	7
Temperature (°C)	X ₂	20	30	40	50	60
Initial U Concentration (mgL ⁻¹)	X ₃	50	100	150	200	250
Contact Time (min.)	X ₄	5	45	85	125	165

The matrix for four variables is varied at five levels (- α , -1, 0, +1, + α). The higher level of variable was designed as “+1”, the lower level was designed as “-1”, centre point was designed as “0” and star points were designed as “- α and + α ”. The quadratic equation model for predicting the optimal point was expressed according to Eq. (3).

$$y_i = a_0 + \sum a_i X_i + \sum a_{ii} X_{ii}^2 + \sum a_{ij} X_i X_j \quad (3)$$

Four parameters varied, 14 coefficients has to be estimated, i.e. coefficients for the four main effects, four quadratic effects, six interactions and intercept term. y_i is the predicted response, a_0 is the intercept term, a_i is the i^{th} linear coefficient term, a_{ii} is the i^{th} quadratic coefficient term and a_{ij} is the interaction coefficients term for the model. Second-order polynomial equation can be presented as Eq. (4).

$$y = a_0 + a_1 X_1 + a_2 X_2 + a_3 X_3 + a_4 X_4 + a_{11} X_1^2 + a_{22} X_2^2 + a_{33} X_3^2 + a_{44} X_4^2 + a_{12} X_1 X_2 + a_{13} X_1 X_3 + a_{14} X_1 X_4 + a_{23} X_2 X_3 + a_{24} X_2 X_4 + a_{34} X_3 X_4 \quad (4)$$

Experimental data points used in CCD statistical design and predicted and actual responses are given in Table 2.

3 RESULTS AND DISCUSSION

The relationship between independent variables and response was drawn by second-order polynomial equation. The regression equation coefficients were calculated and data was fitted to a second-order polynomial equation for removal of uranium ions with PA-modified *P. Orientalis*.

$$y = 196.61 - 1.29 X_1 + 13.03 X_2 + 45.67 X_3 + 3.18 X_4 - 30.31 X_1^2 - 4.44 X_2^2 - 5.63 X_3^2 - 23.10 X_4^2 + 5.73 X_1 X_2 + 1.13 X_1 X_3 - 2.06 X_1 X_4 - 1.85 X_2 X_3 + 3.34 X_2 X_4 + 0.99 X_3 X_4 \quad (5)$$

On the basis of second-order polynomial equation of response surface methodology, the effect of independent variables: pH, temperature, initial uranium concentration and contact time on the sorption of uranium were analyzed. Table 3 shows the regression analyses of independent variables.

Table 2 Experimental data points used in CCD statistical design and predicted and actual responses

No	pH	Temperature (°C)	Initial U conc. (mg.L ⁻¹)	Contact time (min.)	PA-P. Orientalis	
					q (mg.g ⁻¹) Actual	q (mg.g ⁻¹) Predicted
1	1	1	1	1	194.19	201.00
2	1	1	1	-1	188.14	190.10
3	1	1	-1	1	121.81	109.13
4	1	1	-1	-1	95.61	102.18
5	1	-1	1	1	161.59	160.49
6	1	-1	1	-1	160.77	162.95
7	1	-1	-1	1	68.18	61.21
8	1	-1	-1	-1	63.30	67.63
9	-1	1	1	1	203.37	193.97
10	-1	1	1	-1	154.83	174.85
11	-1	1	-1	1	95.75	106.61
12	-1	1	-1	-1	95.42	91.45
13	-1	-1	1	1	169.92	176.39
14	-1	-1	1	-1	163.02	170.63
15	-1	-1	-1	1	88.67	81.64
16	-1	-1	-1	-1	73.61	79.83
17	α	0	0	0	69.36	72.79
18	-α	0	0	0	89.36	77.96
19	0	α	0	0	211.01	204.92
20	0	-α	0	0	154.67	152.79
21	0	0	α	0	278.73	265.44
22	0	0	-α	0	77.44	82.76
23	0	0	0	α	100.04	110.54
24	0	0	0	-α	116.31	97.84
25	0	0	0	0	196.66	196.61
26	0	0	0	0	207.43	196.61
27	0	0	0	0	189.67	196.61
28	0	0	0	0	192.88	196.61
29	0	0	0	0	190.57	196.61
30	0	0	0	0	189.22	196.61
31	0	0	0	0	209.84	196.61

Table 3 Analysis of variance (ANOVA) for the regression model for uranium uptake capacity of biosorbent

	df	SS	MS	F	Significance F	R ²
Regression	14	93001.33	6642.95	43.88	4.52x10 ⁻¹⁰	0.97
Residual	16	2422.43	151.40			
Total	30	95423.76				

Table 4 Coefficients, *t* Stat and *P*-values in the uranium sorption with biosorbent

	PA-P. <i>Orientalis</i>		
	Coefficients	t Stat	P-value
Intercept	196.61	42.28	7.58×10^{-18}
X ₁ (pH)	-1.29	-0.51	6.14×10^{-01}
X ₂ (Temperature)	13.03	5.19	8.96×10^{-05}
X ₃ (In. U Concentration)	45.67	18.18	4.13×10^{-12}
X ₄ (Contact Time)	3.18	1.26	2.24×10^{-01}
X ₁ X ₁	-30.31	-13.17	5.27×10^{-10}
X ₂ X ₂	-4.44	-1.93	7.17×10^{-02}
X ₃ X ₃	-5.63	-2.45	2.64×10^{-02}
X ₄ X ₄	-23.10	-10.04	2.59×10^{-08}
X ₁ X ₂	5.73	1.86	8.08×10^{-02}
X ₁ X ₃	1.13	0.37	7.18×10^{-01}
X ₁ X ₄	-2.06	-0.67	5.14×10^{-01}
X ₂ X ₃	-1.85	-0.60	5.56×10^{-01}
X ₂ X ₄	3.34	1.09	2.94×10^{-01}
X ₃ X ₄	0.99	0.32	7.52×10^{-01}

The efficiency values obtained as a result of 31 experiments determined at the Central Composite Design conditions were compared with the calculated efficiency values from the applied model. Table 3 represents analysis of variance (ANOVA) for the regression model for uranium uptake capacity of *PA-P. Orientalis*. The value of R^2 was found 0.97 for uranium sorption on biosorbent. Probability F value ($F < 0.05$) and high R^2 value ($R^2 \geq 0.95$) indicate that the model fits the experimental data well for each samples. Coefficients and P- values to understanding importance of parameters are shown in table 4.

3.1 Effect of solution pH

pH was found statistically non significant ($P = 6.14 \times 10^{-1}$) for the biosorbent. Maximum uranium adsorption from aqueous solution by *PA-P. Orientalis* was obtained at pH 4.5 – 5.5 interval (Figure 2). Below pH 4.5 and above pH 5.5 uranium sorption was reduced dramatically. The uranium sorption is increased by pH with another variables being fixed at centre points.

3.2 Effect of Temperature

Temperature was found statistically significant ($P = 8.96 \times 10^{-5}$) for *PA-P. Orientalis* biosorbent. The positive value of coefficient belong to pH ($X_2 = 13.03$) indicates that pH has a positive effect on sorption of uranium from aqueous solution by *PA-P. Orientalis*

(Figure 3). The increasing of uranium sorption depends on increasing temperature with another variables being fixed at centre points.

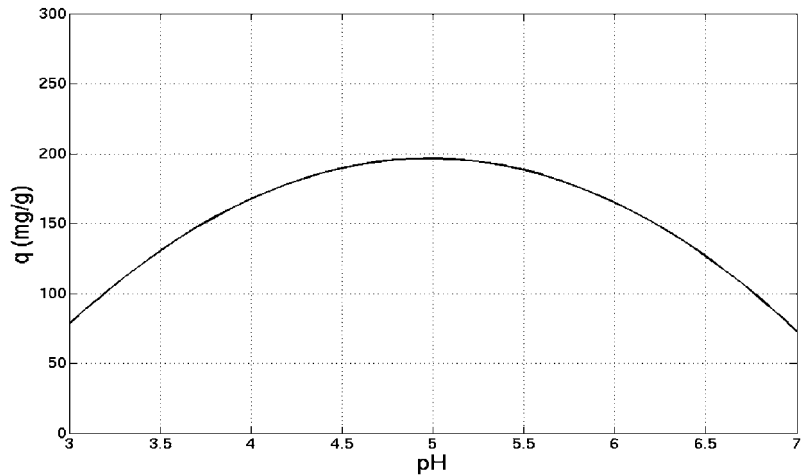


Figure 2 Effect of solution pH on uranium biosorption onto PA modified *P. Orientalis* leaf powder.

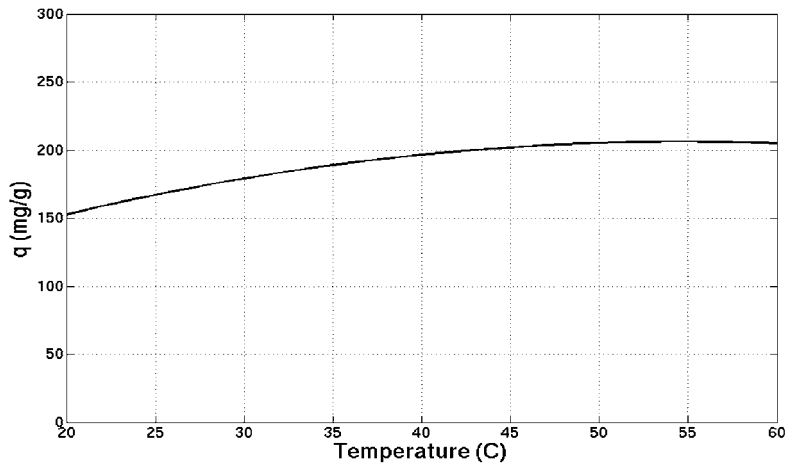


Figure 3 Temperature effect of uranium biosorption onto PA modified *P. Orientalis* leaf powder

3.3 Effect of Initial Uranium Concentration

Initial uranium concentration was found statistically significant ($P= 4.23\times10^{-12}$) for biosorbent. The positive value of coefficient belongs to initial uranium concentration for biosorbent ($X_3= 45.7$) indicate that initial uranium concentration has a positive effect on sorption of uranium from aqueous solution by *PA-P. Orientalis* biosorbent. It means the

sorption of uranium increases when initial uranium concentration increases (Figure 4). The increasing of uranium sorption depends on increasing initial uranium concentration with another variables being fixed at centre points.

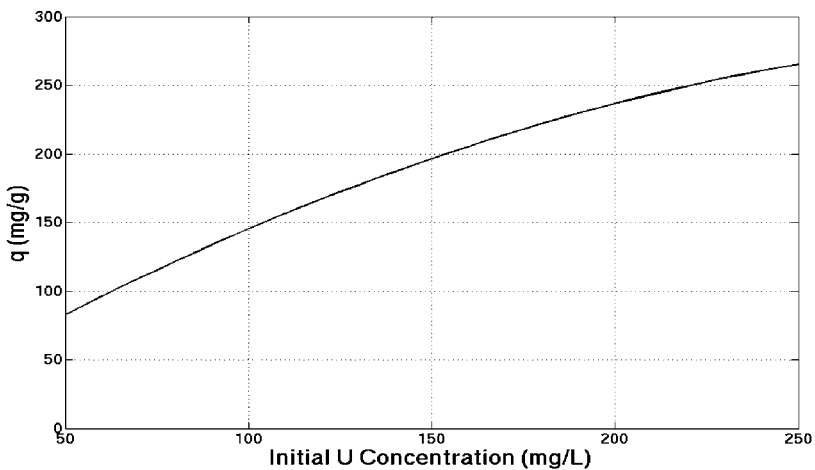


Figure 4 Effect of initial uranium concentration of the uranium biosorption onto PA modified *P. Orientalis* leaf powder

3.4 Effect of Contact Time

Contact time was found statistically non-significant ($P = 0.22$) for biosorbent. Between 5-90 minutes adsorption increases by increasing of contact time and after that decreases due to the desorption of uranium ions (Figure 5). The uranium sorption is increased by contact time with another variables being fixed at centre points.

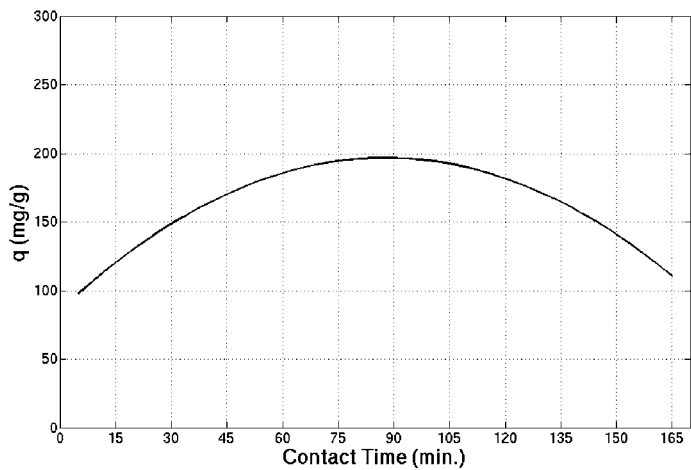


Figure 5 Effect of contact time on uranium biosorption onto PA modified *P. Orientalis* leaf powder.

3.5 RSM Plots

Interactions between independent variables are shown in 3D surface plots with other variables being at fixed levels (Figures 6 – 11).

Combined effect of two independent variables pH (X_1) and temperature (X_2) indicate that maximum uranium adsorption onto *PA-P. Orientalis* obtained at pH 4.5 – 5.5 interval in all temperature ranges (Figure 6). There is the distinct maximum in the adsorption isotherm of uranium at pH 4.5–5.5 and the adsorption dramatically decreases passing to the acidic and alkaline regions. At low pH (below pH 4.5), the observed trend of the decrease of adsorption capacity may be due to the protonation of donor sites. While in acidic solutions the uranyl ion UO_2^{2+} is practically the only complex-forming uranium species, with increasing pH uranium species bearing lower positive charge, neutral, or even negatively charged species (hydrolysis products) such as UO_2OH^+ , $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})^{5+}$, $\text{UO}_2(\text{OH})_2$, UO_2CO_3 , $(\text{UO}_2)_2\text{CO}_3(\text{OH})^{3-}$, etc are formed. However the relative concentration of these species depends on the pH and the concentration of uranyl solution, the higher pH favouring the bulky or high nuclearity species, i.e., $(\text{UO}_2)_3(\text{OH})^{5+}$. Thereby the hydrolysis of uranyl ions begins at a solution pH of 3.0 and between pH 3.0 and 4.0 the uranyl ion UO_2^{2+} its hydrolysis species UO_2OH^+ and $(\text{UO}_2)_2(\text{OH})_2^{2+}$ exist in different amounts. The formation of trinuclear uranyl species, $(\text{UO}_2)_3(\text{OH})^{5+}$ begins at pH 4.0, and becomes dominant at pH >4.5²⁶⁻²⁷. As it is presented the uranium adsorption increased with pH of the uranyl solution and reached the maximum at pH 4.5–5.5 interval. This pH range corresponds to the formation of $(\text{UO}_2)_3(\text{OH})^{5+}$, and thus the maximum loading of uranium can be attributed to the formation of trinuclear, $(\text{UO}_2)_3(\text{OH})^{5+}$ species.²⁸

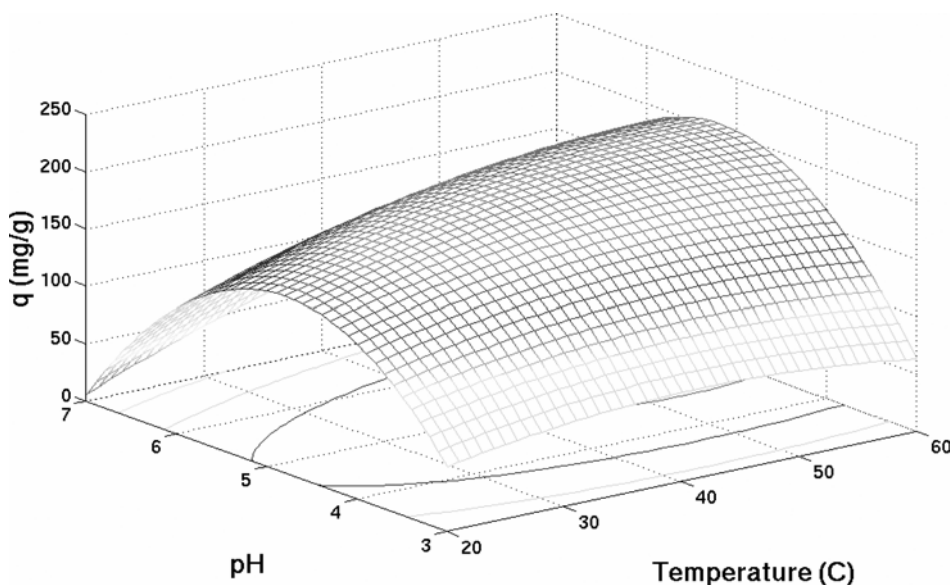


Figure 6 Interaction between pH (X_1) and temperature (X_2)

The uptake of uranium was found to increase as the initial metal ion concentration increased because the number of ions adsorbed from solutions of higher concentrations is more than that removed from less concentrated solutions (Figure 7). Maximum uranium uptake (265.44 mg/g) is observed at 250 mg l^{-1} initial uranium concentration and pH 5.

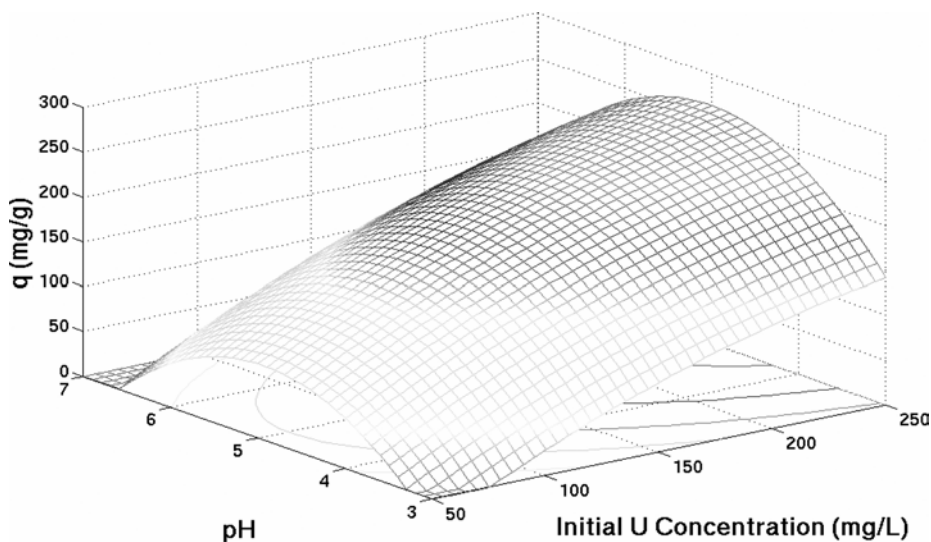


Figure 7 Interaction between pH (X_1) and initial uranium concentration (X_3)

Interaction between pH (X_1) and contact time (X_4) show uranium uptake as a function of both of them. Maximum uranium uptake (196.6 mg/g) is observed at 85 min contact time and pH 5 (Figure 8).

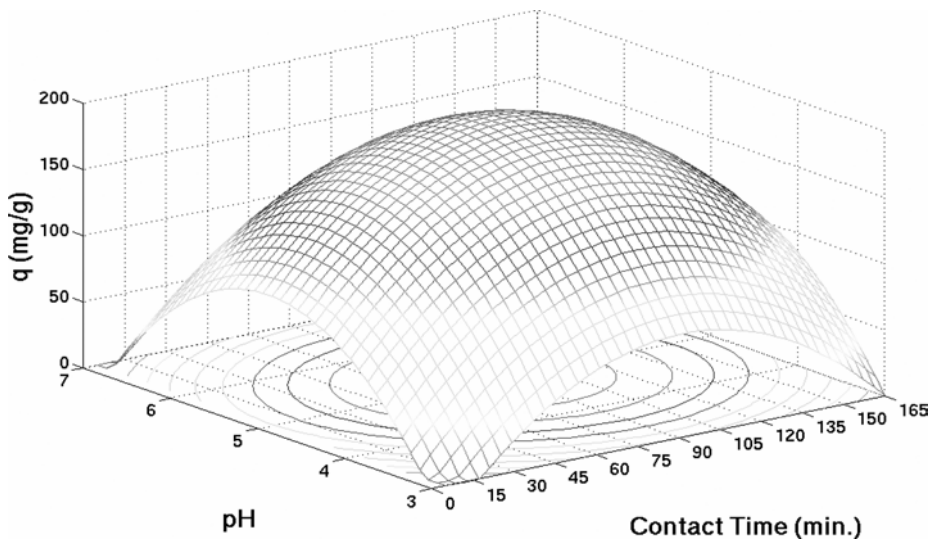


Figure 8 Interaction between pH (X_1) and contact time (X_4)

Combined effect of temperature (X_2) and initial uranium concentration (X_3) was analyzed and graph indicate that both of them increase the uranium uptake (Figure 9). Maximum uranium uptake (270 mg/g) is observed at 250 mg/L initial uranium concentration and temperature at 50°C.

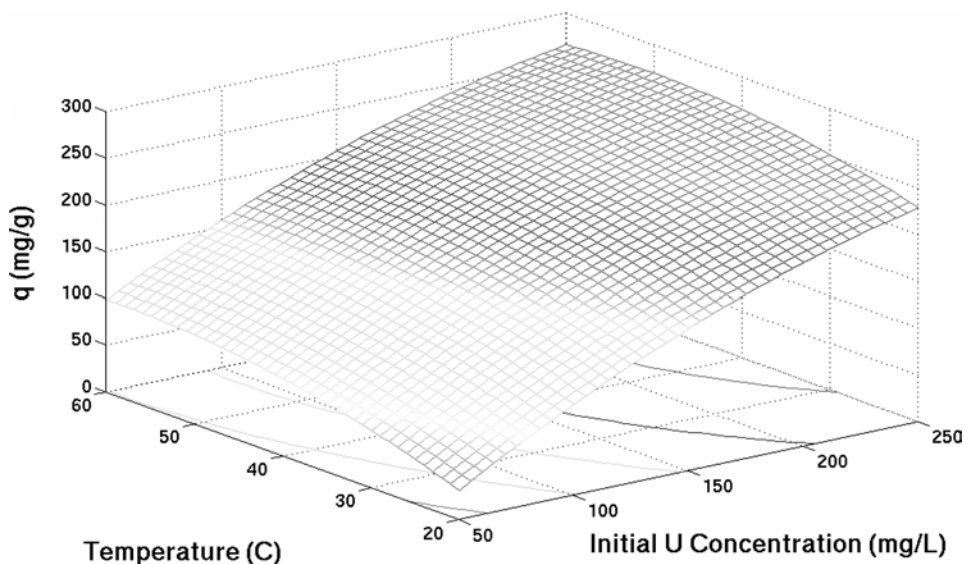


Figure 9 Interaction between temperature (X_2) and initial uranium concentration (X_3)

If the graph was plotted interaction between temperature and contact time, it seems that temperature and contact time changes on uranium sorption onto *PA-P. Orientalis* biosorbent (Figure 10). Maximum uranium uptake (205.2 mg/g) is observed at 50°C temperature and 250 mgL⁻¹ initial uranium concentration.

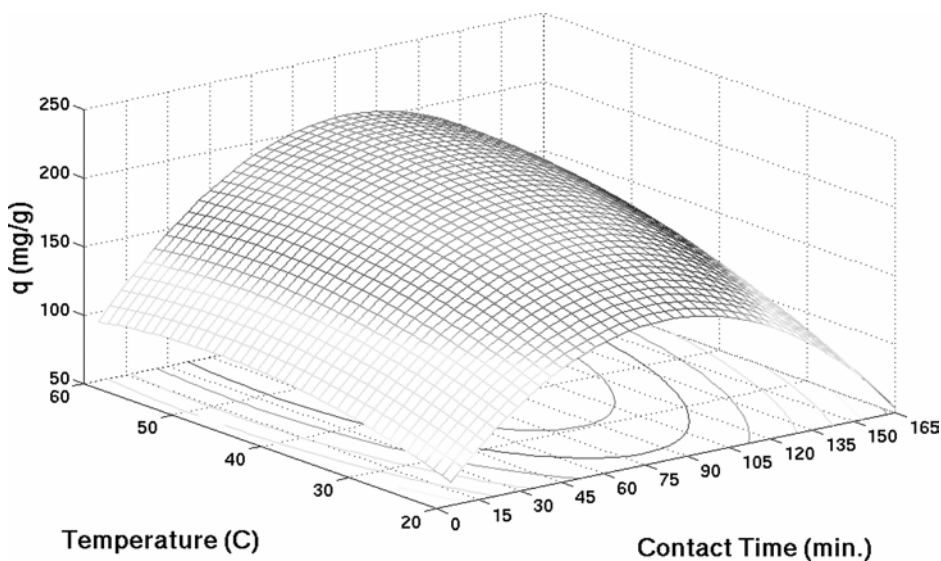


Figure 10 Interaction between temperature (X_2) and contact time (X_4)

Adsorption of uranium ions onto biosorbent increases when initial uranium concentration increases in all contact time intervals (Figure 11). Maximum uranium uptake (265.4 mg/g) is observed at 85 min. contact time and 250 mg/L initial uranium concentration.

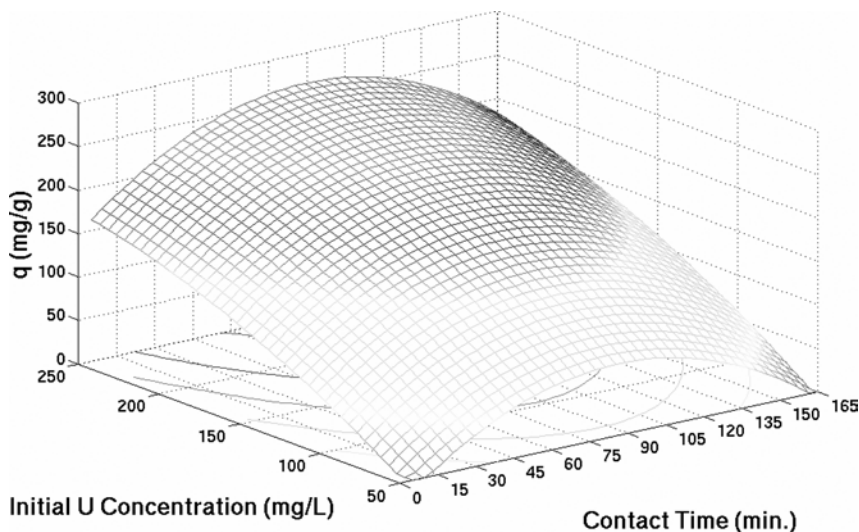


Figure 11 Interaction between initial uranium concentration (X_3) and contact time (X_4)

3.6 Sorption Isotherms

In order to understand the sorption capacity of the adsorbents, the equilibrium data were evaluated according to the Freundlich and Langmuir and D-R isotherms.

The Langmuir equation, which has been successfully applied to many sorptions, is given by:

$$\frac{C_e}{q_e} = \frac{1}{bn_m} + \frac{C_e}{n_m} \quad (6)$$

where, C_e is the equilibrium concentration (mg/L), q_e is the amount absorbed at equilibrium (mg/g), n_m and b are the Langmuir constants related to monolayer capacity and energy of sorption. Langmuir isotherm models the monolayer coverage of the sorption surface. This model assumes that sorption occurs at specific homogeneous sorption sites within the adsorbent and intermolecular forces decrease rapidly with the distance from the sorption surface. The Langmuir sorption model further based on the assumption that all sorption sites are energetically identical and sorption occurs on a structurally homogeneous adsorbent.²⁹

The Freundlich equation, which was applied for the sorption of uranium is given as:

$$q_e = KC_e^n \quad (7)$$

Eq. (7) can be rearranged to linear form:

$$\log q_e = \log K + n \log C_e \quad (8)$$

where q_e is the amount of solute adsorbed per mass unit adsorbent, C_e is the equilibrium concentration, K and n are the Freundlich constants characteristic of a particular sorption isotherm and can be evaluated from the intercept and slope of the linear plot of $\log q_e$ versus $\log C_e$.

The experimental data were fitted using the Dubinin–Radushkevich (D–R) equation in order to understand the sorption type.

The linearised D–R equation can be written as:

$$\ln X = \ln X_m - K\varepsilon^2 \quad (9)$$

where ε is Polanyi potential and is equal to,

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (10)$$

X is the amount of metal adsorbed per unit mass of adsorbent, X_m is the theoretical sorption capacity, C_e is the equilibrium concentration of metal, K is the constant related to sorption energy, R is the universal gas constant and T is the temperature in Kelvin.

D–R isotherm constants K and X_m were evaluated from the slope and intercept of the plot $\ln X$ versus ε^2 , respectively. The mean free energy of sorption (E_{DR}) is the free energy change when one mole of a solute is transferred to the surface of the adsorbent from infinity in the solution, and that has been calculated by

$$E_{DR} = (2K)^{1/2} \quad (11)$$

The magnitude of E_{DR} (kJ mol^{-1}) is useful for estimating the type of sorption reaction, and if it ranged between 8.0 and 16.0 the sorption should be taken place by ion exchange reaction.

Sorption isotherm investigations were made under the conditions as; pH 5, 50°C temperature, 85 min contact time, and 250 mg l^{-1} initial uranium concentrations. q values of the biosorption experiments were obtained by the evaluation of Eq.5.

The D–R parameters and mean free energies evaluated are shown in Table 5. In the present case, the E_{DR} value obtained (11.07 kJ mol^{-1}), which indicates ion exchange mechanism. The corresponding Freundlich, Langmuir and D–R parameters along with correlation coefficients are reported in Table 5. The correlation coefficients indicate that the Langmuir model fits better than the Freundlich model for the uranium sorption onto *PA-P. Orientalis* biosorbent (correlation coefficient is 0.99).

3.7 Thermodynamic Results

The thermodynamic studies were carried out under the conditions as; pH 6, 85 min contact time and 150 mg l^{-1} initial uranium concentrations. K_d values of the biosorption experiments were obtained by the evaluation of Eq. 5.

Sorption enthalpy was measured using the method based on the Van't Hoff plot. The values of ΔH° and ΔS° are calculated from the slopes and intercepts of the linear variation of $\ln K_d$ with reciprocal temperature, $1/T$, using the relation:

Table 5 Sorption isotherm constants for the sorption of uranium onto *PA-P. Orientalis* biosorbent

<i>Freundlich</i>			
R ²	n	K	
0.97	0.47	45.7	

<i>Langmuir</i>			
R ²	n _m (mg/g)	b (l/mg)	
0.99	564.7	0.02	

<i>Dubinin-Radushkevich</i>			
R ²	K (mol ² kJ ⁻²)	X _m (mol/g)	E _{DR} (kJ/mol)
0.98	0.004	0.009	11.07

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{12}$$

where ΔH^0 and ΔS^0 are the standard enthalpy and entropy changes of sorption, respectively (Table 6). Positive ΔH^0 values for uranium sorption onto biosorbent indicate that sorption of uranium is endothermic.

The free energy of specific sorption ΔG^0 is calculated using the equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{13}$$

The calculated negative values of ΔG^0 for all cases indicate that the sorption process of each is spontaneous and preferentially driven toward the products. Temperature change has significant effect on ΔG^0 values for *PA-P. Orientalis* biosorbent. Temperature effect on uranium sorption onto biosorbent was discussed previously in experimental design results and we found that temperature had positive effect on sorption. Thermodynamic results are in same sense and prove that conclusion.

Table 6 Thermodynamic parameters for cerium sorption onto *PA-P. Orientalis*

	ΔH^0	ΔS^0	ΔG^0 (kJ/mol)			
	(kJ/mol)	(J/molK)	293K	303K	313K	323K
<i>P. Orientalis</i>	24.90	144.01	-17.30	-18.74	-20.18	-21.62

3.8 Kinetics of Adsorption

The kinetic studies were carried out under the conditions as; pH 5, 40°C temperature and 150 mg l⁻¹ initial uranium concentrations. q values of the biosorption experiments were obtained by the evaluation of Eq. 5.

In order to explain the mechanism of adsorption processes such as mass transfer and chemical reaction, the first and second-order equations are used to test the experimental data.

Two kinetic models were used to analyse uranium adsorption kinetics, namely, pseudo-first-order and pseudo second-order.

The pseudo-first-order model is presented by the following equation:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (14)$$

The plot of $\ln(q_e - q_t)$ against t provides a linear relationship from which k_1 , constant of pseudo-first-order adsorption (min^{-1}) and q_e , adsorption capacity at equilibrium (mg/g) are determined from the slope and intercept of the plot respectively, given that q_t is the adsorption capacity at time t (mg/g).

The pseudo-second-order model is presented by the following equation:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (15)$$

The plot of t/q_t against t provides a linear relationship from which k_2 , rate constant of pseudo-second-order adsorption ($\text{g}/(\text{mg min})$) and q_e , adsorption capacity at equilibrium (mg/g) are determined from the slope and intercept of the plot, respectively.

The validity of both kinetic models is checked and depicted in Figures 12 and 13 by each linear plot of $\ln(q_e - q_t)$ against t and t/q_t against t , respectively. Based on the correlation coefficients values show a good agreement of dynamical data with first-order kinetic model. The results of the kinetic parameters for uranium biosorption are given in Table 7. The first-order kinetic process has been used for reversible reaction i.e. ion exchange reaction with an equilibrium being established between liquid and solid phases. As discussed in previously E_{DR} value has shown that the type of biosorption reaction is ion exchange in this work. Therefore, kinetic results are in a good agreement with the D-R isotherm values. Whereas, the second-order kinetic model assumes that the rate-limiting step may be chemical adsorption³⁰.

Table 7 Grams of Solute Sorbed per gram of Sorbent at Equilibrium (q_e), Pseudo First and Second Order Rate Constant (k_i) and Correlation Coefficient Values

	q_e (mg/g)	k_i	R^2
<i>Pseudo first order</i>	134.52339	0.01964	0.99
<i>Pseudo second order</i>	224.00397	0.000352	0.994

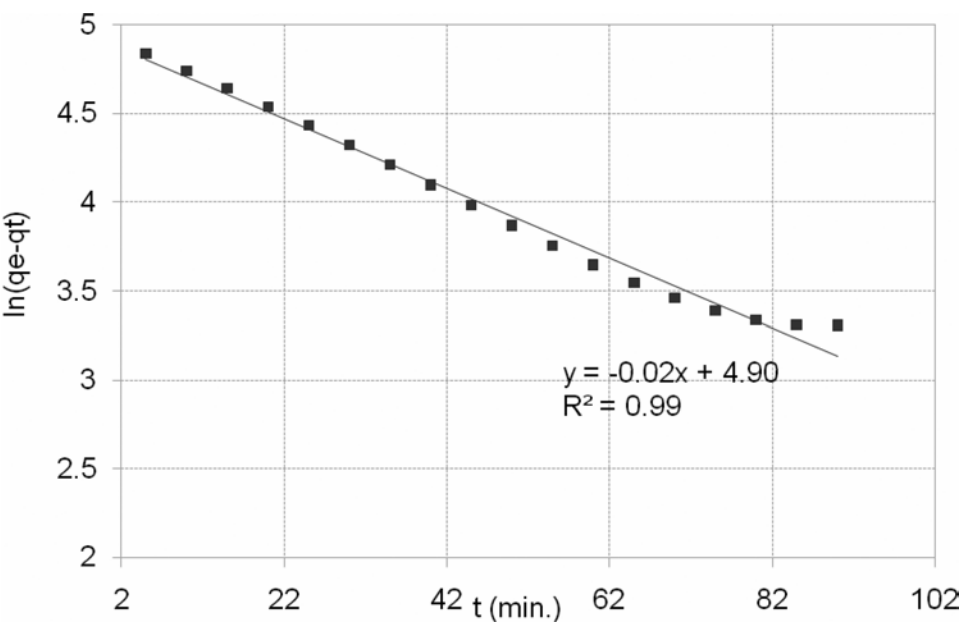


Figure 12 Pseudo-first-order kinetics plot for the adsorption of uranium onto PA-P. *Orientalis*

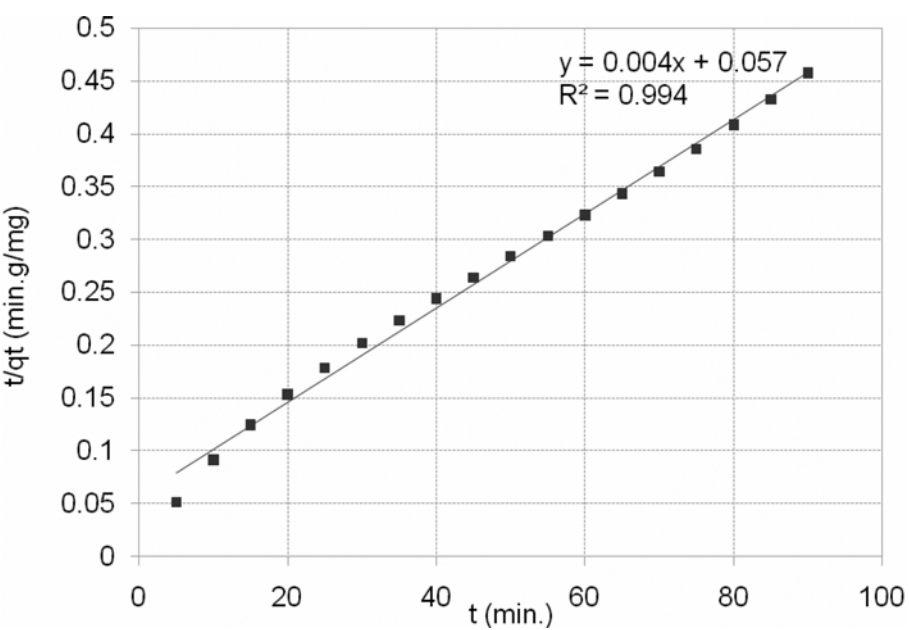


Figure 13 Pseudo-second-order kinetics plot for the adsorption of uranium onto PA-P. *Orientalis*

4 CONCLUSION

In this study, the biosorption of uranium which is one of the most important element because of its toxicity and radioactivity was investigated. Uranium adsorption from aqueous solution by phosphoric acid (PA) modified *P. Orientalis* leaf powder was demonstrated in a batch system as a function of initial pH, temperature, initial concentration of adsorbate and contact time. Central Composite Design was used in the experiments. Optimum uranium uptake was found as 270.33 mg/g at the following conditions; pH 5, temperature 50°C, initial uranium concentration 250 mg l⁻¹, contact time 85 min, by evaluation of eq. 4. The results show that modified *P. Orientalis* leaf powder has high biosorption capacity. The temperature and initial concentration of uranium of the aqueous phase affected the uptake of the ions, but according to the results pH is non significant on biosorption of metal ions. The Langmuir, Freundlich and D-R adsorption models were used and their constants were calculated for mathematical description of the biosorption of the uranium ions onto biosorbent. Cation sorption data were interpreted in terms of Langmuir equation which assumes monolayer adsorption due to its correlation coefficient was found as 0.99. In D-R model, E_{DR} value has shown that the type of biosorption reaction is ion exchange in this work. Consequently, monolayer capacity according to Langmuir isotherm was found as 564.73 mg g⁻¹. Thermodynamic parameters such as standard enthalpy (ΔH°), entropy (ΔS°) and free energy (ΔG°) were calculated and the results indicated that biosorption was endothermic. According to kinetic results, the biosorption of uranium is best described by the first-order equation. As the results show that, modified leaf powder of *P. Orientalis* has great biosorption capacity and usage of this method can be suggested as an alternative and low-cost method for uranium recovery from waste solutions.

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DEVELOPMENT AND VALIDATION OF THE RADIOCHEMICAL DETERMINATION OF ^{99}Tc IN ENVIRONMENTAL SAMPLES

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1 INTRODUCTION

A recent study carried out by the Health Protection Agency's Centre for Radiation, Chemical and Environmental Hazards (HPA-CRCE), investigated the transfer of ^{99}Tc through the terrestrial environment from seaweed to food crops and animal products.¹

To quantify the transfer of technetium, it was necessary to measure radioactivity concentrations in crops of less than 1 Bq kg^{-1} . To achieve this limit of detection requires the use of large samples (approximately 1 kg fresh mass). Many published methods including the one being used in CRCE's Chilton laboratories², make use of small sample sizes, with technetium-99m ($^{99\text{m}}\text{Tc}$) being used as a yield tracer. The half life of $^{99\text{m}}\text{Tc}$ is 6 hours and so the published methods need to be completed up to the point at which the yield (also known as the chemical recovery) is determined, before the tracer has decayed. This normally means a time limit of less than 48 hours, depending on the amount of tracer activity that has been added. These methods are adequate for routine surveillance monitoring of ^{99}Tc in the environment because the limits of detection that can be achieved on small samples are low enough to demonstrate that the resultant radiation doses are small – a consequence of the low dose coefficient for ingestion for this radionuclide.³ However, they are not sufficiently sensitive to achieve the limit of detection required to investigate the transfer of ^{99}Tc through the environment.

Initial investigations showed that the method being used in the Chilton laboratory gave very low recoveries when used on the larger sized samples required to achieve limits of detection below 1 Bq kg^{-1} . Dry ashing of the sample was undertaken over a few hours because of the time limit imposed by the tracer and it was apparent that for larger samples visible carbonaceous material was present after the ashing stage. Subsequently, these analyses gave very low technetium recoveries. If samples are dry ashed before addition of the tracer then a longer more complete ashing would be possible, although it is known that in some circumstances technetium can be volatile at ashing temperatures. Uchida and Tagami^{4,5} have published several papers showing that technetium in environmental samples is not volatile provided that the sample has not been subjected to recent contamination. The effect of longer ashing and sample sizes on the limits of detection achievable has therefore been investigated. Based on this investigation a revised method has been developed appropriate for large environmental samples.

To validate the revised method the HPA and Westlakes Scientific Consulting organised an interlaboratory intercomparison exercise under the auspices of the UK Analysts Informal Working Group using seaweed and sand samples. The exercise and its results are described.

2 DEVELOPMENT OF THE ANALYTICAL METHOD

The established method used for the determination of ⁹⁹Tc was based on one published by Holm and Rioseco.² Briefly, the sample is ashed for 1 hr at 600°C in the presence of hydrochloric acid to minimise losses of technetium. After dissolving in 3M sulphuric acid, the technetium is oxidised to the heptavalent state with potassium persulphate and hydrogen peroxide and extracted with tri-n-butyl phosphate. A source is prepared by electroplating onto stainless steel discs. Technetium-99m is added at the start of the ashing process so that the chemical recovery of the technetium can be estimated by counting the ^{99m}Tc by gamma-ray spectrometry. After the ^{99m}Tc has decayed, the ⁹⁹Tc is measured using a gas proportional counter.

Technetium-99m is particularly useful in the development of analytical methods because the amounts of activity used are relatively high and the technetium can be “followed” qualitatively through the method using simple hand – held instruments. A loss of technetium at any particular stage can then be detected quickly, without the need to take the method through to completion.

2.1 The Effect of Increases in Sample Size on Method Sensitivity

An increase in the amount of sample that can be analysed will improve the overall sensitivity provided that the chemical recovery is unaffected. Differing sample masses of dried and ground potato and seaweed were taken from samples collected as part of the HPA study¹ and the ^{99m}Tc tracer was added. The samples were slurried with hydrochloric acid, dried on a hotplate and ashed for 40 minutes at 600 C and then a further 20 minutes with ventilation to promote the ashing process. The ashed sample was then treated with dilute sulphuric acid and potassium persulphate to extract the technetium.

After the ashing step there was clear visual evidence of partially ashed organic material, especially in the 100 g aliquot of potato. Ashing for a further hour still did not completely destroy the remaining organic matter. The analytical results from these experiments are given in Table 1, and illustrate the effect of incomplete ashing. In the case of the largest sample of potato, the chemical recovery was only 25%, and ^{99m}Tc was detectable in the solid residue. The effect was less marked in the smaller sample sizes with significantly less tracer left in the residues. The data for ⁹⁹Tc in seaweed suggested that in most cases equilibrium with the ⁹⁹Tc tracer had been reasonably established up to sample sizes of about 30g. Overall, the conclusions were that the use of larger sample sizes would give little improvement in overall sensitivity because of the reduction in chemical recovery, and that this reduction resulted from incomplete ashing of the sample material. Even though larger samples were not considered for seaweed because of the difficulty of sample digestion due to the presence of large amounts of calcium from shells in the sample, similar results would be expected as seen for large sample sizes of potato. The next step was therefore to evaluate the potential for changes in the ashing conditions.

2.2 The Effect of Acid Pre-treatment and Ashing Times on Method Sensitivity

The effect of the pre-treatment with hydrochloric acid was investigated using 50 g portions of seaweed. Samples pre treated with acid and ashed for 2 hours at 600°C gave low and variable recoveries (1-8%) and the measured ^{99}Tc concentration was lower than the values in Table 1. However, those ashed overnight at 500°C with no pre-treatment gave recoveries of about 60% and the measured ^{99}Tc concentration was in agreement with those in Table 1. This led to the conclusion that pre-treatment with acid did not improve the ashing process and could lead to loss of technetium during the ashing.

Table 1 Results of the analysis of different sample sizes of potato and seaweed

Sample	Sample mass (g)	Chemical yield based on $^{99\text{m}}\text{Tc}$ (%)	^{99}Tc activity (Bq kg^{-1})
Potato	20.16	70.5	ND
Potato	20.47	64.3	ND
Potato	40.44	60.1	ND
Potato	39.30	81.5	ND
Potato	101.2	25.2	ND
Seaweed A	10.0	67.7	237 ± 13
Seaweed A	10.3	61.2	243 ± 14
Seaweed A	32.3	58.1	205 ± 9
Seaweed A	29.7	43.1	240 ± 11

ND = Not detected. Activity concentrations for potato samples were below the limits of detection which were typically $<1 \text{ Bq kg}^{-1}$. This is in line with other samples of potatoes collected and analysed from the same area.

To investigate the effect of ashing time, 50 g samples of a second seaweed sample were ashed overnight: for one aliquot the $^{99\text{m}}\text{Tc}$ was added before ashing and for the others the tracer was added to the ashed material. The results are given in Table 2. As can be seen, there was no significant difference in chemical recovery or the measured ^{99}Tc concentration for all three aliquots. The effect of longer ashing times were investigated by ashing three aliquots of the original seaweed sample for one week before tracer addition and analysis.

These results give strong evidence that ^{99}Tc in environmental samples is not volatile at 500°C. This conclusion is supported by the work of Uchida and Tagami^{4,5}, who concluded that technetium in environmental soil samples, is not volatile unless the soil had been recently contaminated.

Table 2 Analytical results for seaweed ashed with and without tracer

Sample	Ashing time (h)	$^{99\text{m}}\text{Tc}$ added	Sample mass (g)	Chemical yield based on $^{99\text{m}}\text{Tc}$ (%)	^{99}Tc activity (Bq kg^{-1})
Seaweed B	16	Before ashing	50.1	80.7	287 ± 21
Seaweed B	16	After ashing	50.9	68.1	302 ± 23
Seaweed B	16	After ashing	49.8	89.7	270 ± 19
Seaweed A	168	After ashing	19.8	58.9	215 ± 14
Seaweed A	168	After ashing	29.7	80.7	219 ± 13
Seaweed A	168	After ashing	40.4	80.0	238 ± 14

3 INTERCOMPARISON EXERCISE

At the time of the method development, the authors could not find a solid reference material or intercomparison sample containing ^{99}Tc . The UK Analysts Informal Working Group therefore decided to organise an informal intercomparison exercise. Two samples were used, seaweed A used earlier in this study and a sand sample that was used as an internal quality control sample in the Westlakes laboratory. These samples were not prepared with the rigour used for a certified reference material to guarantee homogeneity between different aliquots. Nevertheless both laboratories had sufficient measurements to satisfy themselves that the sample was sufficiently homogeneous at the normal sample size taken for analysis.

Samples were sent out in early 2008 and results were collated late in that year. Eight UK laboratories participated in the exercise although not all laboratories reported results for both materials. The results for the seaweed and sand samples are shown in Figures 1 and 2, respectively. The exercise mean and standard deviations were calculated firstly by calculating a mean for each laboratory then performing a Grubbs' test⁶ on them. If an outlier was identified this was removed from the data set before calculating the mean and standard deviation of the laboratory means.

More recently the authors have become aware that the soil sample in the MAPEP scheme⁷ does include analysis for ^{99}Tc , although for some rounds of the exercise no ^{99}Tc is added. This will be used as part of an ongoing validation of the method.

3.1 Seaweed Sample Results

The Grubbs test indicates that there are no outlier values in the dataset for seaweed. The mean concentration was 215 Bq kg^{-1} with a standard deviation of 30 Bq kg^{-1} . With the exception of one result from laboratory 7, all reported results were within two standard deviations of the mean. Deviations from the mean of laboratories 7 and 8 were -23% and +24%, respectively; all other laboratories were within $\pm 10\%$ of the mean. These results support the hypothesis that the material was homogeneous.

3.2 Sand Sample Results

Grubbs test for the sand sample identifies the mean result from Laboratory 6 as an outlier and so the results for this laboratory have been excluded from the mean and standard deviation calculations. The mean concentration was 9.5 Bq kg^{-1} with a standard deviation of 1.5 Bq kg^{-1} . This compares favourably with the long term average from the Westlakes laboratory of $10 \pm 1.5 \text{ Bq kg}^{-1}$. It is not surprising that there was a greater relative variability in the sand results when compared to the seaweed, because the technetium concentration in the sand was over an order of magnitude lower than that in the seaweed. With the exception of the excluded result and taking into account the larger relative uncertainties reported, the mean values for all laboratories are not significantly different from the exercise mean. Laboratory 7 has reported much lower uncertainty than the other laboratory and these uncertainties appear to be inconsistent with the spread of their results.

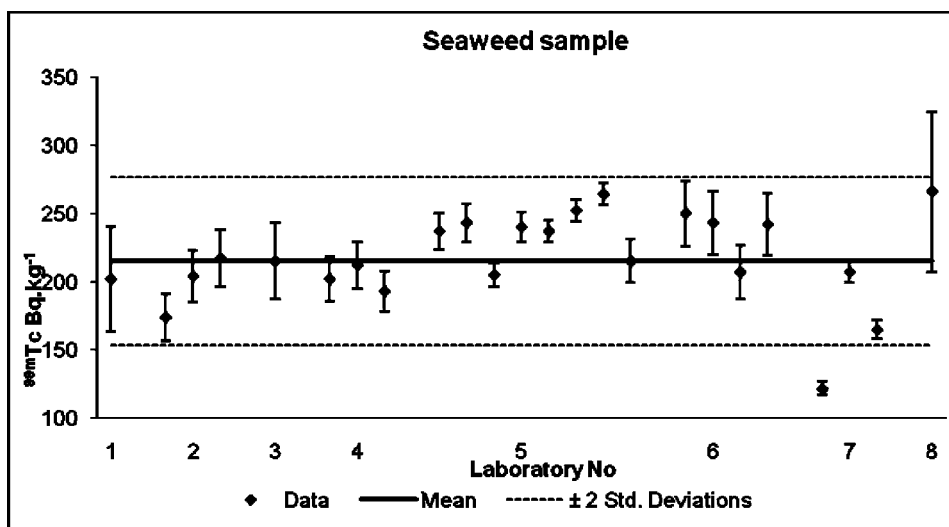


Figure 1 Results of Seaweed intercomparison exercise

4 CONCLUSIONS

The pre-treatment of samples with hydrochloric acid prior to ashing was shown to lead to loss of technetium during ashing. This strongly suggests that prolonged heating of samples containing technetium under reducing conditions aids volatility and should be avoided.

The method published by Holm and Rioseco² gives low and variable recoveries on large environmental samples due to incomplete ashing. It has been shown that the method can be modified by furnace ashing samples at 500°C for up to one week prior to the addition of the ^{99m}Tc yield tracer. Following the addition of the tracer to the ashed sample, the analysis follows the published procedure. Modifying the analytical scheme in this way allows the successful analysis of samples up to 100g dry mass, which is equivalent to 1kg or more fresh mass vegetation.

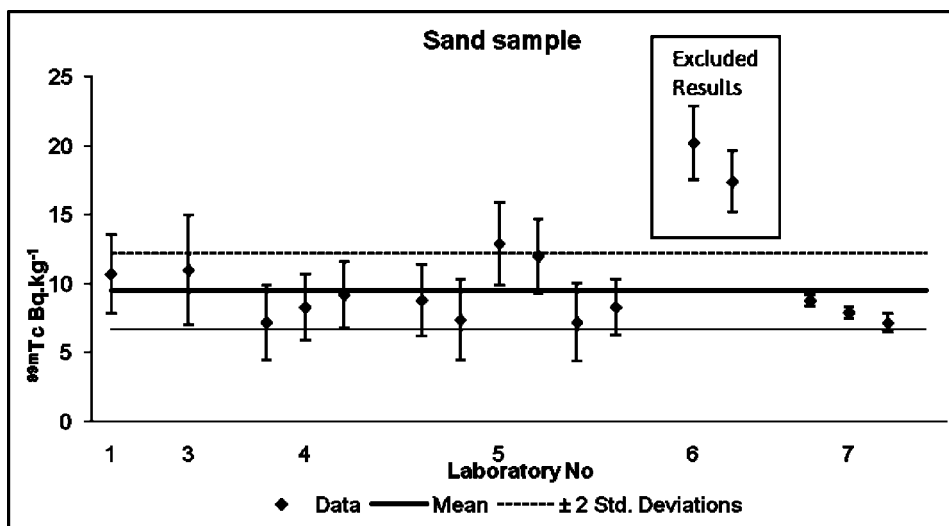


Figure 2 Results of sand intercomparison exercise

As the tracer is added after the ashing process several batches of samples can be ashed prior to starting the rest of the procedure. As the ^{99m}Tc tracer is short lived this can offer improvements in sample throughput and more efficient use of the tracer.

The results of the informal intercomparison exercise support the hypothesis that the samples were homogeneous at the mass required for analysis. With the exception of the sand result from laboratory six, all results were in reasonable agreement with the mean.

Informal exercises like this are very useful where a more formal exercise is not available for particular matrices or isotopes. While they can not be considered as rigorous as formal accredited schemes, they can be set up rapidly in response to a perceived need and give reasonable confirmation that laboratories results are in agreement with others working in the field.

Acknowledgements

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RADIOACTIVITY IN THE IRISH SEA

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1 INTRODUCTION

Authorised discharges of radionuclides into the eastern Irish Sea from the Sellafield site (formerly Windscale) have been underway since 1951.¹ Such a practice over the last six decades has resulted in hundreds of peer-reviewed publications being produced in the scientific literature. Topics that have been covered are numerous and include: *physical transport processes* – water body movement, sedimentation, suspended loads, sea to land transfer, geochemical associations, saltmarsh accretion and erosion; *radiochemistry* – analysis of radionuclides in environmental media, determination of oxidation states in the water column, surface sediments and bulk sediments; *dosimetry* – to critical groups and relatively recently to biota; *radionuclide behaviour in biota* - biological uptake, biokinetic modelling, exposure routes; *radionuclide inventory budgets*.

To cover all subjects to a reasonable degree would result in the production of a book rather than a manuscript, therefore some focus has been given here to provide an up to date overview of the current distribution of discharged radionuclides to the Irish Sea.

2 IRISH SEA – PHYSICAL ATTRIBUTES

The Irish Sea is a semi-enclosed body of water with Atlantic water entering from the south at St George's Channel and leaving from the North Channel. The volume of the Irish Sea is 2,400 km³ of which 80 % lies to the west of the Isle of Man. Its surface area is 103,600 km² (209 km long and up to 140 km wide). The deepest point of the Irish Sea is at Beauforts Dyke in the North Channel at 315 m. The western Irish Sea is a relatively deep channel maintaining depths greater than 100 m with depths typically less than 40 m being present closer to the Irish coast. The eastern Irish Sea however, has much gentler shelving less than 50 m depth. The circulation of the waters within the Irish Sea is typically driven by the tides (up to 10 m in the Solway Firth) and winds.²

3 SELLAFIELD LTD HISTORICAL DISCHARGES

At present there are over 30 radionuclides regularly monitored within the liquid effluent prior to discharge to the Irish Sea, 16 of which have authorised limits. These 16

radionuclides have such limits due to the quantities discharged and their role when assessing the radiological impacts of discharges on critical groups.³ Not all of the radionuclides have discharge data recorded from 1951. Details of discharges have been presented elsewhere^{1,3-8}, but a brief overview will be given here. Discharges from Sellafield have been used in many scientific studies. One field they have been used in is in attempting to provide a chronology to natural processes within the Irish Sea⁹⁻¹⁴, in particular the timing of mixing of waters and in what direction they go.¹⁵ To this end the conservative radionuclides ¹³⁴Cs and ¹³⁷Cs have been used for several decades with ⁹⁹Tc being used in a similar vein since the mid 1990's.¹⁶⁻¹⁸

Because of the history of the reprocessing plant, there have been maximum annual discharge rates of radionuclides at different times. In the mid 1970's maximum annual discharges were recorded for ¹³⁷Cs, Pu-alpha and ²⁴¹Pu whereas for ¹⁰⁶Ru peak annual discharges were in the late 1950's¹, for ⁹⁹Tc in 1995¹⁷ and for ¹⁴C in 2003.⁴ Such information is vital when extrapolating measurements from field samples to discharge trends. In particular, great care has to be practiced when trying to determine a chronology of sediment deposition in bed sediments and saltmarsh sediments when using such radionuclides.^{11,19-21} The discharge trend is a simplified trend and is an obvious marker to be used. Mechanisms between radionuclide discharge and deposition, however, need to be understood to interpret observed depth profiles with some confidence.

4 NUCLIDES OF MAJOR INTEREST

For the remainder of the consideration of radioactivity in the Irish Sea, it is necessary to streamline the number of radionuclides to be considered. Due to the quantities discharged, their radiological importance and the amount of environmental data available, the four radionuclides to be considered further are ⁹⁹Tc, ¹³⁷Cs, ^{239,240}Pu and ²⁴¹Am.

Details of the quantities discharged to date are given in Table 1. From the list it is evident larger activities of ¹³⁷Cs and ²⁴¹Pu have been discharged compared to the others listed. This is partly due to them being relatively short lived (half lives of 30 and 14 years respectively) and being beta/gamma emitters. The alpha-emitting radionuclides in Table 1 have relatively lower inventory values. Also included in Table 1 is the decay corrected values of these discharged inventories as, due to some of the half lives involved, the discharge of material over 50 years will result in a significant quantity of material having decayed away. To this end, it is evident that those radionuclides whose half life is much greater than 50 years there is no change in the decay corrected values e.g. ⁹⁹Tc ($t_{1/2}$ 211,000 years, ²³⁹Pu $t_{1/2}$ 24,110 years). Those that have shorter half lives, ¹³⁷Cs and ²⁴¹Pu, there have been a significant drop in the decay corrected inventory values.

In order to keep some perspective on these values, the abundance of naturally occurring radionuclides in the Irish Sea, for comparison, is made. There is typically 11 Bq L⁻¹ of ⁴⁰K and 0.033 Bq L⁻¹ of ²³⁸U in marine waters.²² From volumes presented earlier this results in a natural inventory of around 26 TBq of ⁴⁰K and 0.008 TBq of ²³⁸U present in the Irish Sea.

5 RADIONUCLIDE BEHAVIOUR OF Tc

Many studies have been performed on the behaviour of ⁹⁹Tc in the marine environment.^{16-18,23,24} It has been demonstrated that Tc is discharged in a dissolved form as the

Table 1 Liquid discharge inventories from Sellafield from 1951 to 2008 (TBq)^{1, 3-8}

Radionuclide	Cumulative Discharge	Decay-corrected Cumulative Discharge
⁹⁹ Tc	1 700	1 700
¹³⁷ Cs	41 350	20 100
²³⁸ Pu	126	98
^{239,240} Pu	612	612
²⁴¹ Am	544	514
²⁴¹ Pu	21 600	4 490

pertechnetate ion, TcO₄⁻, representing the +7 oxidation state of technetium. This chemical species of technetium is abundant in oxic conditions which predominate in the water column of the Irish Sea and in its surface sediments. However, once deposited with sedimentary material, if this material begins to be buried and the Tc is moved from the surface sediments, then anoxic conditions may occur where the abundant chemical species of Tc is TcO₂, representing the +4 oxidation states. This form of Tc is less mobile and binds more strongly to its surroundings. The recommended partition coefficient (K_d) of Tc by the IAEA is 100.²⁵ These are taken to be generic values. If more relevant data is available for the area of interest then those data should be taken. In this instance studies in the Irish Sea have determined values of 1900.¹⁸ Tc is considered as a ‘conservative’ radionuclide in that it is easily dispersed and diluted on discharge as it stays within the water column relatively easily. Tc-99 has a radioactive half-life, t_{1/2}, of 211,000 years.

6 RADIONUCLIDE BEHAVIOUR OF Cs

Caesium is a ‘conservative’ element similar to Tc. Its environmental chemistry is straightforward in that it exists in the marine environment as Cs⁺. Measured and recommended K_d values for Cs are in good agreement – 10³ to 10⁴ measured²⁶ and 3.5 x 10³ recommended²⁵. These values are higher than for Tc which would indicate that Tc is a better water movement tracer than Cs. Cs-137 has a t_{1/2} of 30.1 years.

7 RADIONUCLIDE BEHAVIOUR OF Pu

Plutonium in the marine environment behaves as a ‘non-conservative’ or ‘particle reactive’ radioelement. Once discharged it rapidly associates itself with particulate material and is quickly deposited onto the seabed close to the discharge point.²⁷ The environmental chemistry of Pu is very complex as it can exist under four different oxidation states in natural conditions. In the marine environment, under oxic conditions in the water column, Pu can possess +5 or +6 oxidation state although the predominant species in the water column is +5.²⁸

Once deposited onto particulate material Pu exists in either the +3 or +4 oxidation state. The predominant species on surface sediment is +4.²⁷ Again the chemistry of Pu can change under varying environmental conditions. Measured and recommended K_d values for Pu are in good agreement – 10⁴ to 10⁶ measured^{29,30} and 10⁵ recommended.²⁵ The 10⁵ value appears to be a compromise between the 10⁴ value with the more conservative

species of Pu (+5, +6) predominant in the marine water column and the more particle reactive species (+3, +4) predominant in bed sediment. Pu-239 has a $t_{1/2}$ of 24,110 years.

8 RADIONUCLIDE BEHAVIOUR OF Am

Less is known about the behaviour of Am in the marine environment but it is similar to Pu in that Am is very particle reactive. It has a relatively simple environmental chemistry compared to Pu as Am exists as a single oxidation state (+3) in the environment.²⁸ Measured and recommended K_d values for Am are in close agreement – 10^6 from both sources^{25,30}. Am-241 has a $t_{1/2}$ of 432 years.

Further attention on the presence of ^{241}Am in the environment is required due to the discharges of the beta-emitter ^{241}Pu . Pu-241 has a $t_{1/2}$ of 14 years. On decay, ^{241}Am is produced as a decay product of ^{241}Pu . From Table 1 it is evident that ^{241}Pu discharges were up to two orders of magnitude greater than ^{241}Am . Calculations have been made considering the cumulative decay corrected discharge of ^{241}Am , and the cumulative decay corrected discharge of ^{241}Am produced from the discharge and decay of ^{241}Pu . The inventory trends are shown in Figure 1 along with the total ^{241}Am cumulative inventory (black triangles). The ^{241}Am produced from the decay of ^{241}Pu is a theoretical maximum value as the calculations have assumed that no ^{241}Pu has left the Irish Sea region. From Figure 1, it can be seen that in the early 2000's the environmental inventory of ^{241}Am was such that more ^{241}Am from the discharge and decay of ^{241}Pu was present than the ^{241}Am discharged and since then is continuing to do so as long as the current discharge trends are maintained. A result of this is that the total ^{241}Am environmental inventory is still gradually increasing (black triangles). This increasing trend is a factor to be considered when Am and Pu data in sediment (sea bed or saltmarsh) depth profiles are available. Care needs to be taken in applying the appropriate Am/Pu ratio for chronological purposes.

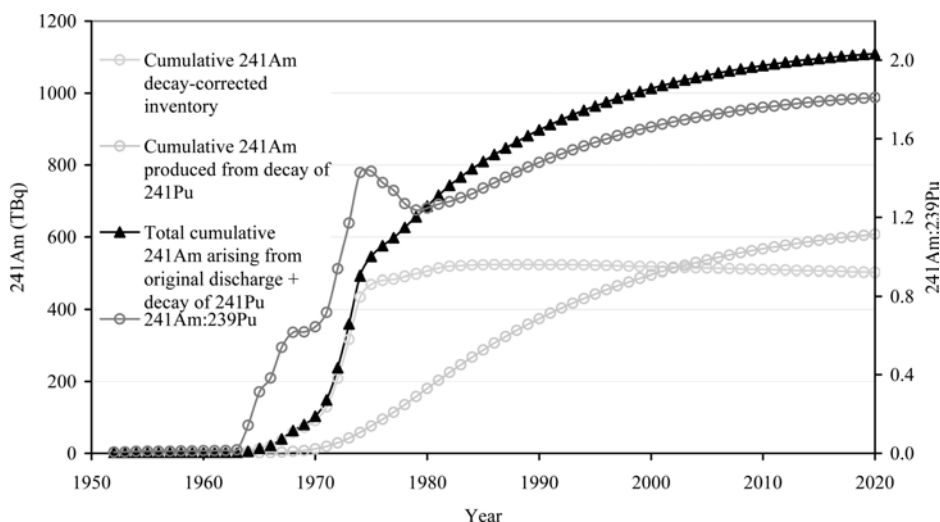


Figure 1 Inventory of ^{241}Am in the Irish Sea environment

9 WHERE ARE THESE RADIONUCLIDES NOW?

The current radionuclide environmental budget of ^{99}Tc , ^{137}Cs , $^{239,240}\text{Pu}$ and ^{241}Am discharged from the Sellafield site since 1951 has now been presented. However, where do these radionuclides reside now? Generally, as expected from the descriptions given in Sections 7 and 8 above, the conservative radionuclides, ^{99}Tc and ^{137}Cs , have followed the prevailing currents of the Irish Sea and have been effectively flushed from the Irish Sea environment, along the western coast of Scotland and into the North Sea and beyond.¹⁵ This route of dispersion was first presented for ^{137}Cs and is consistent with any conservative radionuclide discharged. Although ^{99}Tc and ^{137}Cs are conservative there is still a presence of these radionuclides in the sediments of the Irish Sea. It is estimated that there is approximately 37 TBq of ^{99}Tc and <900 TBq of ^{137}Cs associated with the sediments of the Irish Sea^{31, 32}.

The particle-reactive radionuclides, $^{239,240}\text{Pu}$ and ^{241}Am , are less mobile than the conservative radionuclides and are associated with the finer sediments of the Irish Sea particularly the finer sediments present within the eastern Irish Sea.^{9, 10, 29, 33-35} The surface sediments of the Irish Sea are varied in nature. A 'column' of gravel is present down the middle of the Irish Sea from the Scottish Solway coast in the north, through the Isle of Man to the north Wales coast in the vicinity of Anglesey and Bangor. To the west of the gravel lies a channel of fine sediment with a large mud-patch lying between the Isle of Man and the Irish coast.³⁶ This mud-patch area is a site a commercial fishing for the Dublin Bay Prawn (*Nephrops norvegicus*) which thrive on mud to live and breed. To the east of the gravel, in the shallower side of the Irish Sea, sands and silty sands predominate with the exception of a mud-patch, much smaller than the one in the western Irish Sea lying 10 to 20 kilometres from the Cumbrian shore and running parallel to it from Workington in the north to Walney Island in the south.³⁶ Inventory calculations for $^{239,240}\text{Pu}$ and ^{241}Am were performed in the late 1990s based on data from 1974 to 1995 for $^{239,240}\text{Pu}$ and 1978 to 1995 for ^{241}Am ³⁵. These calculations accounted for 67% of Pu and Am to be in the Cumbrian 'mud-patch' and its environs. More recent inventory calculations have been performed³⁷ using deeper sediment cores in coarser sediments collected from the eastern Irish Sea. This resulted in up to 90% of the Pu inventory being accounted for.

10 POST DEPOSITIONAL PROCESSES – REDISSOLUTION

Current discharge quantities from Sellafield are very low compared to peak discharge periods (1995 for ^{99}Tc , 1975 for ^{137}Cs , 1973 for $^{239,240}\text{Pu}$ and 1974 for ^{241}Am). However, activities of these radionuclides in the waters off Cumbria are such that they cannot be supported from the annual discharges. Therefore there is another 'source' of radionuclides to the water column – the historic discharges contained within the bed sediments. Investigations into the re-dissolution rates of radionuclides from Irish Sea sediments have been made and modelled.^{9, 10, 26, 29-31, 35, 38} The conservative radionuclide ^{137}Cs , has been calculated to being released at a rate of 50 – 90 TBy per year resulting in a halving time (time taken for the specific activity of ^{137}Cs to drop by 50% by considering radioactive decay and rate of removal) of the order of 10 years. Similarly for $^{239,240}\text{Pu}$, an annual rate of loss of 0.6 to 1.2 TBq per year was calculated resulting in a halving time in the order of 100 years. Data was not as abundant for ^{241}Am , but the data available did indicate that the halving time for ^{241}Am was in the order of 1000 years.

11 NORM IN THE EASTERN IRISH SEA

To provide a perspective on the artificial radionuclides discharged from the Sellafield site over the last 6 decades, it is interesting to consider the discharge practices of a phosphate ore processing plant also situated on the Cumbrian coast at Whitehaven, 10 km north of Sellafield. This site processed phosphate ore between 1954 and 1992. A change of the manufacturing process resulted in phosphoric acid being delivered by road from 1992 until the process ceased in 2001, with the plant being demolished in 2004.^{39,40} Phosphate ore is known to contain elevated levels of naturally occurring radionuclides (NORM) and depending on what process is being used, other radionuclides within the natural decay chains may also be enhanced prior to discharge. Discharge data show that between 1954 and 1992, 14 TBq of ^{238}U and 11 TBq of ^{210}Po were discharged into the Irish Sea.⁴⁰ Although discharges to sea ceased in 1992, monitoring of the shoreline for ^{210}Po in winkles was maintained and reported annually by the UK regulators within the RIFE reports.⁴¹ The most recent report has stated that the dose to the relevant critical group from NORM was 0.39 mSv y^{-1} , with the total dose from both NORM and artificial radionuclides being 0.62 mSv y^{-1} .⁴¹ This calculated dose value was the highest reported for the whole of the UK in 2008. Hence despite discharges to sea having ceased over 15 years ago, the radiological impact on members of the local critical group are greater than those from the Sellafield site. One factor that is very sensitive to the final value calculated is annual habit data. Although the specific activity of ^{210}Po in the monitored winkles have remained relatively level at 35 Bq kg^{-1} fresh weight since 1992, the quantities consumed over the years have varied. In 2008 winkle consumption had risen from the previous year resulting in this relatively large contribution to the overall dose assessment⁴¹.

12 SUMMARY

Numerous studies have been performed on radioactivity in the Irish Sea over the last 6 decades. The environmental chemistry of the individual radionuclides as well as their physical half lives have a large bearing on their persistence in the marine environment. The bulk of the conservative radionuclides discharged from the Sellafield site, e.g. ^{99}Tc and ^{137}Cs , have left the environs of the Irish Sea according to the prevalent currents, tides and wind conditions. The particle-reactive radionuclides discharged, e.g. $^{239,240}\text{Pu}$ and ^{241}Am still reside within the sediments of the eastern Irish Sea. These sediments, however, are losing this activity due to re-dissolution into a relatively clean water column. Halving times of activity have been calculated and are of the order of tens of years for ^{137}Cs , hundreds of years for $^{239,240}\text{Pu}$ and thousands of years for ^{241}Am .

As a result of past discharge practices of ^{241}Pu , there is now more ^{241}Am in the Irish Sea environment due to the decay of previously discharged ^{241}Pu than from the ^{241}Am discharged directly into the Irish Sea. Such changing inventories need to be considered when dealing with Pu and Am ratios within chronological studies.

Historic NORM discharges contribute significantly to the critical group dose, more so than radionuclides discharged from Sellafield. This highlights how lasting impacts can occur although the discharge practice may have ceased years ago. The impact of Sellafield derived radionuclides to the Cumbrian critical group is mainly due to historic discharges and not current ones.

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1 INTRODUCTION

The macroalgae *Fucus vesiculosus* is a good bioindicator for radioactive iodine. In this work the algae have been used for studying ¹²⁹I along the Swedish coast at 40 sampling stations from 1982-1983, 1986-1988, 1991-1995 to 2007. In 2007 also water samples were taken and analyzed by AMS at Centro Nacional de Aceleradores (Seville, Spain). In addition ¹³⁷Cs was analyzed. ¹²⁹I in the area may originate from natural occurrence, fallout from atmospheric nuclear tests, releases from the Chernobyl accident and discharge from European nuclear fuel reprocessing facilities.

It is obvious that the European reprocessing facilities are the most important sources for ¹²⁹I at the Swedish west coast. The transit time from La Hague reprocessing plant is about 2 years and 4 years from Sellafield.¹ Over the past decade, liquid and gaseous discharges of ¹²⁹I from BNG's spent nuclear fuel reprocessing facility at Sellafield (UK) have increased from 10 to 70 kg/year as a result of the operation of the Thermal Oxide Reprocessing Plant (THORP), which started in 1995. The principal source of ¹²⁹I in the English Channel, of course, is AREVA's reprocessing plant located at Cap de la Hague (France). Annual discharges from this site increased sharply in the early 1990s from 100 to 500 kg/year (Figure 1) and are currently considerably higher than those from Sellafield.

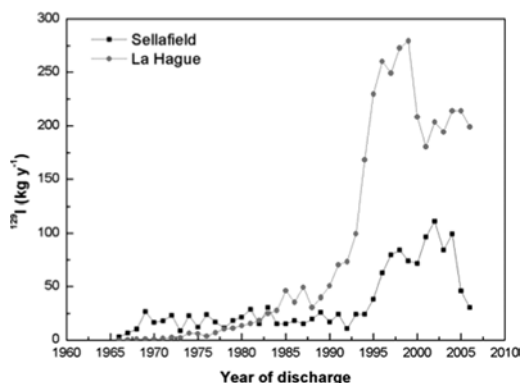


Figure 1 ¹²⁹I in liquid effluent discharges annually from Sellafield and La Hague²

There is an inflow of saline sea water from the North Sea to the Baltic Sea reaching only the north western part (Figure 2). Most of the ^{129}I in the Baltic Sea is mainly due to fallout from the atmospheric emissions from nuclear facilities and emissions from contaminated seawater as organic iodide³. In contrast to ^{137}Cs , the Chernobyl accident had a rather limited impact on the Baltic Sea with respect to ^{129}I compared to ^{129}I from other sources.

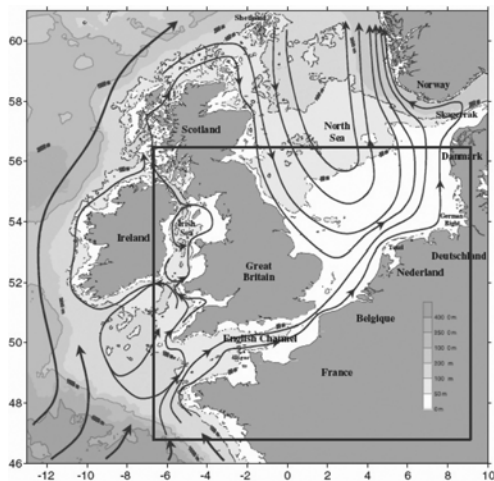


Figure 2 Simplified scheme of water masses general circulation in north-western European seas⁴

^{129}I has been identified⁵ as potentially one of the most important radionuclides in global scale long-term radiological assessment of discharges from reprocessing plants and is also important for tracing water masses. Here we present a study of ^{129}I concentration in *Fucus vesiculosus* sampled around the coastline of Sweden at 40 different stations in the periods 1982-1983, 1986-1988, 1991-1995 and 2007. The resulting data were evaluated in terms of spatial and temporal trends and compared, in case of samples from year 1986, with ^{137}Cs concentrations recorded in the same samples. Using these data, $^{129}\text{I}/^{137}\text{Cs}$ ratios in seawater at the same coastal sites were deduced. The spatial variation in this ratio (in seawater) from year 1986 was then compared to that in fallout from Chernobyl accident. The temporal trend is used to verify the influence of nuclear reprocessing facilities liquid emissions in Swedish coastline. Also, ^{129}I concentrations in *Fucus* were compared to concentrations in seaweed from other regions of the world, including those remote from reprocessing plant discharges. Finally, ^{129}I concentration in a recent (2007) set of seawater samples from the Swedish coast were recorded in an attempt to determine the concentration factor of iodine in the brown alga *Fucus vesiculosus*.

2 MATERIALS AND METHODS

2.1 Seaweed

Fucus vesiculosus was sampled at locations selected to provide a representative geographical distribution on all aspects of the Swedish coast (Figure 3). Sampling took

place between 1982-1983, 1986-1988, 1991-1995 and 2007 and about 1 kg of each sample was collected, dried, grinded and homogenised.

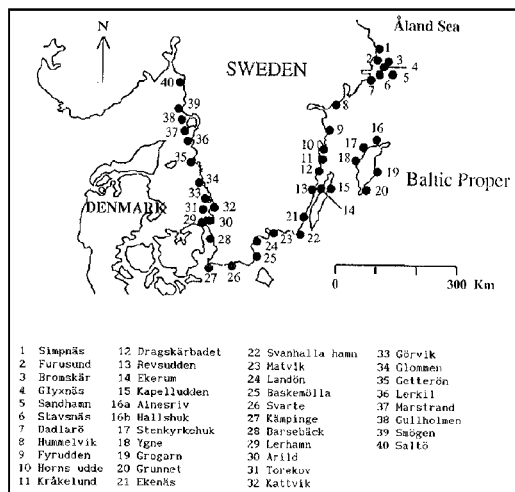


Figure 3 Sampling sites of *Fucus vesiculosus*⁶

All samples were digested using an alkaline fusion method⁷: 0.5 g of the solid material was mixed with 5 mg of ^{127}I carrier solution, 6 mL of a 30% KOH and 3% KNO_3 solution as a fluxing agent in a crucible. The crucible was then placed in a 90 °C oven and allowed to evaporate to dryness, after which it was covered and transferred to a muffle furnace preheat to 550°C. Fusion was completed by heating the sample for 60 min. After this, the crucible was cooled to ambient room temperature. The fused solid sample was then dissolved with water ($>18 \text{ V cm}^{-1}$) produced in a Milli-Q apparatus (Millipore Co., Bedford, MA, USA). The iodine extraction was then made with an organic compound.⁸ Iodine was precipitated as AgI by the addition of AgNO_3 .

2.2 Seawater

Seawater samples were collected at twelve locations around the west Swedish coastline (from sites 27 to 40, Figure 3) during 2007. The chemical extraction of iodine from water is usually based on the solubility of I_2 in CCl_4 . However, here we preferred to use CHCl_3 instead of CCl_4 because of its lower chemical toxicity. The procedure is straightforward: 5 mg of ^{127}I carrier solution is added to each 400 ml sample of water. First this solution is extracted with CHCl_3 and then re-extracted in NaHSO_3 , following a published method.⁸ Iodine is precipitated as AgI in the same manner as for *Fucus*.

2.3 Accelerator Mass Spectrometry Measurements

Determination of $^{129}\text{I}/^{127}\text{I}$ ratios in the samples was conducted at the 1 MV multielement compact AMS facility SARA (Spanish Accelerator for Radionuclides Analysis) at the Centro Nacional de Aceleradores (CNA) in Seville (Spain). Charge state 3+ after stripping was chosen to make the measurements. Background effects were evaluated through measurement of iodine blanks (Woodward Iodine, from Woodward Iodine Corporation, USA), with a measured $^{129}\text{I}/^{127}\text{I}$ value of $3\text{--}4 \times 10^{-13}$. This is typically lower than 10% of

the isotopic ratios measured for real samples. A more detailed description of the system and the measurement details can be found.⁹

3 RESULTS AND DISCUSSION

¹²⁹I concentrations in *Fucus* and in seawater sampled in 2007 around the Swedish coastline (Figure 3) are shown in Tables 1 and 2, respectively. Concentrations in *Fucus* are expressed as atoms of ¹²⁹I per gram of dry *Fucus*, while concentrations in seawater are expressed as atoms of ¹²⁹I per gram of seawater.

Table 1 ¹²⁹I concentrations (dry weight) in *Fucus* sampled around the Swedish coastline in 1982-1983, 1986-1988, 1991-1995 and 2007. Quoted uncertainties are ±1σ

Sampling zone	¹²⁹ I concentration (x10 ⁹ at./g)					
	1991	1992	1993	1994	1995	2007
40						574.97±21.73
39	72.43±3.26	251.01±10.42			176.32±7.48	517.92±25.91
38					245.37±10.32	300.83±11.27
37		75.05±3.19	141.93±8.29		134.38±5.88	324.54±12.14
36			82.18±3.84		132.82±6.59	299.66±14.65
35	46.63±1.94	112.89±5.05	147.48±6.77		149.79±6.35	251.65±9.37
34	77.62±3.36	121.86±5.42			143.58±6.02	305.12±11.76
33						154.77±6.66
32						175.38±8.94
31	34.47±1.50				99.56±4.30	
30						182.93±6.91
29	39.52±1.63				97.73±4.29	
28			55.89±2.44	122.70±5.02		77.81±2.95
27	9.39±0.49					43.82±1.74
26						
25						
24						
23						
22						
21						
20						
19						
18						
17						
16						
15						
14						
13						
12						
11						
10						27.89±1.61

Sampling zone	¹²⁹ I concentration (x10 ⁹ at./g)				
	1982	1983	1986	1987	1988
40					
39					
38					
37					
36					
35					
34					
33			38.83±2.12		
32			29.43±2.04	35.30±1.71	
31			30.97±1.61	43.39±2.25	
30			28.77±1.20	27.82±2.26	
29			29.55±1.22	30.35±3.27	
28		5.89±0.15	17.89±0.78		
27	4.02±0.21		6.87±0.30	6.90±0.27	6.94±0.23
26	3.22±0.23		3.36±0.17		
25	2.05±0.10		2.66±0.12		
24	2.18±0.10	2.69±0.17	1.88±0.13		
23	2.81±0.16		2.14±0.36		
22	2.51±0.11		2.89±0.21		
21					
20		2.48±0.13	2.81±0.16		
19			2.19±0.11		
18			1.89±0.30		
17		2.09±0.11	1.97±0.19		
16		2.11±0.12	1.82±0.11		
15			2.55±0.13		
14	3.39±0.15		1.88±0.32		
13	1.44±0.10		1.50±0.10		
12	1.12±0.10		1.6±00.10		
11	0.96±0.06				
10	0.96±0.06		1.72±0.10		
9	0.18±0.06		1.88±0.18		
8	0.82±0.06		1.59±0.07		
7	1.03±0.06		1.81±0.15		
6			1.55±0.21		
5			1.33±0.06		
4			1.80±0.11		
3			3.87±0.22		
2			1.77±0.10		
1			3.49±0.16		

3.1 Spatial distribution and temporal evolution of ¹²⁹I in Swedish seaweed

The data reveal an spatial enhancement of approximately one order of magnitude in the ¹²⁹I concentration in seaweed sampled along the west coast of Sweden in 1986 and 2007, with respect to concentrations in seaweed taken from the Baltic Sea coastline at similar times (Figure 4). ¹²⁹I concentrations peak in the North Sea coastline sites 40-27 (range: 5.89×10⁹ at./g at site 28 in 1983 to 5.75×10¹¹ at./g at site 39 in 2007). This is clear evidence that ¹²⁹I discharges from Sellafield and La Hague to the North Sea have had a significant impact to the northwest coast of Sweden.

Table 2 ^{129}I concentrations in seawater sampled at selected sites around the west Swedish coastline in 2007. Quoted uncertainties are $\pm 1\sigma$

Sampling zone	^{129}I concentration ($\times 10^6$ at./g)
40	49.39 $\pm$ 2.11
39	51.27 $\pm$ 2.54
38	38.32 $\pm$ 0.99
37	25.00 $\pm$ 1.19
36	22.50 $\pm$ 2.11
35	16.98 $\pm$ 0.71
34	29.56 $\pm$ 2.38
33	18.69 $\pm$ 0.73
32	20.11 $\pm$ 1.54
31	
30	14.76 $\pm$ 1.65
29	
28	9.83 $\pm$ 0.46
27	5.44 $\pm$ 0.22

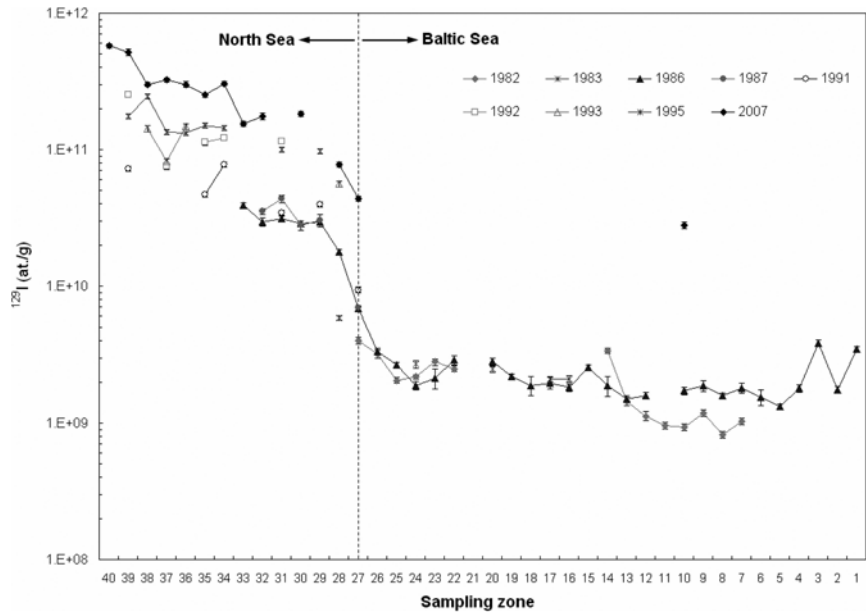


Figure 4 ^{129}I concentrations (at./g) in *Fucus* from the Swedish sites sampled in 1982-1983, 1986-1988, 1991-1995 and 2007. Quoted uncertainties are $\pm 1\sigma$

^{129}I concentrations in Swedish *Fucus* were found to be in the order of $(5\text{-}500)\times 10^9$ at./g on the North Sea coast and $(1\text{-}40)\times 10^9$ at./g on the Baltic Sea coast (Table 1). To illustrate how these measurements rate on a global scale, we can compare them to ^{129}I concentrations recorded in seaweed worldwide (Table 3).

Comparing results from these experiments with the published ones, we found¹⁰ results obtained by RNAA (Radiochemical Neutron Activation Analysis) in seaweed *Fucus*

*virsoides*1 sampled during the summers of 2005 and 2006 in the coastline of the Adriatic Sea (Table 3). ¹²⁹I concentrations in these samples ranged between $(1.5-3.4) \times 10^9$ at./g. These values are in the same order of magnitude that those found in this study for seaweed sampled in 80's in the coast of the Baltic Sea (sites 1-27). This similarity in ¹²⁹I concentrations in samples that have 30 years of difference is due to the fact that the Adriatic Sea is not directly influenced by nuclear reprocessing plant liquid discharges. Results¹¹ obtained by Gamma Spectrometry in seaweed sampled between 1998 and 1999 in Goury, sited in the vicinity of La Hague nuclear reprocessing plant, show very high ¹²⁹I concentrations, ranging $(14000-32000) \times 10^9$ at./g, two orders of magnitude higher to that found in this study in seaweed sampled at the end of 90's. Results¹³ show ¹²⁹I concentrations in seaweed sampled in Denmark and Iceland between 1988 and 1992. These values ranged between $(0.6-115) \times 10^9$ at./g and were in the same order of magnitude that results found in this study. Results¹² showed ¹²⁹I concentrations obtained in seaweed sampled in Novaya Zemlya2 between 1967 and 1993 and measured by AMS (Accelerator Mass Spectrometry). Found values ranged between $(0.4-13.3) \times 10^9$ at./g, and are lower than obtained in this study in samples collected in the North Sea. This Russian archipelago has been influenced by the impact of the Soviet nuclear tests and, indirectly, its waters are contaminated by Sellafield and La Hague liquid emissions that arrive through the NCC (Norwegian Coastal Current)¹⁴.

Table 3 ¹²⁹I concentrations reported in various seaweeds sampled worldwide

Algae	Sampling zone		¹²⁹ I concentration ($\times 10^9$ at./g)	Measure method	Reference
	Date	Zone			
<i>F. vir.</i>	Sept. 2005	Slovenia	2.0 $\pm$ 0.6	RNAA	[10]
<i>F. vir.</i>	June 2006	Italy	1.5 $\pm$ 1.1		
<i>F. vir.</i>	Oct. 2006	Croatia	3.4 $\pm$ 1.1		
<i>F. ves.</i>	Oct. 1998	Goury, France	14000 $\pm$ 900	γ Spectrometry	[11]
<i>F. ves.</i>	March 1999	Goury, France	32000 $\pm$ 2300		
<i>F. ves.</i>	July 1967	Kruglaya Levaya	0.4 $\pm$ 0.02	AMS	[12]
<i>F. ves.</i>	July 1972	Sosnovetz	1.2 $\pm$ 0.03		
<i>F. ves.</i>	August 1993	Gribovaya Fjord	13.3 $\pm$ 0.3		
<i>F. ves.</i>	Dec. 1988	Iceland	0.6 $\pm$ 0.04	RNAA	[13]
<i>F. ves.</i>	Nov. 1989	Klint, Denmark	62.1 $\pm$ 4.6		
<i>F. ves.</i>	April 1992	Klint, Denmark	115.3 $\pm$ 10.4		
<i>F. ves.</i>	1982	(8) Hummelvik	0.82 $\pm$ 0.06	AMS	[This work]
<i>F. ves.</i>	2007	(27) Kämpinge	43.82 $\pm$ 1.74		
<i>F. ves.</i>	1983	(28) Barsebäck	5.89 $\pm$ 0.15		
<i>F. ves.</i>	2007	(40) Saltö	579.97 $\pm$ 21.73		

The impact of the significant increase in releases of ¹²⁹I from Sellafield and La Hague (commencing in the mid-1990s) on the northwest Swedish coast is illustrated best by comparing the ¹²⁹I concentrations in *Fucus* samples from 1986, with those from 1995 and

1 Although *Fucus vesiculosus* and *Fucus virsoides* are two different algae families, both belong to same species (Phaeophyceae, brown algae), so have similar iodine sorption and concentration factor (CF).

2 Novaya Zemlya is an archipelago in the Arctic Ocean in the north of Russia, between Kara Sea and Barents Sea.

2007. The ^{129}I concentration along the northwest coast increased by a factor of 10 between 1986 and 2007 (Table 1), in response to a seven-fold increase in annual discharges in the same period (Figure 1).

3.2 Impact of Chernobyl Accident in the Swedish Coasts

Anthropogenic radioactivity in the Swedish coasts originates from several sources such as global fallout from nuclear weapons tests and releases from nuclear power plants and European nuclear fuel reprocessing plants. Since the 26th of April 1986 the Chernobyl accident constitutes another important source of radionuclides in the Swedish coast²³, as shown in Figure 5. In an attempt to determine whether there was any correlation between the $^{129}\text{I}/^{137}\text{Cs}$ ratio in seawater surrounding Sweden and that in discharges from Chernobyl accident, the $^{129}\text{I}/^{137}\text{Cs}$ ratio in seawater at the various (*Fucus*) sampling sites was deduced from the ^{129}I and ^{137}Cs concentrations in the same *Fucus* samples, using the Equation 1:

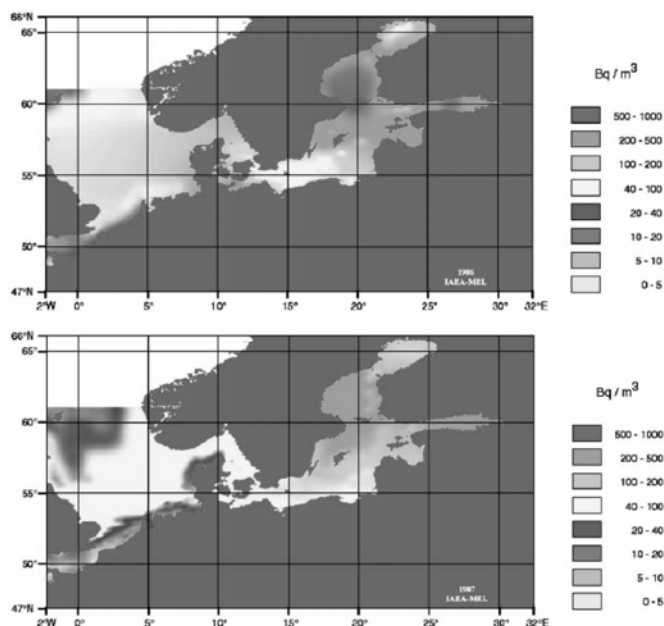


Figure 5 ^{137}Cs in surface waters of the Baltic and North Seas in 1986 (up) and 1987 (down)²³

$$\begin{bmatrix} ^{129}\text{I} \\ ^{137}\text{Cs} \end{bmatrix}_w = \frac{\begin{bmatrix} ^{129}\text{I} \\ ^{127}\text{I} \end{bmatrix}_F}{\begin{bmatrix} ^{137}\text{Cs} \end{bmatrix}_F} \times \begin{bmatrix} ^{127}\text{I} \end{bmatrix}_w \times \text{CF}(^{137}\text{Cs}) \quad (1)$$

where: $^{129}\text{I}/^{137}\text{Cs}$ is the $^{129}\text{I}/^{137}\text{Cs}$ atom ratio in seawater at the various *Fucus* sampling sites; $^{129}\text{I}/^{127}\text{I}$ is the atom ratio in *Fucus*, using ^{129}I concentration obtained in this study and ^{127}I concentrations¹⁵; ^{127}I is the stable iodine concentration in coastal water around Sweden, taken to be 15 $\mu\text{g/l}$ for Baltic Sea and 40 $\mu\text{g/l}$ for North Sea¹⁵; $\text{CF}(^{137}\text{Cs})$ is the measured concentration factor for radiocaesium from seawater to *Fucus* in Swedish coastal

waters, taken to be 180^{16} ; and $[^{137}\text{Cs}]_F$ is the ^{137}Cs concentration in *Fucus*.⁶ It is demonstrated⁶ that ^{137}Cs concentrations in *Fucus* along the Baltic Sea coast sampled in 1986 are due to the Chernobyl accident, and this is because the activity ratio $^{134}\text{Cs}/^{137}\text{Cs}$ was (0.45 ± 0.05) in July 1986, which is in agreement with the ratio calculated from IAEA¹⁷ values, which correspond to $(0.47\text{--}0.48)$ in July 1986. Once it is known that the Chernobyl accident is the origin of ^{137}Cs concentrations present in *Fucus* (and, therefore, also in waters) in the Swedish coastline in July 1986, the following step is to determine the origin of ^{129}I concentrations measured in this study to calculate $^{129}\text{I}/^{137}\text{Cs}$ atomic ratio in these waters and to verify if it corresponds to values due to atmospheric fallout ($^{129}\text{I}/^{137}\text{Cs}=0.2$)⁵ or to the Chernobyl accident ($^{129}\text{I}/^{137}\text{Cs}=1.4$).¹⁸ This ratio, calculated according to Equation 1, is shown in the Figure 6. The resulting data indicate that this ratio, i. e., the $^{129}\text{I}/^{137}\text{Cs}$ ratio in seawater around Sweden, varies significantly with geographical location of sampling sites. Inferred ratios $^{129}\text{I}/^{137}\text{Cs}$ in seawater along the Baltic Sea coastline (positions 7-26) have a mean value of (1.25 ± 0.30) , which is in agreement with the ratio corresponding to the Chernobyl accident.¹⁸ In most of the samples, a significant positive correlation between the ^{129}I and ^{137}Cs concentration is observed (Figure 7), indicating that these two radionuclides have the same source.²⁴ In northwest positions (27-33), corresponding to the North Sea, ^{129}I concentration in seawaters can be correlated with the liquid discharges of Sellafield and La Hague reprocessing plants.

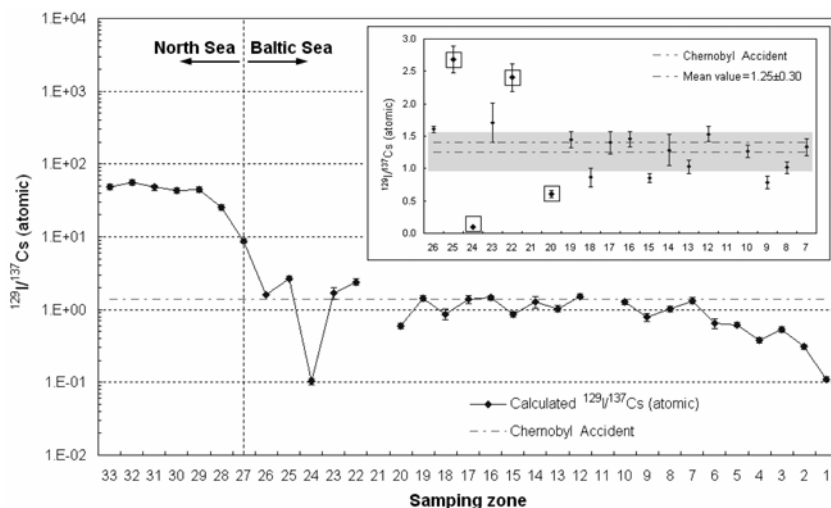


Figure 6 $^{129}\text{I}/^{137}\text{Cs}$ atom ratio in seawater at the various (*Fucus*) sampling sites deduced from the ^{129}I and ^{137}Cs concentrations in the same *Fucus* samples in July 1986, calculated according to Equation 1

3.3 Impact of Sellafield and La Hague Liquid Emissions in the Swedish Coasts

^{129}I had been discharged into the environment from two reprocessing facilities at Sellafield and La Hague (Figure 1). This amount is one order of magnitude larger than the estimated total ^{129}I in the pre-nuclear era, 30 times higher than the released from nuclear weapon tests and several hundreds times higher than that from the Chernobyl accident¹⁵. The $^{129}\text{I}/^{127}\text{I}$ ratio had already been increased to 10^{-8} to 10^{-6} in the North Sea and 10^{-9} to 10^{-8} in the Arctic¹⁹ by 1993.

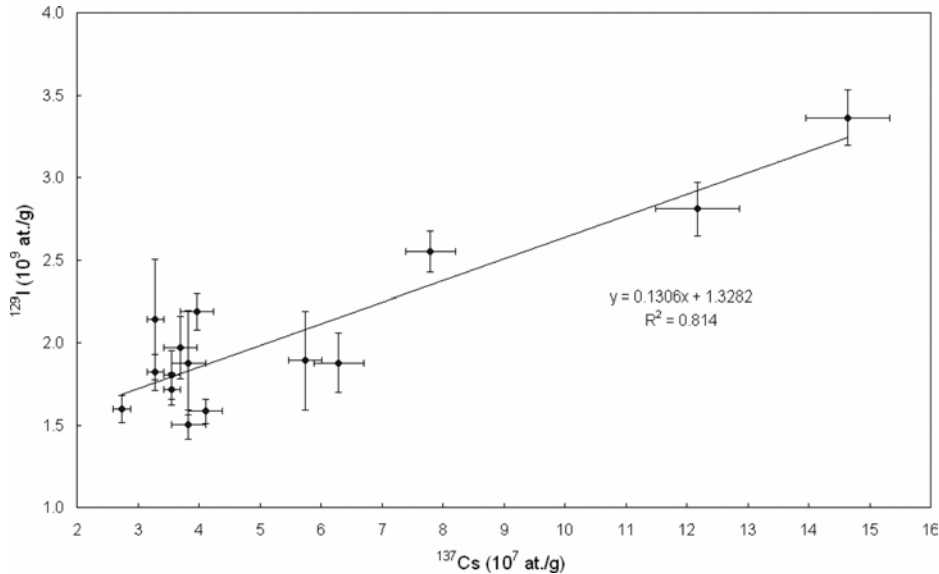


Figure 7 Correlation between ^{129}I and ^{137}Cs in seaweed along the Baltic Sea coastline (positions 7-26) in 1986

It has been well established¹⁵ that the discharged radioactive effluents from the reprocessing facilities at La Hague is first transferred northwards to the coast of north-western Europe via the English Channel, mixed with effluent from Sellafield at the North Sea, and then further transferred by the NCC (Norwegian Coastal Current) to the Arctic. Time series seaweed collected from positions 39 (Smögen), 31 (Torekov) and 24 (Landön) and completed with data from Utsira, Klint and Bornholm¹⁵ respectively, have been used to study the transport of ^{129}I from Sellafield and La Hague to these positions (Figure 8). In this case, the ratio $^{129}\text{I}/^{127}\text{I}$ instead of ^{129}I concentration in seaweed should be used as an index of the ^{129}I level in the surrounding seawater of sampling location, which is based on the assumption¹⁵ that seaweed has a similar capability to take up an assimilate ^{129}I and ^{127}I .

Table 4 The transit times and transfer factors¹⁵ of ^{129}I

Sampling location	Transit time (year)		Transfer factor (ng m ⁻³ /ton yr ⁻¹)	
	La Hague	Sellafield	La Hague	Sellafield
Klint	1-2	3-4	54.3±10.2	8
Utsira	1-2	3-4	60.1±16.0	24

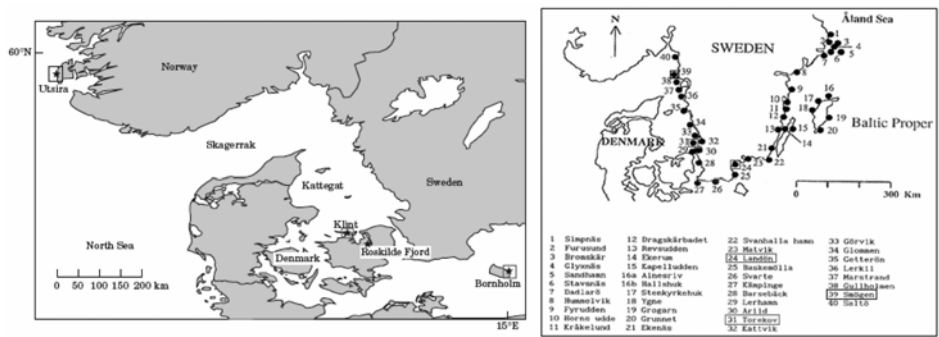


Figure 8 The sampling locations for time series seaweeds: Torekov+Klint, Smogën+Utsira and Ländön+Bornholm. Left map¹⁵ and right map⁶

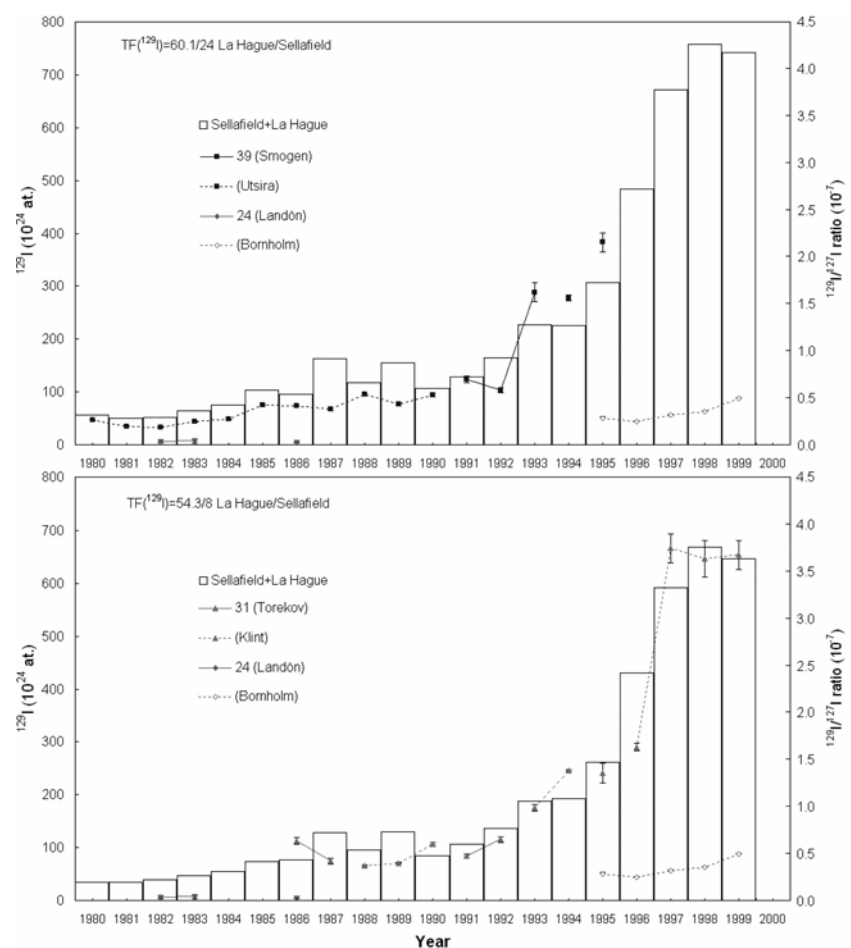


Figure 9 The $^{129}\text{I}/^{127}\text{I}$ ratios (right scale) in seaweed from Smogën+Utsira, Torekov+Klint and Ländön+Bornholm and the combined discharges (bars) of ^{129}I (left scale) from La Hague and Sellafield. The combined discharges were calculated by assuming transit time and transfer factors shown in Table 4

Considering the transit time and transfer factor of ^{129}I shown in Table 4 and comparing the $^{129}\text{I}/^{127}\text{I}$ ratios in the seaweed with the combined discharges of ^{129}I from Sellafield and La Hague (Figure 7), it can be clearly seen that the variation of $^{129}\text{I}/^{127}\text{I}$ ratios at (Torekov+Klint) and (Smögen+Utsira) followed the combined discharges of these facilities, which indicates that a significant amount of discharge from the reprocessing facilities had been transferred to the Swedish water through the Kattegat by the NAC (North Atlantic Current). In the other hand, the $^{129}\text{I}/^{127}\text{I}$ ratio at (Landön+Bornholm) in the Baltic Sea is much lower than (Torekov+Klint) site for the same sampling date (Figure 9). This indicates that a minor fraction of the contaminated seawater reaches the north of Denmark from the North Sea through Kattegat and is transferred further to the Baltic Sea; most of it returning to the North Sea²⁰.

3.4 Determination of the Concentration Factor of Iodine in Algae *Fucus Vesiculosus*

The quantity of an element or radionuclide in biological tissue is almost always discussed in terms of concentration, either on a dry or wet weight basis. For modeling purposes, this value is then usually represented in terms of a concentration relative to that of the ambient seawater, traditionally expressed as a Concentration Factor (CF). If the seawater concentration is derived in terms of unit volume, the CF is expressed in L/kg (Equation 2):

$$\text{CF(L/kg)} = \frac{\text{Concentration per unit mass of organism (atoms/kg or kg/kg)}}{\text{Concentration per unit volume of seawater (atoms/L or kg/L)}} \quad (2)$$

The concentration factor CF (in L/kg) of iodine in *Fucus* presented in this study (Figure 10) were calculated from dry weight data (Table 1) divided by their average concentrations in seawater (Table 2) for year 2007. CF calculated, (10275 ± 184) is in agreement with recommended value $(10000)^{21, 22}$.

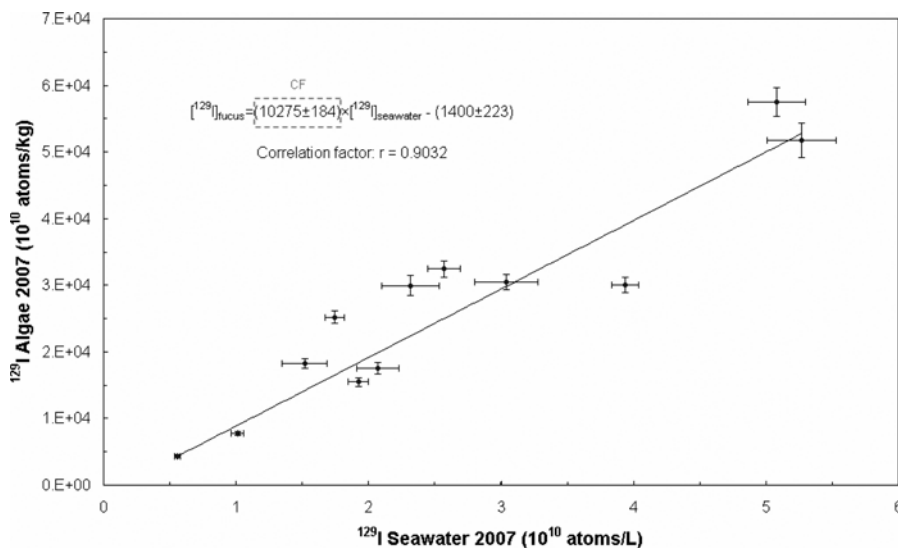


Figure 10 ^{129}I concentrations in *Fucus* versus ^{129}I concentrations in seawater for the same sampling sites in 2007

It is assumed the same CF in seaweed for different iodine isotopes because it increases only with the atomic radius.²¹ As a consequence, an element with a larger atomic radius (as iodine) can be easily absorbed by the surface of the algae cell and combined with the macromolecules in algae, can be highly enriched.

4 CONCLUSIONS

The impact of anthropogenic ^{129}I on Swedish seaweed *Fucus Vesiculosus* and coastal waters is clearly evident from this study:

- a) In case of samples from year 1986, inferred ratios $^{129}\text{I}/^{137}\text{Cs}$ in seawater along the Baltic Sea (positions 7-26) were found to be (1.25 ± 0.30) , which is in agreement with the ratio 1.4 which corresponds to that in fallout from Chernobyl accident.¹⁸
- b) A temporal trend was used to verify the influence of Sellafield and La Hague liquid emissions in Swedish coastline. The variation of $^{129}\text{I}/^{127}\text{I}$ ratios at (Torekov+Klint) and (Smögen+Utsira) followed the combined discharges of these facilities, which indicated that a significant amount of discharge from the reprocessing facilities had been transferred to the Swedish water through the Kattegat. In the other hand, the ratio $^{129}\text{I}/^{127}\text{I}$ at (Landön+Bornholm) in the Baltic Sea is much lower than (Torekov+Klint) site, which indicates that a minor fraction of the contaminated seawater reaches the north of Denmark from the North Sea through Kattegat and is transferred further to the Baltic Sea.
- c) Using ^{129}I concentrations in algae and in seawater from 2007 in northwest Swedish coastline (positions 27-40), concentration factor (CF) of iodine in brown algae *Fucus vesiculosus* was found to be (10275 ± 184) , which is in agreement with recommended value $(10000)^{21, 22}$.

Acknowledgements

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THE EFFECT OF CEMENT SUPERPLASTICISER ON THE SOLUBILITY OF RADIONUCLIDES UNDER REPOSITORY CONDITIONS

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1 INTRODUCTION

One of the illustrative disposal concepts considered by the NDA- RWMD (Nuclear Decommissioning Authority – Radioactive Waste Management Directorate) for the disposal of intermediate-level wastes and some low-level wastes is that of grouted waste packages surrounded by a cementitious backfill. The potential use of superplasticisers to improve flow properties of waste encapsulation grouts offers benefits in some applications, e.g. for infilling or self-levelling. However their impact on the post closure performance assessment of a geological disposal facility (GDF) needs to be considered.

The addition of organic compounds into a radioactive waste matrix is, in general, discouraged since metal complexation with the organics has shown to increase in the concentration of the metal measured in solution.^{1,2} Superplasticisers are potentially complexing agents and the impacts of their addition must be fundamentally understood before use to allow accurate predictions of their behaviour under the conditions of the near field of a radioactive waste disposal facility.

First generation superplasticisers such as naphthalene formaldehyde and sodium lignosulphonate showed the ability to increase the aqueous concentrations of radionuclides.³ The observed effects were not consistent and the use of such additives was, in general, discouraged, however, the composition of modern superplasticisers ('comb' type polymers) is better controlled than the composition of compounds used in the past. This suggests that their effects may be better understood and they may behave in a more predictable manner.

The present study will focus on the solubility of U(VI), Ni(II) and Eu(III) in high pH aqueous solution. This will represent the high pH conditions within and surrounding a geological disposal facility. The expected pH of this system is between 12 and 13.5 and this is due to the influx of groundwater through the facility over time. With the groundwater flow, parts of the cement (NaOH and Ca(OH)₂) dissolve resulting in a very high pH solution.

2 EXPERIMENTAL

2.1 Reagents and Preparation of Solutions

All solutions were prepared using boiled and N_2 sparged deionised water and then stored under nitrogen. 95% saturated $Ca(OH)_2$ was prepared by adding an excess of $Ca(OH)_2$ power (Alfa Aesar) to boiled and sparged deionised water and allowing equilibration with agitation for 48 hours. The solution was then filtered and diluted to 95% using boiled and sparged deionised water. 0.1 mol dm^{-3} NaOH was prepared by dilution from a 2 mol dm^{-3} stock of carbonate free NaOH (Fisher) with boiled and sparged deionised water. The cement equilibrated water solutions were prepared by contacting the cement powders with boiled and sparged deionised water at a ratio of 50:1 for 28 days before filtration.³ BFS (Civil+Marine), OPC (Castle Cement) and PFA (Cemex) were equilibrated individually. 2 equilibrated solutions containing BFS:OPC at a ratio of 9:1 and PFA:OPC at a ratio of 3:1⁴ were also prepared. ADVA Cast 551 (GRACE Construction Products) was used 'as received' and prepared in each aqueous solution at 0%, 0.1%, 1% and 10% (w/v). These concentrations were chosen as the manufacturer recommends the use of ADVA Cast at between 0.3% and 0.8%. 10% ADVA Cast was also added to represent a worst case scenario, if a large concentration of ADVA Cast were to become available to a radionuclide in solution.

2.2 Procedures

All experiments were conducted in a N_2 atmosphere glove box at ambient temperature ($21^\circ\text{C} \pm 2^\circ\text{C}$). The solubility measurements were approached from oversaturation with and without the presence of ADVA Cast 551.

20 cm^3 of each solution was placed into a sample tube. Samples were produced in quadruplicate for each concentration of ADVA Cast 551 in each aqueous solution studied. To each sample (except the blank control samples) an excess of the metal of interest was added so that a precipitate was formed. Uranium was added in the form of $UO_2(NO_3)_2$, Nickel in the form $Ni(NO_3)_2$ and Europium in the form $EuCl_3$ with an added spike of radioactive ^{152}Eu in order to measure the Eu (III) radiometrically. The samples were allowed to equilibrate with agitation for a total of 28 days. At 7 day intervals, a 2 cm^3 aliquot was removed from each vial to investigate the kinetics of oversaturation. The sample was filtered through a $0.45\mu\text{m}$ syringe filter and then analysed for the metal of interest.

U(VI) and Ni(II) were analysed by ICP-OES or ICP-MS for very low concentrations of metal in solution. The samples were acidified with HNO_3 (Fisher Scientific, Trace Metal Grade) after filtration and dilutions prepared where necessary. Eu(III) was analysed radiometrically by gamma spectroscopy.

3 RESULTS AND DISCUSSION

The kinetics of oversaturation was studied for each metal by measuring the concentration of metal in solution after 7, 14, 21 and 28 days.

3.1 Solubility of Uranium (VI)

Uranium was measured by ICP-OES for the most part and ICP-MS for very low concentrations of U(VI) in solution. Shown in **Figure 1** are the solubility results observed for U(VI) in each aqueous solution of interest. The error bars shown in the graphs correspond to the standard deviation of four sample replicates. Steady state was observed to have been reached by day 7 in most cases with the exception of the PFA:OPC equilibrated water samples which reached steady state at day 14. In each case for U(VI) an increase in solubility was observed in the presence of 1% and 10% ADVA Cast 551. In the 0.1% samples, the increase in solubility was not as high, such as in the PFA and BFS equilibrated samples where there was little change from the baseline solubility at 0% ADVA Cast 551.

In order to make meaningful comparisons of the solubility of U(VI) in each individual aqueous solution, the Solubility Enhancement Factor (SEF) was calculated. The solubility of U(VI) in the presence of 10% ADVA Cast 551 was divided by the baseline solubility (0% ADVA Cast 551). These values are shown in Table 1.

The most significant enhancement in solubility is observed in the 95% saturated $\text{Ca}(\text{OH})_2$ solution. This enhancement is much greater than any of the other solutions. The lowest increases in solubility were noted in NaOH and also BFS water.

Table 1 Solubility Enhancement Factors for U(VI) in the Presence of ADVA Cast 551

Test Solution	SEF in the presence of 10% ADVA Cast
$\text{Ca}(\text{OH})_2$	4826
NaOH	23
BFS:OPC water	325
PFA:OPC water	65
OPC water	305
BFS water	37
PFA water	316

3.2 Solubility of Nickel (II)

The solubility of Ni(II) was also measured under the same conditions. The most significant increases were observed in the BFS water and OPC water samples. Figure 2 shows the kinetics of oversaturation for Ni(II) in each of the aqueous solutions investigated. The $\text{Ca}(\text{OH})_2$, BFS:OPC and PFA:OPC samples reached steady state after 7 days. The BFS samples reached steady state after 14 days. NaOH and PFA samples reached steady state at 21 days. The Ni(II) measured in the OPC samples was less consistent over time at 1% and 10%, suggesting that the samples had not yet reached steady state.

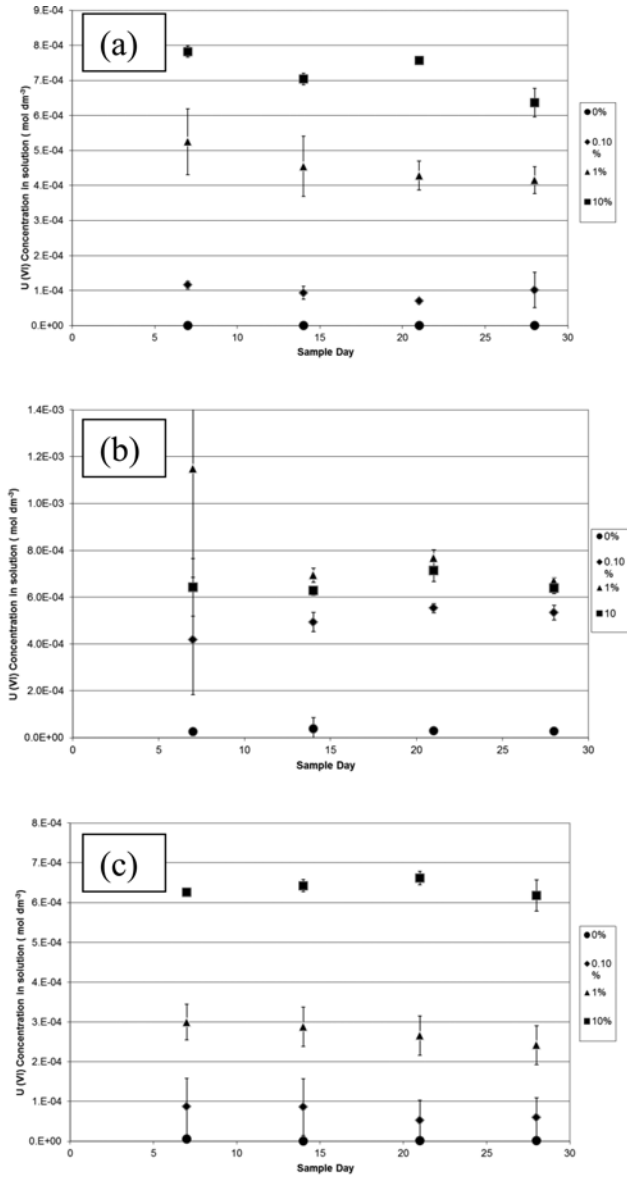


Figure 1 Kinetics of oversaturation of U(VI) in the presence of ADVA Cast 551 in (a) Ca(OH)_2 , (b) NaOH , (c) BFS:OPC water, (d) PFA: OPC water, (e) OPC water, (f) BFS water and (g) PFA water

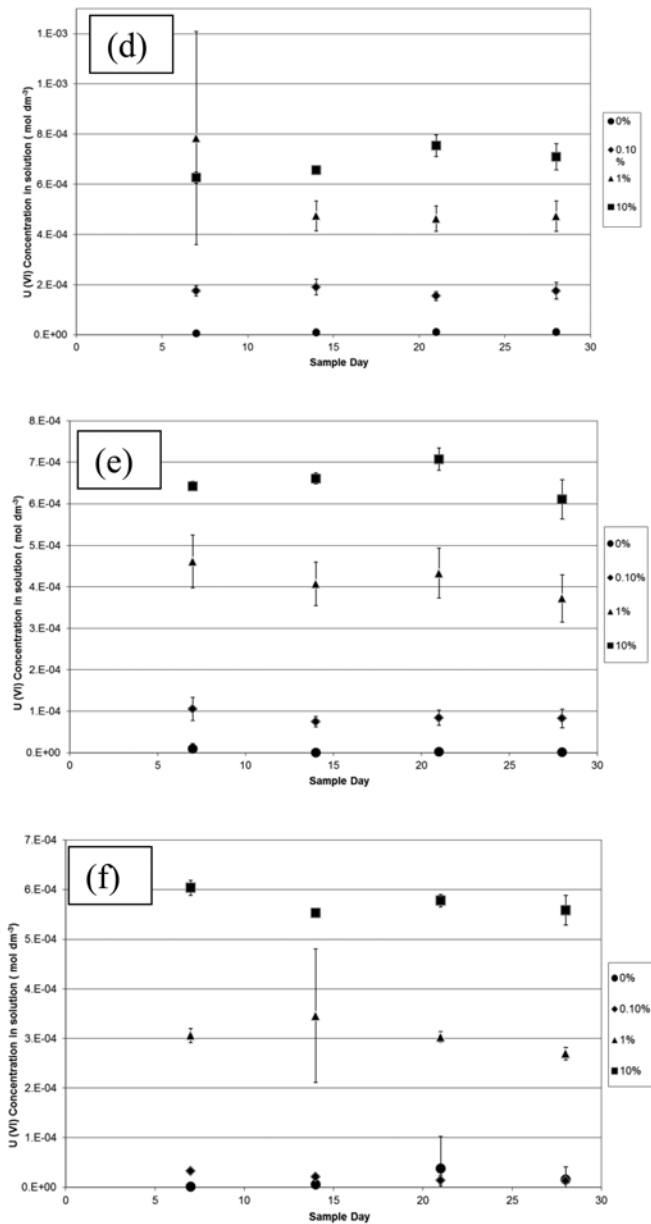


Figure 1 (continued)

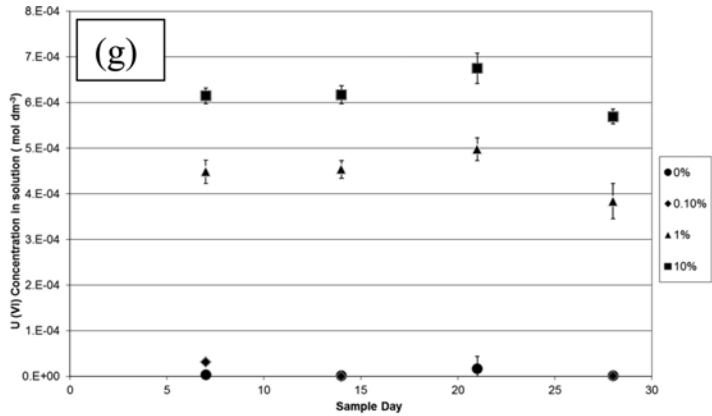


Figure 1 (continued)

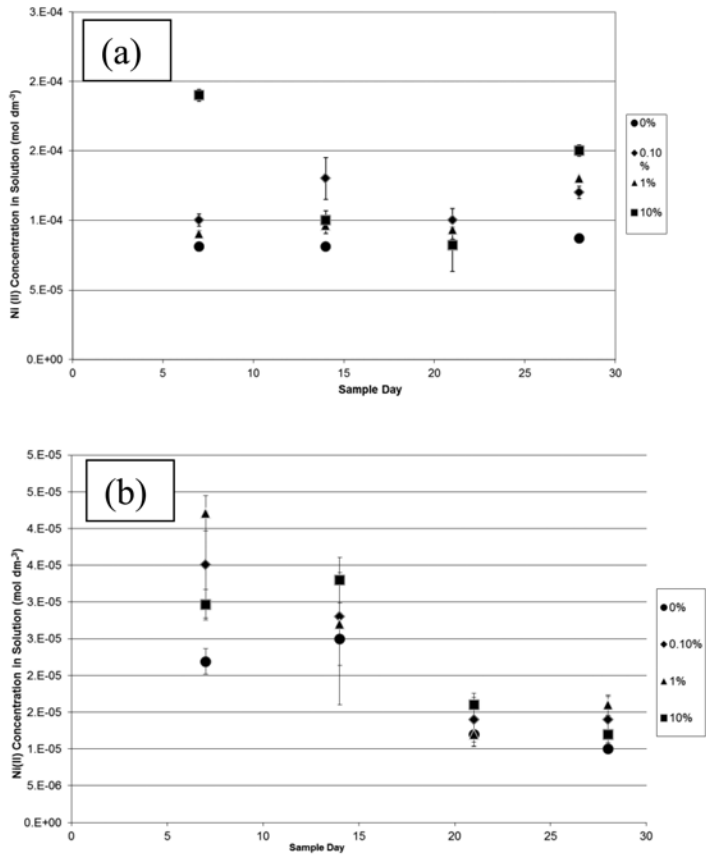


Figure 2 Kinetics of oversaturation of Ni(II) in the presence of ADVA Cast 551 in (a) Ca(OH)₂, (b) NaOH, (c) BFS:OPC water (d) PFA:OPC water (e) OPC water, (f) BFS water and (g) PFA water.

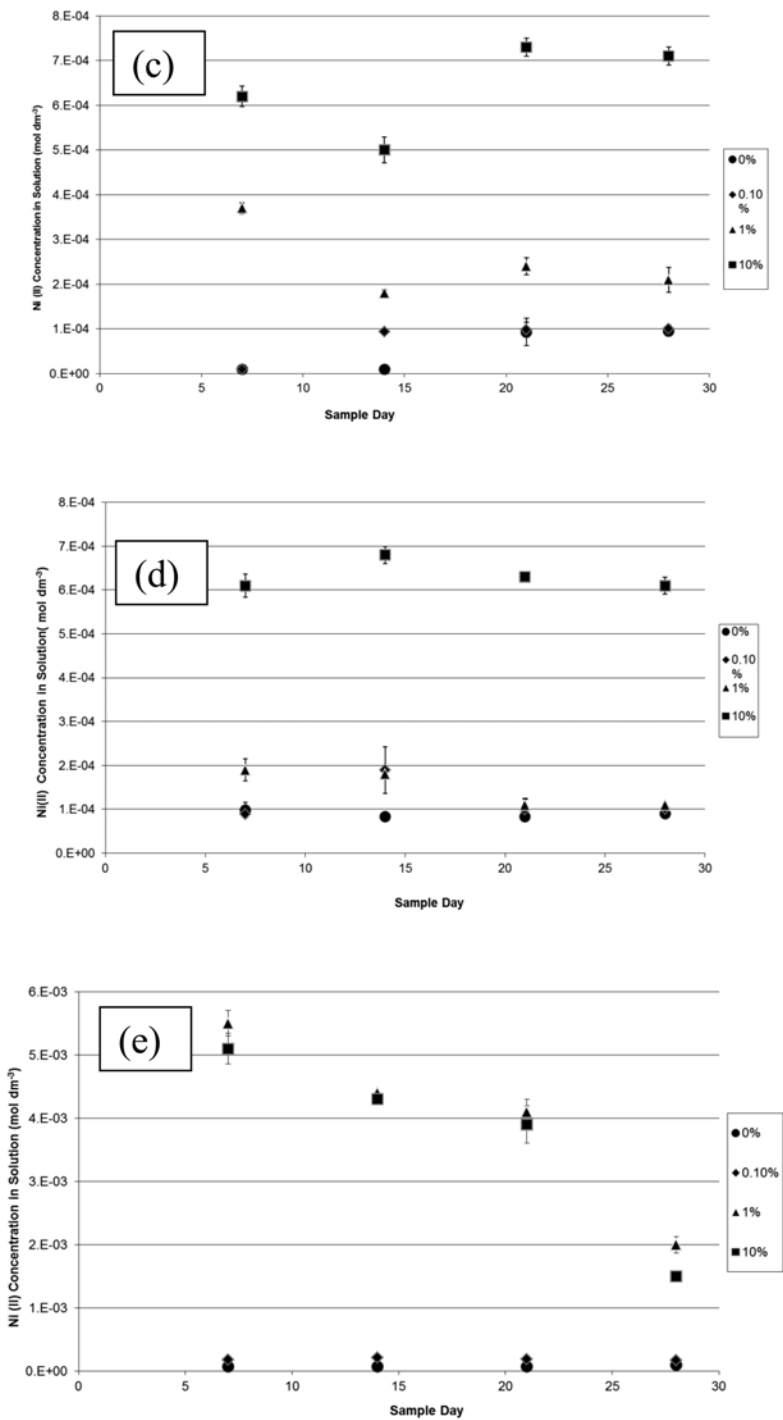


Figure 2 (continued)

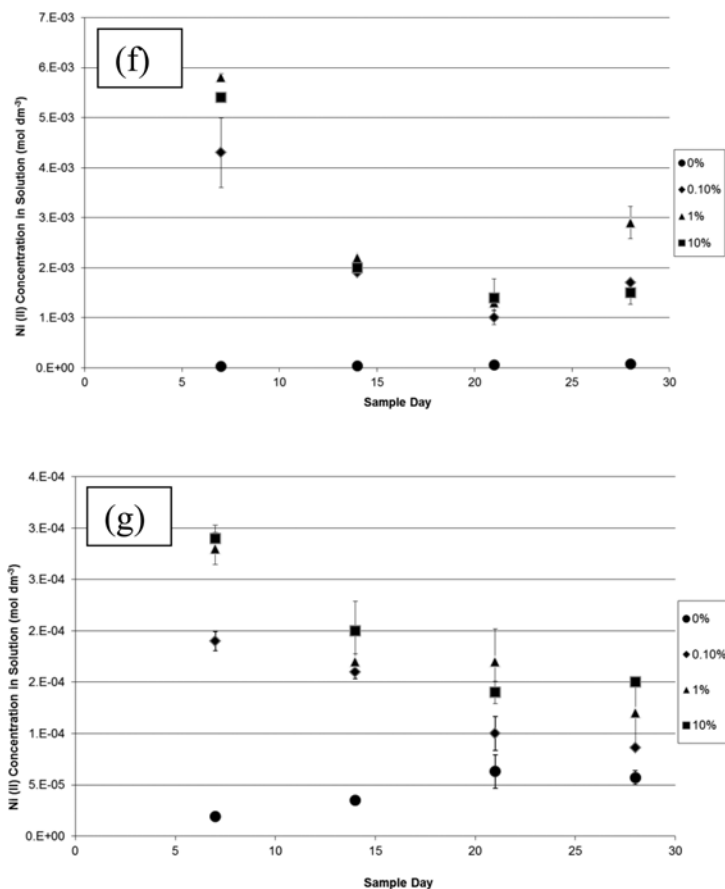


Figure 2 (continued)

The solubility enhancement factors for Ni(II) in the presence of ADVA Cast 551 are shown in **Table 2**. The solubility of Ni(II) is less significantly enhanced than U(VI) with the highest SEF calculated as 20 and this was Ni(II) solubility in BFS water solution. Whereas U(VI) solubility in Ca(OH)₂ has a SEF of 4826 with the presence of 10% ADVA Cast 551, Ni(II) shows little enhancement with a SEF of 2 in the same solution.

3.3 Solubility of Europium (III)

The third metal solubility to be measured under these conditions was Eu(III). Eu(III) is widely known to be highly sorbing. To avoid any negative effects on the measured solubility of Eu(III) under the experimental conditions (such as Eu(III) sorption to glass sample vials), polyethylene sample tubes, syringes and pipettes were used at all times throughout the experiment. Eu(III) concentration in solution was measured radiometrically by gamma spectroscopy. Figure 3 shows the kinetics of oversaturation of Eu(III) in each of the investigated solutions. In the case of Ca(OH)₂, NaOH, BFS:OPC water and PFA:OPC water, steady state was reached by day 7. The PFA, BFS and OPC water samples had reached steady state by day 14.

Table 2 *Solubility Enhancement Factors for Ni(II) in the Presence of ADVA Cast 551*

Test Solution	SEF in the presence of 10% ADVA Cast
Ca(OH) ₂	2
NaOH	1
BFS:OPC water	8
PFA:OPC water	7
OPC water	16
BFS water	20
PFA water	3

3.3 Solubility of Europium (III)

Eu(III) has the lowest baseline solubility of the metals investigated. The concentrations measured in solution are around 4 times lower than for uranium and nickel. In the simple test solutions of Ca(OH)₂ and NaOH, there was little notable increase in the Eu(III) solubility. In particular the concentration of Eu(III) in the NaOH samples was constant (within errors) for the duration of the experiment and at each concentration of ADVA Cast 551. It may be said therefore that in NaOH, the ADVA Cast 551 has little or no effect on Eu(III) solubility.

The SEF for the Eu(III) samples is shown in Table 3. The greatest solubility enhancement was observed in the PFA water samples. The BFS:OPC, OPC and BFS water samples have similar SEF values. In the case of Eu(III) it is clear that with a more complex matrix, there is an effect on the solubility of the metal of interest.

Table 3 *Solubility Enhancement Factors for Eu(III) in the Presence of ADVA Cast 551*

Test Solution	SEF in the presence of 10% ADVA Cast
Ca(OH) ₂	11
NaOH	1
BFS:OPC water	131
PFA:OPC water	25
OPC water	88
BFS water	100
PFA water	211

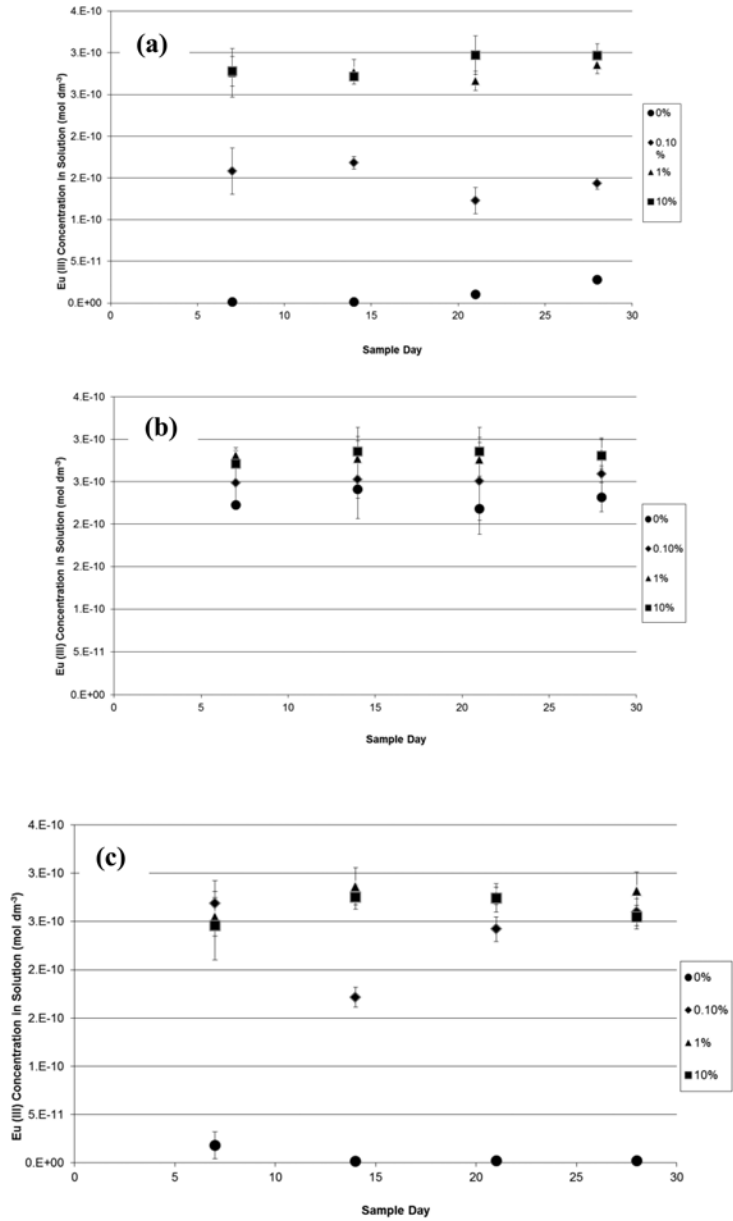


Figure 3 Kinetics of oversaturation of Eu (III) in the presence of ADVA Cast 551 in (a) Ca(OH)_2 , (b) NaOH , (c) BFS:OPC water (d) PFA:OPC water (e) OPC water, (f) BFS water and (g) PFA water.

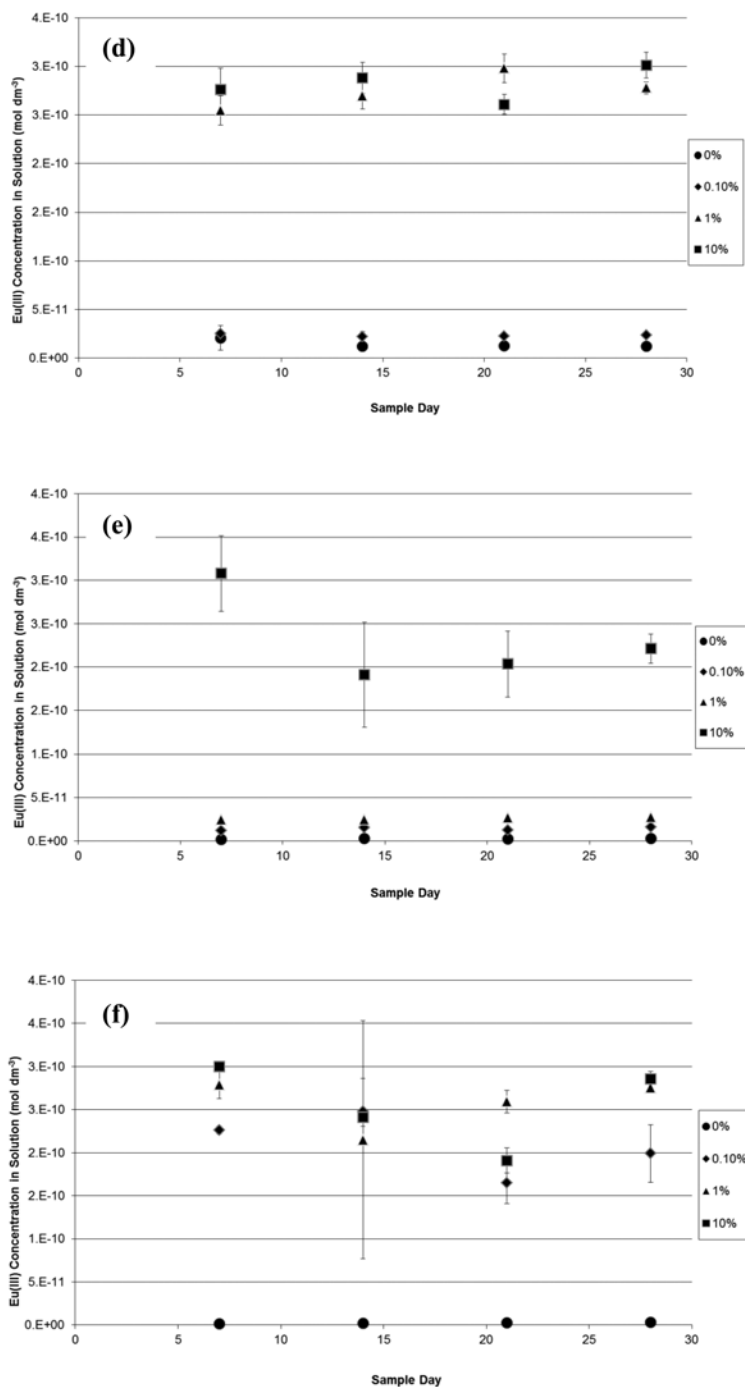


Figure 3 (continued)

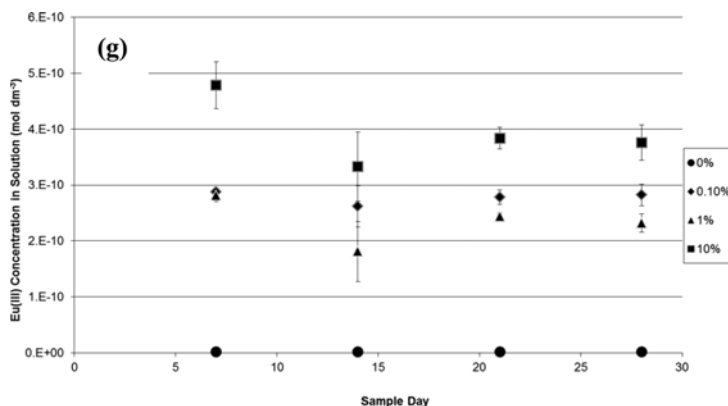


Figure 3 (continued)

4 CONCLUSION

There is a measurable effect on the solubility of U(VI), Ni(II) and Eu(III) in the presence of ADVA Cast 551. This effect is varied depending on the metal and the aqueous test solution investigated. In all cases, the effect is an increase of the concentration of metal measured in solution. For example, the greatest increase in solubility was observed to be U(VI) in Ca(OH)₂ in the presence of 10% ADVA Cast 551 (SEF of 4826). This is in contrast to both Ni(II) and Eu(III) where in the same Ca(OH)₂ solution, there was little increase measured with SEF values of 2 and 11 respectively. In all 3 cases, the least increase in solubility was measured in NaOH solution with U(VI), Ni(II) and Eu(III) having SEF values of 23, 1 and 1 respectively.

5 FUTURE WORK

The experiments shown here demonstrate only one scenario, where the superplasticiser is freely available in solution. The behaviour of the superplasticiser within the repository environment is not yet known and so leaching and sorption behaviour need to be understood also to be able to accurately predict the amount of superplasticiser that will be free in groundwater solution.

There is also the potential for the superplasticiser to degrade under the high temperature and radiolytic conditions of the repository. With this in mind, the effect of the degradation of ADVA Cast 551 on the solubility of U(VI), Ni(II) and Eu(III) will be investigated. The ADVA Cast will be degraded by thermal (80°C), chemical (alkaline) and radiolytic degradation (⁶⁰Co irradiation) and then solubility experiments conducted using the degradation products.

Acknowledgements

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PERFORMANCE AND CHARACTERISTICS OF A LOW-BACKGROUND GERMANIUM WELL DETECTOR FOR LOW-ENERGY GAMMA-RAY NUCLIDES

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1 INTRODUCTION

Many environmental samples are low activity and small, typically a few grams, with the typical nuclides of interest emitting gamma rays in the range of 10 to 50 keV. These samples are most efficiently counted with a well-type detector, where the sample is inserted into a well or hole in the detector. This geometry almost surrounds the sample with active detection volume giving a subtended solid angle of 4π steradians. A Hyper Pure Germanium (HPGe) well detector has been constructed with a well tube of carbon fiber material. The carbon fiber is naturally low background, mechanically strong, and has good transmission (65%) down to 10 keV. Previously, low-background aluminium was used for the well tube, but the transmission is less than 1% at 10 keV for the thicknesses required for mechanical strength. The IEEE 325-2010 standard describes the method to characterize detectors for efficiency and resolution, including the well detector, over the energy range from 50 keV to 2 MeV. The source-detector geometry defined in IEEE 325 for well detectors is the most common geometry for small samples. The HPGe detector was installed in a low-background shield of 15 cm of lead, 1 mm tin, and 6 mm OFHC copper. The shield is approximately 275 m above sea level. The 4π solid angle increases cascade summing (TCS) which reduces the net areas of the full energy gamma ray peaks for all nuclides with cascade decays, such as ^{60}Co and ^{88}Y . These nuclides are commonly used for calibration. To correct for the cascade summing, the efficiency calibration was done using the TCC methods of GammaVision. The efficiency, both uncorrected and corrected for TCC, and resolution from 50 keV to 2 MeV are presented. The background from 10 keV to 3 MeV will be shown. The minimum detectable activities for common nuclides based on the measured efficiency, background, and different counting times will also be presented.

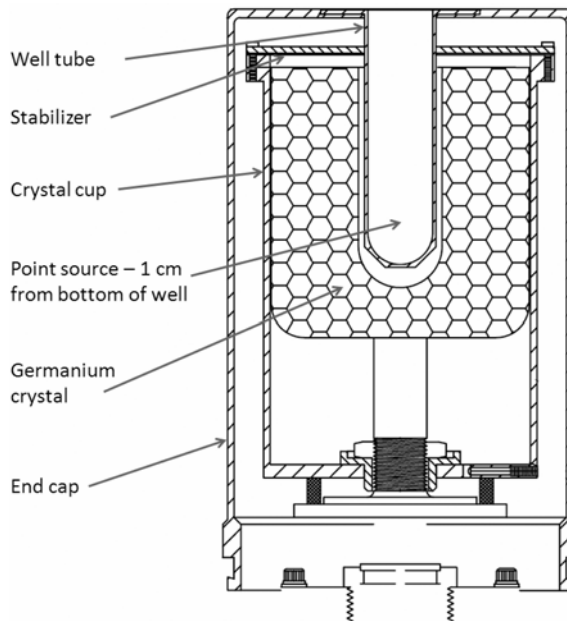


Figure 1 Cross Section of Well Detector

2 EXPERIMENTAL

The HPGe detector has a crystal with 150 ml active volume with an outside diameter of 6.17 cm and a length of 6.49 cm with an internal bore of 2.22 cm. This gives a germanium “wall” thickness of 1.97 cm, which corresponds to 40% absorption of the 1.33 MeV gamma rays. The cross section of a typical crystal and cryostat is shown in Fig.1. The inner contact is ion-implanted boron and the outer contact is diffused lithium. The boron has a thickness of less than 0.3 microns and the lithium thickness is about 600 microns. The endcap and detector mounting cup are made of OFHC copper. The total thickness of copper is less than 3 mm on the sides and 2.4 mm on the front face. The well tube is made of carbon fiber material bonded with epoxy. The carbon fiber thickness is nominally 0.8 mm which has an attenuation of about 15% at 15 keV (that is, 85% of the full energy gamma rays are transmitted). The inside diameter of the well tube is 15.5 mm.

The well tube is held in place by the endcap and an additional stabilizer. The stabilizer is constructed of Mylar and thin copper which reduces the efficiency for low-energy gamma rays originating outside the well in front of the detector.

The detector was placed in the center of a shield constructed of low activity lead bricks in a rectangular shape and lined with tin and copper on all internal surfaces. The internal cavity is 30 cm wide by 51 cm tall by 71 cm long. The lead walls and bottom are nominally 15 cm thick. The lead top is supported by a thin steel sheet and is nominally 15 cm. The copper is 6 mm thick and the tin is 1 mm thick. The shield is located in a building constructed mainly of concrete. It is at an altitude of 275 m.

The background spectrum was collected for 2×10^6 s and is shown in Fig. 2. The average count rate in the energy range of 15 keV to 3 MeV is 5.6×10^{-4} counts/s/keV. The three largest peaks are 511 keV (0.022 c/s), 1461 keV (2.4×10^{-3} c/s), and 2614 keV (8.6×10^{-4} c/s). The cosmic neutron inelastic scattering peaks are also clearly visible.

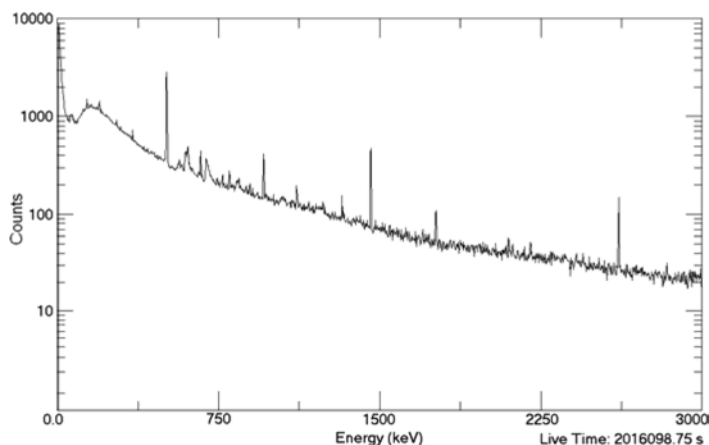


Figure 2 *Background in Shield, Live Time of 2,000,000s*

The source was a point source in a recessed cavity 2 mm from the end of an 8 mm diameter plastic rod. The source was positioned at 1 cm from the bottom of the well tube by inserting the source in a thin wall plastic tube such that the plastic tube rested on the bottom of the well tube and centered horizontally in the well. This is the position for the efficiency measurement of a well detector specified in IEEE 325-2010 (draft).¹ Blaauw² suggested the use of an absorbing layer in well detectors to reduce the effects of X- and gamma-ray self-absorption. Measurements were made with the unshielded source and with the source surrounded by 0.25 mm of copper or 0.065 mm of aluminum.

The source is traceable to NIST and contained ^{109}Cd , ^{113}Sn , ^{139}Ce , ^{203}Hg , ^{134}Cs , ^{137}Cs , ^{88}Y , ^{54}Mn , and ^{241}Am . The nuclides ^{134}Cs and ^{88}Y have cascade summing (true coincidence summing) and were included in order to make the summing correction calibration in GammaVision. The correction is necessary for small source-detector distances (less than 10 cm)³ and the well-detector geometry is very close.

The efficiency was calculated using GammaVision with and without consideration of true coincidence summing using the same spectrum. The carbon fiber cup and the thin contact make the detector sensitive to low-energy gamma- and X-rays, which can be in coincidence with the gamma rays used in the calibration. In addition, the high efficiency of the detector can cause considerable random summing which distorts the full-energy net peaks of the gamma rays needed for the efficiency calculation. The normal rise time setting is 12 μs , but at this setting, the random summing was too severe to produce usable spectra. The amplifier rise time was then set to 1 μs (shaping time of 0.5 μs) to reduce random summing, but the summing with X-rays is still evident. The bare source spectrum is shown in Fig. 3. This shows the background under the peaks is not able to be determined which means that the efficiency will not be correctly calculated.

The addition of the thin aluminum foil showed minimal improvement in the random summing or pileup. The use of the copper foil showed enough improvement for the spectrum to be used for energy and efficiency calibration. Figure 4 shows the spectrum with the addition of the copper foil around the source. The 750 to 900 keV region of the two spectra is shown in Figure 5. Comparing these two spectral regions shows the reduction in the pileup is enough to enable the software to accurately define the background and the net peak area.

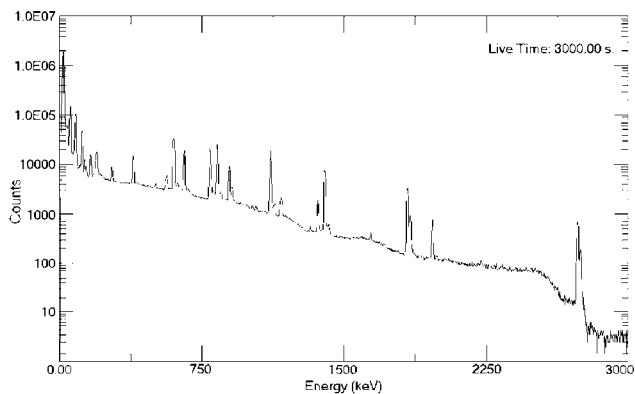


Figure 3 Calibration Source Spectrum with no Absorber

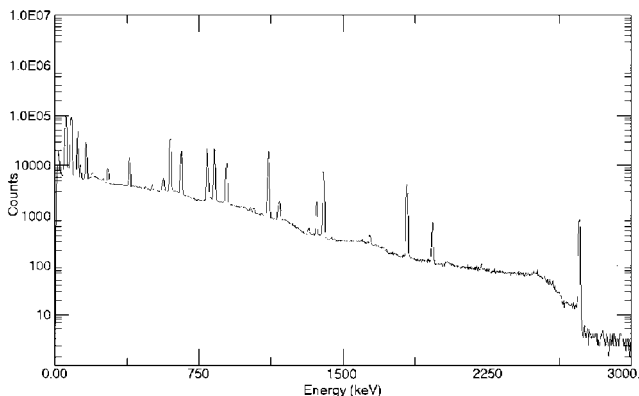


Figure 4 Calibration Source Spectrum with Copper Absorber

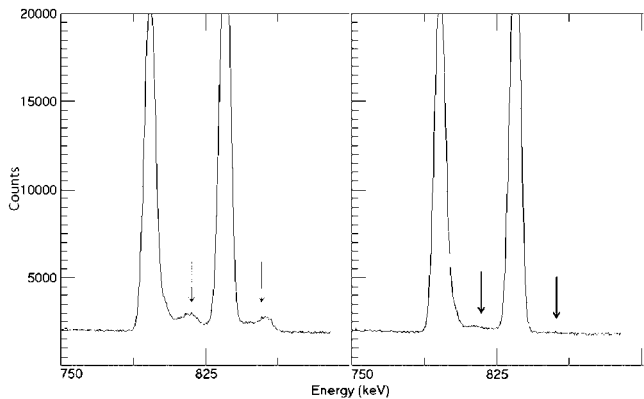


Figure 5 Comparison of Spectrum Region with and without the Copper Foil Absorber

3 RESULTS

The spectra shown in Figures 4 and 5 were used to measure the resolution for the two rise times (shaping times). Note that neither of these spectra is in the geometry specified in the IEEE 325 standard, so the resolution values are not comparable to normally specified values. Figure 6 shows the FWHM for both Rise Times for the energy range from 50 keV to 3 MeV.

The spectrum collected with the copper foil was calibrated for energy using all the gamma ray energies from the source. The efficiency calibration was first done without consideration of any true coincidence summing by using only the nuclides in the source that do not have cascade decays. The analysis of the spectrum using this calibration for activity is shown in Table 1 along with the declared activities. Note that the differences between the declared activities and the measured activities for most nuclides are within 2%. The exceptions are ^{134}Cs and ^{88}Y , both of which are subject to cascade summing. The ^{134}Cs result is under reported by 58% (that is, less than half of the actual activity) and ^{88}Y is under reported by 36%, indicating that significant coincidence summing is impacting the results.

Table 1 Comparison of Calculated and Known Activity without True Coincidence Correction

Nuclide	Measured	Known	Difference
^{241}Am	5544.4	5571.4	-0.5
^{109}Cd	50471.0	50639	-0.3
^{57}Co	1325.7	1343.2	-1.3
^{139}Ce	1761.1	1749.7	0.7
^{203}Hg	4225.6	4224.5	0.0
^{113}Sn	2768.5	2715.6	1.9
^{134}Cs	2583.1	6183.2	-58.2
^{137}Cs	1482.6	1476.4	0.4
^{54}Mn	3496.1	3521.8	-0.7
^{65}Zn	9292.2	9245.1	0.5
^{88}Y	4177.8	6563	-36.3

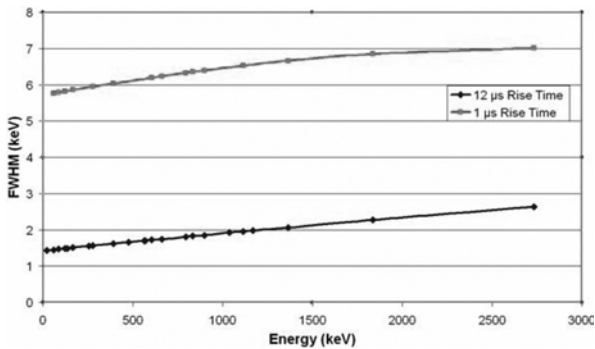


Figure 6 Resolution for Different Rise Times as a Function of Energy

The same spectrum was calibrated for efficiency (using the energy calibration above) using the true coincidence correction feature (TCC) of GammaVision. The TCC calibration includes ¹³⁴Cs and ⁸⁸Y, as well as all of the other nuclides in the source. With this calibration, it is possible to account for the cascade summing in the calibration and correct the net peak areas for the loss of counts due to cascade summing. The analysis will utilize peaks in the spectrum from the summing of two or more primary gamma rays and escape peaks (where a 511 keV gamma ray leaves the active volume of the detector) thus increasing the accuracy of the results. Table 2 shows the analysis results using this calibration along with the declared activities. Note that the activity of ¹³⁴Cs and ⁸⁸Y are much closer to the declared values than the analysis that did not considering coincidence summing. This calibration is valid to the low energy of 59 keV and is extrapolated to energies below that value. The activity of ¹³⁹Ce is over reported by 9.6% because of the over correction for the summing of the 163 keV gamma ray and the 33 keV X-ray. A more accurate correction can be obtained using the 2-source method described by Blaauw.

Table 2 Comparison of Calculated and Known Activity Using True Coincidence Correction

Nuclide	Measured Activity	Known Activity	Difference (%)
²⁴¹ Am	5539.3	5571.4	-0.6
¹⁰⁹ Cd	52351.0	50639	3.4
⁵⁷ Co	1328.0	1343.2	-1.1
¹³⁹ Ce	1918.2	1749.7	9.6
²⁰³ Hg	3998.5	4224.5	-5.3
¹¹³ Sn	2632.6	2715.6	-3.1
¹³⁴ Cs	6095.2	6183.2	-1.4
¹³⁷ Cs	1459.0	1476.4	-1.2
⁵⁴ Mn	3509.6	3521.8	-0.3
⁶⁵ Zn	9057.2	9245.1	-2.0
⁸⁸ Y	6826.7	6563	4.0

Table 3 Minimum Detectable Activity (mBq) for Various Counting Times and Nuclides

Time (hours)	⁶⁰ Co mBq	¹³³ Ba mBq	¹³⁷ Cs mBq	²¹⁰ Pb mBq	²¹⁴ Bi mBq	²³⁵ U mBq	²⁴¹ Am mBq
43	1.06	0.81	0.89	7.34	2.04	0.55	0.72
111	0.68	0.51	0.56	4.61	1.26	0.34	0.45
200	0.49	0.38	0.42	3.45	0.94	0.25	0.33
333	0.37	0.29	0.32	2.66	0.72	0.20	0.26
406	0.34	0.27	0.29	2.42	0.66	0.18	0.23
560	0.29	0.23	0.25	2.06	0.56	0.15	0.20
611	0.28	0.22	0.24	1.97	0.53	0.15	0.19
833	0.24	0.19	0.20	1.69	0.46	0.12	0.16
944	0.22	0.18	0.19	1.58	0.43	0.12	0.15

Using the TCC calibration and the background spectrum, the MDAs were calculated using the KTA Rule formula. The KTA Rule formula was chosen because it is relatively simple, uses a fixed width (based on the FWHM) for the peak region, and is similar to the methods used in many areas of the world. The nuclides considered were ²¹⁰Pb, ²⁴¹Am,

^{214}Bi , ^{137}Cs , ^{235}U , and ^{60}Co . Table 3 and Fig. 7 show the MDA values for these nuclides as a function of counting time. Note that the MDA depends on the nuclide yield for the gamma rays used to calculate MDA (typically the most intense), the efficiency and background count rate at that energy, and the counting time. The major contribution to the low measured values is the high efficiency of the well detector, especially for low energies.

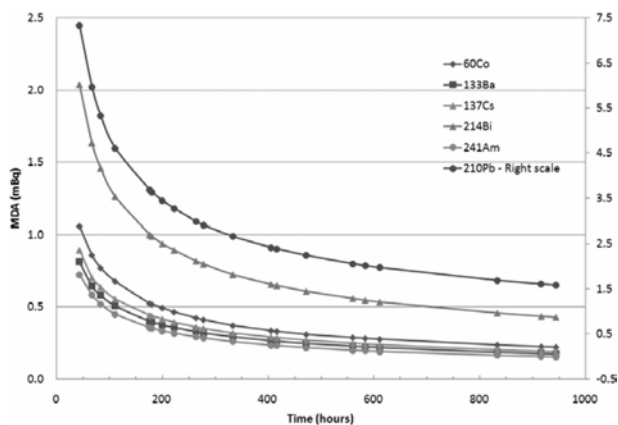


Figure 7 MDA vs Time for Several Nuclides

4 CONCLUSIONS

The HPGe well detector with copper endcap and cup, and carbon fiber well tube is a highly efficient detector for low energies and has acceptable efficiency for energies above 400 keV. The carbon fiber well tube transmission improves the efficiency over the traditional aluminum thin wall tube by a factor of 95 at 10 keV. The transmissions are about equal above 60 keV. This converts to an improvement in the MDA for ^{210}Pb of about 2.5% and about 5.8% for ^{125}I with the carbon fiber. The reduction in the attenuation of low-energy X- and gamma-rays does increase both the random and coincidence summing. Calibration and data collection for the low-energy gamma rays must be done at low countrate to reduce the random summing. However, TCS depends on the nuclide decay scheme and not on count rate. Thus, the TCC calibration method is necessary for most situations because of the high low energy efficiency. To accumulate useable spectra, the use of absorbers during efficiency calibration for energies above 200 keV to limit the dead time and pileup is recommended. A separate efficiency calibration for low energies requires calibrated sources with low energy gamma rays and low activities. The two calibrations are then combined.

One important reason for using well detectors is to reduce the MDA to the required low value for environmental and forensic studies. The close geometry does increase the efficiency, but it also increases the impact of TCS on the results. The GammaVision TCC method for calibration and activity calculation allow the use of these detectors for low-count, small sample studies to produce the lowest MDAs possible.

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INTERLABORATORY COMPARISON ON THE DETERMINATION OF RADIO-NUCLIDES IN RAW MILK IN THE YEAR 2008

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1 INTRODUCTION

The coordinating laboratory for the surveillance of environmental radioactivity in the Max Rubner-Institut in Kiel is part of the German “integrated measurement and information system for monitoring radioactivity in the environment” (IMIS). Within IMIS the laboratory is responsible for the surveillance of man-made radionuclides in soil, vegetation, fodder and foodstuffs of animal or plant origin. The activities of the laboratory are defined by the Precautionary Radiation Protection Act of 1986 and by the Ordinance on Radiation Protection of 2002 and by the Guidelines for Monitoring the Emissions and Immissions from nuclear facilities. This legislation stipulates that the laboratory should organize and carry out interlaboratory comparison exercises (ring experiments) on the environmental sample types for which it is responsible. The ring experiments aid to improve the quality of measurements in environmental monitoring programmes. Such measurements are important in assessing the dose to the public by the food chain and in a nuclear accident situation would be important in making decisions on radiation protection measures.

Mandatory participants in the ring experiments are the official monitoring laboratories of the 16 German federal states (Laender). However, for the sake of comparison other radioactivity measurement laboratories at nuclear facilities, in industry, in research in Germany and in neighbouring countries are also invited to participate.

The ring experiments are carried out in collaboration with the Physikalisch-Technische Bundesanstalt (PTB) in Braunschweig. The PTB is the national metrology institute in Germany and determines reference values for the activity concentrations of the nuclides of interest in the sample material.

In the year 2008 raw milk was chosen as the sample material because it is an important basic foodstuff, particularly for infants, and is a useful indicator for radioactive contamination of the environment. The following nuclides were added to the milk samples: strontium-89 (Sr-89), strontium-90 (Sr-90), iodine-131 (I-131), caesium-134 (Cs-134) and caesium 137 (Cs-137). These are the most relevant nuclides in milk in the event of contamination of the environment with nuclear fallout. The participants were requested to determine the strontium nuclides by β -measurement after radiochemical separation while the others along with ubiquitous and naturally present potassium-40 (K-40) were to be determined by γ -spectrometry.

73 laboratories participated in the exercise: 58 from Germany, 5 from the United Kingdom, 3 each from The Netherlands and Switzerland and 1 each from Austria, France, Italy and Luxembourg.

2 EXPERIMENTAL

2.1 Sample Preparation

Sample material: Fresh raw milk was obtained from the experimental farm of the MRI at Schaedtbek, homogenized then conserved with sodium azide (0.018 % relative to the total samples mass). The milk was kept at 20°C under gentle stirring until spiking with the radionuclide mixture was completed. Throughout this period the milk remained homogenous.

Mixed radionuclide stock solution: a few ml of each of aqueous standard solutions of the radionuclides Sr-89, Sr-90, I-131, Cs-134 and Cs-137 were transferred by pipette to a standard 1 Litre volumetric flask. Each standard solution contained about 2 to 6 ug of the appropriate carrier per ml solution. The standards were traceable to standards of the PTB. Finally the mixed standards in the volumetric flask were diluted to 1 litre with skimmed UHT milk. The pH-value of this stock solution was in the range 6.8 to 7.0.

Spike addition of sample material with the radionuclides: Each approximately 1.1 litre sample for the participants was prepared directly on an electrical single-pan balance (weighing uncertainty less than 0.2%, $k = 2$) as follows: The sample container was placed on the balance then 8.0 ml of the mixed radionuclide stock solution were added. 1200 g of the conserved, homogenized raw milk were then weighed into the container. (The exact mass of the addition was noted). The samples were immediately dispatched to the participants as well as to the PTB for reference value determination.

2.2 Evaluation of Reported Measurement Data

Data transformation and normalization was carried out to correct the activity concentrations for the slightly different amounts of milk weighed into each sample container. The corrections, however, were in all cases less than 1.2% and therefore almost insignificant relative to the measurement uncertainty incurred in nuclide counting and in the radiochemical separation. This correction was of course unnecessary for natural K-40.

The data for assessing the results of the interlaboratory comparison were calculated according to DIN/ISO 5725 and DIN 38402-42. The relevant terms, symbols and formulae are summarized in the appendix. First the general mean and the standard deviation were calculated. Then all single values (triplicates were requested) and measurement values that differed from the reference value by more than 2.58-fold the standard deviation of the general mean were considered as outliers and eliminated. This procedure was repeated until no outliers occurred.

The general mean $\bar{x}_i$ and the reproducibility standard deviation (S_R) in Table 1 were calculated from the outlier-free data. Z-scores were calculated for all laboratory means including outliers according to ISO Guide 43-1 [^{3,4}]. However, as the general mean and the reference values differed strongly for some nuclides the z-scores were calculated relative to the reference value as well as to the general mean.

3 RESULTS

The PTB reference values and the general results of the interlaboratory comparison are summarized in table 1. Figure 1 shows the frequency distributions of various deviations of the laboratory means from the PTB reference values for each nuclide. Outliers are included in this representation. The vertical dashed line in the middle of these diagrams indicates the position on the axis of no difference from the PTB reference value i.e. ($\bar{x}_i$ - ref = 0). Thus, bias in the distribution of the results (implying some systematic error) may be readily recognized.

Table 1 Summary of results from the interlaboratory comparison

Quantity	Pure β -emitters		γ -emitters			
	Sr-89	Sr-90	K-40	I-131	Cs-134	Cs-137
PTB reference value (ref) [Bq/L]	19.2	4.80	50.7	272	18.2	4.93
expanded uncertainty, (U; k = 2) [Bq/L]	1.0	0.2	1.6	9	0.6	0.15
Outliers [%]	8.5	18.3	8.5	16.6	16.4	8.0
data sets w/o outliers	15	32	77	69	71	79
replicates w/o outliers	43	94	226	206	209	231
minimum value [Bq/L]	13.4	3.3	43.4	248	15.9	4.33
maximum value [Bq/L]	24.5	6.4	59.3	295	20.1	5.48
average absolute deviation from ref [%]	11.3	10.8	4.8	3.1	5.4	3.8
minimum deviation from ref [%]	1.7	0.0	0.1	-0.1	0.0	-0.1
maximum deviation from ref [%]	-29.2	26.5	15.0	-8.4	-12.4	-9.4
general means [Bq/L]	18.9	4.5	50.6	270	17.4	4.82
std. dev. [Bq/L]	2.9	0.6	3.3	10	0.9	0.23
repeatability std. dev. (s_r) [Bq/L]	1.2	0.3	1.8	4	0.3	0.13
coefficient of variation [%]	6.3	6.0	3.5	1.3	1.5	2.8
reproducibility std. dev. (s_R) [Bq/L]	2.9	0.6	3.4	10	0.9	0.23
coefficient of variation [%]	15.5	14.1	6.6	3.9	5.2	4.8
Average recovery [%]	98.5	94.2	99.8	99.1	95.6	97.9

Detailed representations of all results for each nuclide are available from the authors on request.

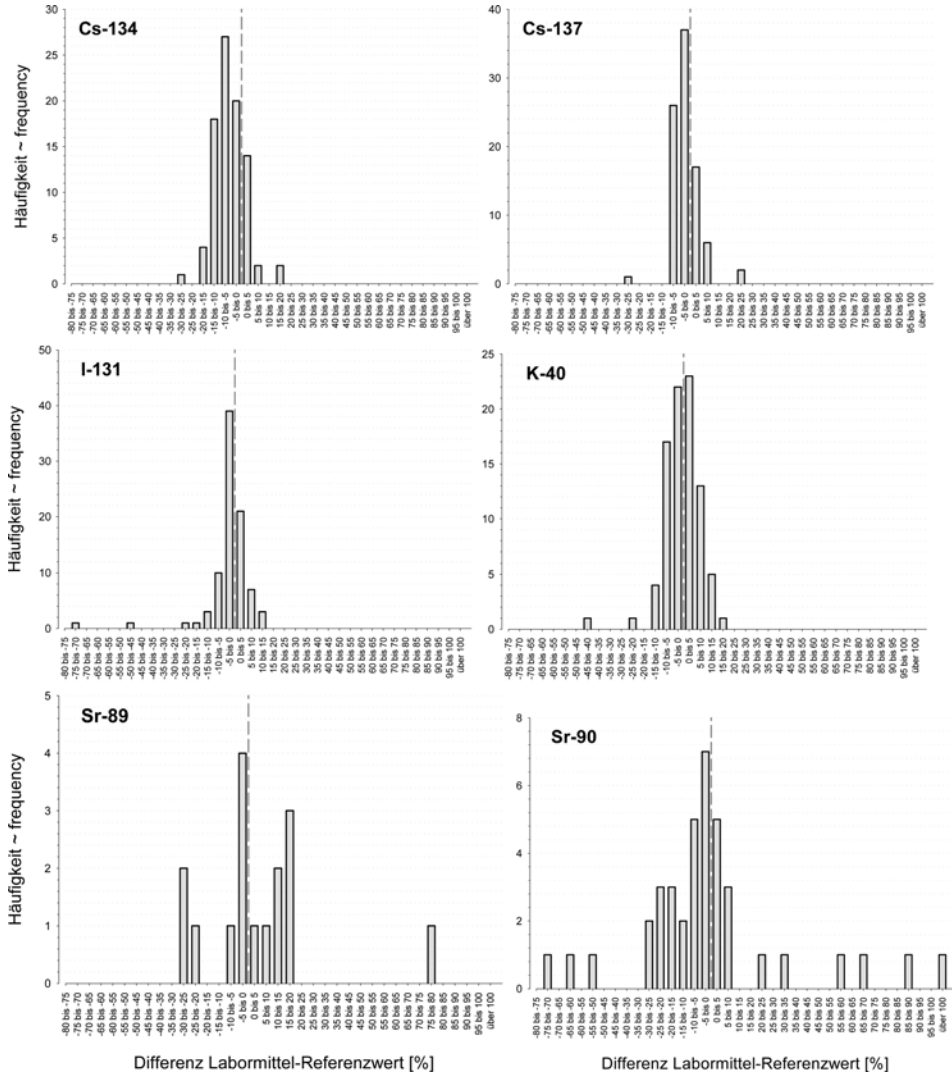


Figure 1 Distributions of the frequencies of different classes of the relative deviation of laboratory means from the reference value in percent: $(\bar{x}_i - \text{ref}) / \text{ref} \cdot 100$.

A useful method for assessing the quality of the submitted results is to calculate the so-called z-scores (see the appendix for the equations and reference 3). Table 2 shows the distribution of the z-score ranges for the different nuclides. According to the z-score classification scheme the quality of results may assigned as follows:

- $0 \leq z \leq 1$: good result
- $1 < z \leq 2$: satisfactory result
- $2 < z \leq 3$: questionable result
- $z > 3$: very questionable result

Table 2 Percentual distribution of z-score ranges i.e. (number of data sets in given z-score range / number of data sets) · 100, for each nuclide.

z-score range	Fraction of values (in percent) in range for nuclide					
	K-40	Sr-89	Sr-90	I-131	Cs-134	Cs-137
Less than -3	2	0	8	6	3	1
-3 to -2	2	0	10	3	16	0
-2 to -1	11	19	15	18	35	31
0 to -1	36	31	31	37	25	39
0 to 1	33	25	21	23	16	19
1 to 2	11	19	0	9	2	7
2 to 3	2	0	5	2	1	0
greater than 3	1	6	10	1	1	2

When $z(ref) > 2$, it is advisable to check the analysis procedure

4 DISCUSSION OF RESULTS

4.1 Gamma-emitters

4.1.1 Potassium 40. 21 outliers were eliminated prior to evaluating the results for K-40. Although the activity concentration is relatively large the values for repeatability (r) and reproducibility (R) are also greater than for the other nuclides. This is explainable by the relatively small emission probability (11 %) and detector efficiency for the 1460 keV photon. Additionally, the count rate of K-40 in the sample must be corrected for the background K-40 signal caused by inefficient shielding of the detector from the radiation of building and construction materials i.e. the relative amount of correction required differs with the construction of the detector, the shielding and the surrounding materials.

4.1.2 Iodine-131. Almost 17 % of the values were identified as outliers. This large outlier fraction may be explained by the fact that this short lived nuclide ($t_{1/2} = 8$ days) is not detectable in normal environmental samples and is therefore not routinely evaluated. Several outliers may be explainable by inadequate correction for decay prior to and during the measurement. The smallest reported value (80 Bq / l) was determined with a NaI scintillation detector while all others were obtained with the aid of HpGe or GeLi detectors.

Repeatability (r) and reproducibility (R) values were smaller than for those of all other nuclides. Such good values for the outlier-free data collective probably results from the large activity concentration (268 Bq I-131 / l milk on the reference date of the sample) and the fact that the I-131 gamma spectrum shows several strong and readily measurable peaks.

4.1.3 Caesium-134. More than 16 % of the reported values were outliers, most of which (87 %) were underestimations. Of the remaining data most underestimated the reference value by 5 to 10 %. This probably results from insufficient correction of coincidence summation effects in the analysis of the gamma spectrum of Cs-134. Considerable losses to coincidence summation occur for all main gamma emission lines e.g. the peaks resulting from the summation of the 605 keV and 796 keV photons are usually significant. The size of the losses, however, is strongly influenced by the geometry of the measurement set up. The losses decrease the measured count rate of the analyzed photopeak and thus to underestimation of the activity concentration of the radionuclide. Only 61% of the participants claimed to have applied corrections for these effects.

As a result of these differences in spectrum evaluation the reproducibility standard deviation (s_R) is relatively large. For example, it is considerably greater than the value for Cs-137 although the count statistical uncertainty - because of the much smaller count rate - for this nuclide is considerably greater than for Cs-134. The value for repeatability (r), on the other hand, is relatively small since in each laboratory the observed count rates are treated similarly.

4.1.4 Caesium 137. The smallest proportion of outliers were observed for this nuclide. The decay of Cs-137 is followed by the emission of a single photon with large emission probability (85%) with an energy of 662 keV that is free of interferences and readily measurable by HpGe and GeLi detectors. In addition this is the most commonly measured radionuclide in environmental samples for radioactivity surveillance. The mean relative deviation from the reference value was only 4% whereby most laboratories underestimated the value.

4.2 Pure Beta-emitters

4.2.1 Strontium-89. After eliminating the outliers the remaining measurement values showed the greatest amount of scatter (relative reproducibility standard deviation of 15.5%) of all nuclide measurements. Accordingly the values for repeatability (r) and reproducibility (R) were also greater than for all other nuclides. The requirements of radiochemical separation as well as complex calculation of results make this analysis difficult. Furthermore only few laboratories routinely carry out Sr-89 analyses.

4.2.2 Strontium-90. The largest proportion of outliers (more than 18%) was observed for the Sr-90 measurement data. Prior to eliminating the outliers the mean relative deviation from the reference value was 24.2%. Without outliers this value decreased to 10.8%. The coefficients of variation of reproducibility with and without outliers were respectively 42 and 14%. As for Sr-89 radiochemical separation is needed for Sr-90 determination and furthermore the calculation of results is more complex because the interfering Sr-89 must be accounted for and corrected.

4.3 General Summary

In general most participants reported at least satisfactory results. This is supported by the distribution of z-score classes summarized in Table 2. According to the classification scheme above the best results were obtained for Cs-137 with 97% satisfactory or good ($-2 < z \leq 2$).

The intra-laboratory scatter is for all gamma nuclides relatively small (coefficient of repeatability less than 4%), implying that during measurement the milk sample remained stable and homogenous, because the observed count rates would be expected to be sensitive to phase separation in the milk owing to the different solubilities of the nuclides in the phases.

The best overall agreement with the reference value was obtained for K-40. Here the general mean and reference values were almost the same and under- as well as overestimates were equally distributed about the reference value (see figure 1). In contrast the mean underestimations of the reference values for Sr-90 and Cs-134 were about 5%.

In the case of Cs-134 this mean level of underestimation is considerably less than in a similar intercomparison study carried out with infant food in 2005 that showed a mean underestimation for Cs-134 of 10 to 15%. This implies that more laboratories now use corrections for coincidence summation or the quality of these corrections has improved.

While almost 90 data sets were reported for each of the γ -emitters only 16 and 39 were reported for the pure β -emitters Sr-89 and Sr-90 respectively. The coefficients of repeatability and reproducibility were greater than 10% for these two nuclides, i.e. considerably larger than for the γ -emitters. This is caused by the need for radiochemical separations prior to β -counting and the determination of the chemical yield of the separations. Furthermore, the measurement procedure is more complex owing to the broad energy spectra of the emitted β -particles. Although the activity of Sr-89 was 4-fold greater than that of Sr-90 the results were substantially poorer. Only very few laboratories seem to have capability and competence in this type of analysis.

Of the 39 reported values for Sr-90 only 5 were determined by liquid scintillation counting (LSC). In a similar ring experiment in the year 2005 on baby food only 3 such determinations were reported. The results determined by LSC do not differ significantly from the others. The particular significance of the LSC measurement technique is that it allows the simultaneous determination of Sr-89 and Sr-90 in a single measurement independent of the equilibrium situation of Sr-90 with daughter Y-90, i.e. it is a relatively fast technique.

The overall results of the study for gamma-spectrometry are satisfactory and show in the case of Cs-134 substantial improvements relative to previous intercomparisons. This probably reflects the widespread use of improved, more standardized low-level detector systems and evaluation software with summation correction capacity. However, the study also shows up some deficiencies and lack of capacity in rapidly determining Sr-89 and Sr-90 together.

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APPENDIX

Symbols, Variables and Formulae

Symbol	Meaning	Formula, Details
p'	Number of laboratories/data sets	
p	Number of laboratories/data sets without single values and outliers	
i	Consecutive numbering of laboratories or data sets	$i = 1, 2, \dots, p$
N'	Total number of reported values	$\sum_{i=1}^p n_i$
N	Total number of reported values without single values and outliers	$\sum_{i=1}^p n_i$
n_i	Number of repetitions for lab. i	
x_{ik}	Value number k in lab. i	$k = 1, 2, \dots, n_i$
$\bar{x}_i$	Laboratory mean	$\frac{1}{n_i} \sum_{k=1}^{n_i} x_{ik}$
$\bar{x}$	General mean	$\frac{1}{N} \sum_{i=1}^p n_i \bar{x}_i$
$\bar{n}$	Average Number of repetitions per laboratory	$\frac{1}{p-1} \times \left(N - \frac{\sum_{i=1}^p n_i^2}{N} \right)$
s_r	Repeatability standard deviation	$\sqrt{\frac{1}{N-p} \sum_{i=1}^p (n_i - 1) s_i^2}$
s_L	Inter-laboratory standard deviation	$\sqrt{\frac{1}{n} \left(\frac{1}{p-1} \sum_{i=1}^p n_i (\bar{x}_i - \bar{x})^2 - s_r^2 \right)}$
s_R	Reproducibility standard deviation	$\sqrt{s_r^2 + s_L^2}$
r	Repeatability	$2,8 \times s_r$
R	Reproducibility	$2,8 \times s_R$
ref	Assigned (reference) value	Determined by the PTB
WFR	Average agreement with assigned value	$\frac{\bar{x}}{ref} \times 100\%$
$z(ref)$	z-score, relative to assigned value	$\frac{\bar{x}_i - ref}{s_R}$
$z(\bar{x})$	z-score, relative to general mean	$\frac{\bar{x}_i - \bar{x}}{s_R}$

DEEP GEOLOGICAL DISPOSAL OF INTERMEDIATE AND LOW LEVEL WASTE IN UK: EXPERIMENTS TO DEMONSTRATE CHEMICAL CONTAINMENT. PART I

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1 INTRODUCTION

A range of geological disposal concepts have been developed in the UK and internationally that employ cementitious materials as one of the main barriers as part of a multi-barrier approach to providing safe and secure geological disposal of low and intermediate level wastes.¹ To complement the high-level isolation safety objective of geological disposal, cementitious materials provide containment of the radionuclides associated with the waste. Containment may be provided both by the characteristics of the wasteform and its container and by the characteristics of the other engineered barriers and the geological setting in which the facility is located. When used for the immobilisation of wastes, cement-based wasteform grouts, together with a suitable waste container, provide containment of radionuclides by limiting the release of radionuclides in groundwater. When employed as buffer and backfill materials, cement-based materials provide containment by creating a favourable chemical environment to limit corrosion of the waste container and by providing chemical and/or physical properties to limit the migration of radionuclides out of the engineered barrier system (note that the term buffer/backfill is here applied to any material that is put in contact with the emplaced waste in the geological disposal facility). Additionally, grouts will limit radionuclide solubility through the rapid achievement and maintenance of highly alkaline conditions through cement leaching mechanisms,^{2,3} which encourages precipitation of many radionuclides as hydroxides. If waste is mixed with anhydrous cements and water is present, there is a possibility that ions produced from the waste material incorporate into the cement during the hydration process. A waste ion may chemisorb, precipitate, form a surface compound to any of several cements component surfaces, form inclusions or be chemically incorporated into the cement structure, or have simultaneous occurrence of several of these situations.⁴ In cements the main binding phase is a calcium silicate hydrogel (C-S-H).⁵

One of the concepts under consideration in the UK for the disposal of intermediate and low level waste includes waste surrounded by grout and immobilised in steel containers. Waste containers would then be placed in disposal areas, and at some appropriate time, backfilled with a suitable candidate cementitious materials, such as the specially formulated hyperalkaline cement, NRVB (Nirex Reference Vault Backfill⁶). Following closure, the disposal area would eventually saturate, and the incoming groundwater would equilibrate with cement backfill resulting in the development of alkaline conditions.

Together with the corrosion of steel waste containers, which would lead to the establishment of reducing redox conditions, solubility limitation of some key safety relevant radionuclides would be achieved.

Also present in some ILW wastes are organic materials such as paper, wood and cotton that through alkaline degradation form water soluble organic compounds known as cellulose degradation products (CDP). These together with water soluble organic anthropogenic complexing agents already present in the wastes⁷ (such as citrate, EDTA and oxalate), are able to form complexes with disposed radioelements, potentially enhancing their migration and increasing the associated radiological risks.

As part of the on-going UK Nuclear Decommissioning Authority Radioactive Waste Management Directorate (NDA-RWMD) research and development programme to support geological disposal of radioactive waste, the Radiochemistry Group at Loughborough University have conducted a series of long-term experiments to demonstrate the concept of chemical containment by showing: (i) precipitation and solubility limitation in a representative high pH cement-conditioned near-field environment, (ii) solubility limitation through the development of a low redox environment and, (iii) sorption to a candidate backfill cement. The aim of the project is to provide confidence that these conditions will reduce the solubilities of a range of radionuclides and, that some radionuclides will be retarded by sorption onto the cement.

The radionuclides included in the project are Cs, Ni, Eu (as an analogue of Am and Cm), U and Th which are representative of +1, +2, +3, +4 (and +6) and +4 cations, and I as a representative anion. The project includes three types of experiments: (i) solubility experiments, using both oversaturation and undersaturation conditions; (ii) advection experiments in which the element of interest is passed through a column of NRVB and (iii) diffusion experiments in which the solute of interest is allowed to diffuse through NRVB. At the end of the duration of the column and diffusion experiments, the NRVB columns will be sliced and analysed to obtain diffusion and advection concentration profiles. Using the determined experimental data together with modelling studies, the profiles will be compared and the agreement of both sets of results would allow for reliable extrapolation to much longer timescales.

The project is expected to last 6 years. In the 1st stage (year 1) of the project, modelling and design of experimental techniques and methods have been conducted and, during the 2nd stage (5 years), long-term experiments will be conducted. Currently, the project is entering the second stage.

The aim of the present paper is to describe the development of the experimental strategy through a combination of scoping experiments carried so far at Loughborough University, and literature review of diffusion and advection studies that consider cement-based systems of relevance to ILW/LLW disposal concepts under consideration in the UK

1.1 Experiments to Demonstrate Containment Safety Functions Provided by a Cementitious-based ILW/LLW Geological Disposal Facility (GDF)

There are many examples in the literature reporting studies of the solubilities of key radionuclides under the alkaline conditions that are expected in a cement-based geological disposal facility, with⁸⁻¹³ or without^{8,14-21} the addition of anthropogenic complexants. There are also papers and reports on sorption studies to different cement components and formulations, both using batch²²⁻²⁷ and diffusion tests.²⁸⁻³³ All these experiments provide crucial information that is used to underpin the safety arguments made in post-closure

environment safety cases and associated performance assessment activities for cement-based ILW/LLW disposal facilities.

Transport of radionuclides from the near-field to the far-field of a geological disposal facility is possible by diffusive transport under water-saturated conditions or by advective transport. It is important to study and understand the processes involved in the transport of radionuclides to be able to differentiate between purely chemical and physical phenomena. Moreover, it is also essential to understand the changing nature of the cementitious material, and how the ageing of cement, both natural and induced by external factors (i.e. interactions with the radwaste, organic additives/waste or groundwater) can affect the mobility of radionuclides. Long term diffusion experiments would provide relevant information on the long-term sorption/mineralisation of radionuclides into the solid phase and changes of porosity caused by chemical reaction, precipitation on the surface, or cracking that cannot be obtained by simpler batch sorption experiments. In some cases distribution ratios (R_d values) derived from such diffusion studies have been found to be one order or magnitude lower than those obtained in batch sorption experiments, due to the higher specific surface area of crushed cement compared with cement monoliths.³⁴

Diffusion experiments provide fundamental information to support the performance assessment of a geological disposal facility. Diffusion can take place by different mechanisms depending on the initial boundary conditions and whether diffusivity is determined under steady state or non-steady state. Steady state diffusion can be determined by studying the mass transport from one solution to another separated by a slice of the solid, whereas non-steady state diffusion can be determined by studying the concentration profile in a solid after contact with a solution containing the species of interest. Several studies have been devoted to investigating the diffusion of key radionuclides using diverse experimental approaches: (i) in-diffusion^{28,29}, (ii) through-diffusion³⁰⁻³³ and (iii) out-diffusion or leaching.^{32,33} Note that all these experiments have been performed under water saturated conditions. However, some authors (see Wellman et al.³⁵) have pointed out that these tests may lead to conservative estimates, as changes in carbonation and wet-dry cycles could have an effect on the diffusion of contaminants.³⁶

In-diffusion experiments usually involve the moulding of the cementitious material followed by curing for a pre-established period of time, followed by covering the specimen with a thin layer of resin on all sides but one so as to limit the diffusion in the specimen to only one direction. Finally, the samples are placed in a container with a solution that has been spiked with a radionuclide. Andersson et al.^{28,37} performed an in-diffusion experiment for a period of 2-3 months to determine the diffusion coefficient of Cs and I in different waters (pore water, groundwater, Baltic seawater and seawater) and different added species (carbonate, sulphate and Mg). Albinsson et al.²⁹ applied this procedure to study the diffusion of Cs, Am and Pu into 5 different types of concrete in contact with pore water, over a period of time that ranged from 0.7 to 5 years. The subsequent grinding and analyses of the different layers of cement by autoradiography indicated no movement (< 0.2 mm) of Am and Pu. The diffusivity of Cs in the different materials was calculated from the results. Sugiyama et al.³⁴ studied the in-diffusion of U(VI) in Portland cement-based materials using the 'solid-in-filter' technique. A precipitate of the radionuclide of interest is formed on a 30 kDa MWCO filter that is in contact with the solution, maintaining a constant aqueous concentration at the solubility limit of the diffusing element. The in-diffusion proceeded during 13 months, after which the concentration profile of U was determined by laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

In through-diffusion experiments, after moulding and curing of the cement specimens, the samples are located between two cells or compartments. In one compartment is a

solution that has been spiked with radionuclides. Extensive studies have been carried out at the Paul Scherrer Institute (Villigen, Switzerland) on the diffusion of ^{36}Cl , ^{125}I and ^{134}Cs ³⁰, ^{36}Cl , ^{63}Ni , ^{125}I and ^{241}Am ³², tritiated water (HTO) and $^{22}\text{Na}^{+}$ ^{33,38} using through-diffusion. Sarrot and co-workers³⁰ observed that when the tests were carried out under atmospheric conditions, there was a significant reduction in the diffusion rate over a period of 170 days, due to carbonation. This agrees with the results of a later study by Chida et al.³⁹, who investigated the diffusion of ^{129}I and ^{14}C (as acetate) through low heat Portland cement over a period of 1-15 months. They observed that the rate of diffusion decreased over the experimental period probably because the changes in the microstructure resulting from the pozzolanic reaction (i.e., formation of calcium silicate hydrates). In another study by Shafique et al.⁴⁰ whereas carbonation slowed the diffusion of Sr, the alteration of the cement increased the release of NO_3^- , Ca, Cd, Pb and Co. They concluded that carbonation lead to a decrease in physical retention despite the diminution in porosity. The reduction in physical retention could indicate microcracking and/or the rearrangement of pores which removes or decreases occluded areas. The net result of carbonation will depend on the specific element of interest. Baker and co-workers⁴¹ reported the work on the diffusion of Th, U(VI) and Pu through NTVB disc, in presence and absence of isosacarinic acid (ISA) or leachate from the alkaline degradation of cellulose (CDPs). After the completion of the experiments the depth-profiling of the radionuclides was determined by incremental grinding and quantification of total actinide concentration by dissolution of full-depth fragments of the discs. In the case of Pu, the Rd values determined in batch studies were higher than in the diffusion experiments, whereas the Rd values for U(VI) showed the opposite trend. However, the authors concluded that no significance can be assigned to the differences found, due to the experimental variability.

In the leaching or out-diffusion experiments, the radionuclides are premixed with the cement prior to moulding and the release of radionuclides is measured after submerging the samples in a solution of interest. In some cases, a leaching test would follow an in-diffusion of through-diffusion experiment³³ in order to test the suitability of the models used to describe through-diffusion. By putting the cement in contact with a radionuclide-free solution, the cement leaches gradually and, from the shape of both nuclide fluxes (in and out), it may be possible to determine the radionuclide distribution in the steady-state.³² Standard procedures, such as the dynamic leach test ANSI/ANS 16.1⁴² or the IAEA proposal⁴³ have been used for leaching tests which involve putting the cement specimen in contact with demineralised water and replacing the solution after designated periods of time. However, these experiments do not provide a realistic insight into the potential conditions in the repository and they can only be used for indexing the radionuclide release and not for defining the long term leaching behaviour. The ANSI/ANS 16.1 procedure has been used to assess the release of Cs and Co from cement-solidified waste produced at a Korean nuclear power plant⁴⁴ and at the Pacific Northwest National Laboratory (PNNL) for leaching of ^{129}I , ^{99}Tc and U⁴⁵, and ^{99}Tc , Cr and Mo from concrete.⁴⁶ At PNNL, the ANSI/ANS 16.1 method was modified by using actual groundwater from the Hanford site (USA) instead of demineralised water. Papdokostaki and Savidou⁴⁷ used the IAEA method at two temperatures, 30°C and 70°C, to study the leaching mechanism of Cr from OPC over a period of 8 years. They observed that in the long-term, the leaching of Cs was accelerated due to the increase in porosity from leaching of the cement matrix (more noticeable at 70°C). Therefore, they concluded that the mechanism of leaching cannot be described only by simple diffusion and other factors such as changes in structure induced by the environment must be considered.

In an environment of low groundwater flow, radionuclide release from the wasteform would be dominated by dissolution kinetics in the short-term until some-saturation would be reached, corresponding to the stabilisation and precipitation of solid phase(s)

incorporating the element of interest. The solubility of key radionuclides has been extensively studied under alkaline conditions, in Ca(OH)_2 ¹⁸, $\text{Ca(OH)}_2 + \text{NaOH}$ ⁸ and in NaOH ^{5,14,16,17,19-21}, in the presence and absence of anthropogenic organic complexants⁸⁻¹² or cellulose degradation products.^{48,49} However, the use of representation of NaOH or Ca(OH)_2 solutions is simplistic and the use of pore waters or cement equilibrated waters would give a better insight into the solubility and species present in repository conditions. For example, Wieland and co-workers⁵⁰ suggested that in the case of Ni, $\beta\text{-Ni(OH)}_2$ may not be the solid phase limiting the concentration of Ni, and that Ni-Al layered double hydroxides could be involved in controlling the Ni concentration in cementations systems. Greenfield and co-workers⁵¹ investigated the solubility of Ni, Tc, Sn, Th, U(IV), U(VI), Pu and Am in cement–equilibrated waters (NRVB and 1:9 ordinary Portland cement : blast furnace slag). In the case of U(VI), they concluded that the concentration of Ca ion in solution influenced its solubility, which would explain the differences in solubility between the solubilities measured in the two cement-equilibrate waters. The author also reported solubilities one order of magnitude lower for Ni and Th in NRVB than other cementitious materials.⁵¹

1.2 NRVB Characteristics

The Nirex Reference Vault Backfill (NRVB) is a mixture of ordinary Portland cement (OPC) (26% w/w), hydrated lime (calcium hydroxide) (9.8% w/w) and limestone flour (28.6% w/w). The backfill was formulated to provide the following requirements⁵²: (i) long-term maintenance of alkaline pore water chemistry, i.e. pH buffering; (ii) long-term maintenance of a high surface area for radionuclide sorption and (iii) relatively high permeability and porosity to facilitate homogeneous performance. The high fractional porosity is achieved by the addition of a high water content in the mix (35.6% w/w). The presence of hydrated lime to OPC increases the proportion of portlandite in the hydrated materials, and therefore enhances its buffering capacity. The function of the limestone flour is to act as inert filler to limit compressive strength of the material, to improve the flow properties and to reduce the bleed in the fresh grout.³¹

The water permeability coefficient of NRVB lies in the range from $6 \cdot 10^{-17}$ to $3 \cdot 10^{-16} \text{ m}^2$. The fractional porosity is 0.55 and the average porous diameter is $0.45 \text{ }\mu\text{m}$.³¹

After hydration of NRVB, the major phases present in the cement are calcium hydroxide (both from the original lime and as product of the hydration of calcium silicate), calcium silicate hydrate gel (CSH), aluminate phases, monocarboaluminate and hydrotalcite.⁵³

2 DESCRIPTION OF THE EXPERIMENTS

2.1. Diffusion

The use of a through-diffusion (steady state diffusion) technique has the advantage of the simultaneous determination of the diffusion and retardation properties of the solid. The method used in this study is similar to the ‘solid-in-filter’ technique developed by Gardiner and co-workers⁵⁴ to study the sorption of Am and Pu onto magnesium hydroxide, zirconium hydroxide, colloidal magnetite and colloidal haematite. This technique has been later applied by Sugiyama et al. for the study on diffusion of U in cement³⁴. Figure 1 shows a simplified schematic of the experimental setup. In this setup, the ‘source’ cell contains a solution saturated with U, Th, Ni and Eu, in contact with their precipitates. As the elements diffuse through the NRVB, the re-dissolution of the precipitate will keep a

constant aqueous concentration at the solubility limits of the elements. The resin coated cement monoliths will be put in place and left to equilibrate with the artificial pore water for a period of at least 7 days. In this kind of setup it is important to keep the solution in both cells at the same level to avoid any gradient of hydrostatic pressure that would disturb molecular diffusion through the cement. After equilibrating, one of the cells will be spiked and the levels will be readjusted.

The concentration of metals, and the pH and Eh, will be measured in both reservoirs on a monthly basis over a period of 48 months. In the case of I and Cs, this approach is not possible. As the diffusion of these two elements is expected to be faster than the others, a more regular daily sampling is planned for the first 3 months of the experiments, during which the breakthrough of these elements is expected. Monitoring will provide data to model the fast decrease of concentration in the 'source' cell and, diffusion through the cement. Note that the diffusion experiments would be conducted simultaneously for all of the elements.

The preparation of the solutions, as well as the through-diffusion experiments will be carried out in a nitrogen-filled glovebox, to remove possible carbonation and to prevent any further changes not only in the solution but also in the microstructure of the cement.

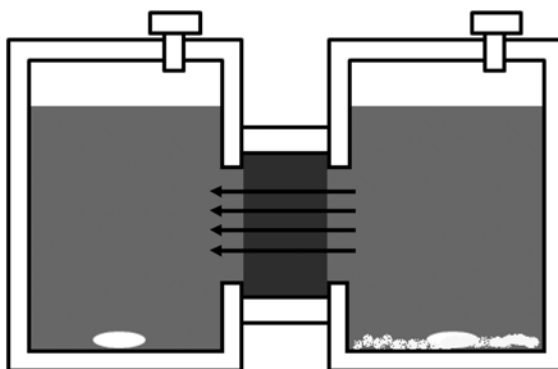


Figure 1 Sketch of the apparatus to perform through-diffusion experiments

Cellulosic wastes, including paper, tissues, filters, cloth and wood form a significant part of the organic materials present in ILW and LLW in the UK. Consideration of cellulose and its degradations products is important in safety assessment as these organics can act as complexants for key radionuclides. The degradation of cellulose can take place by radiolytic, microbial or chemical degradation.⁵⁵ However, the magnitude of cellulose degradation by alkaline degradation is far greater than that by radiolytic degradation.^{56,57} Therefore, within the main objectives of this project, another series of through-diffusion experiments will be carried out in which the artificial pore water will be spiked with cellulose degradation products (CDPs). The CDPs will be produced from tissue papers as starting material, following the procedure described in a report published by NDA-RWMD.⁵⁸ Using these conditions, to produce 10% (w.w) cellulose load CDPs, 30 g of cellulosic material were mixed with 270 g of NRVB in a stainless steel container and 750 cm³ N₂-sparged water were added before re-sparging the mixture. The mixture was then placed in an oven for 30 days at 80°C, after which the solution was filtered in a N₂-atmosphere before use. In the diffusion experiments both cells will contain the same amount of CDPs and the solution will be left to equilibrate with the cement specimen before spiking of the cells with the elements.

Measurement of the concentrations of the elements in the two cells will be performed regularly and at the end of the experiment, the concentration profile along the cement specimen will be determined by ICP-MS.

2.2 Advection

Despite the abundance of reports in the literature on studies of sorption of metals to cement and on leaching and diffusion, no reports of advection experiments through intact cement monoliths have been found pertaining to radioactive waste disposal. This may be because of the difficulties of working with a material that evolves with time and, because of the possibility that these changes are accelerated in a flowing system.

The proposed advection experiment is shown Figure 2. A NRVB-equilibrated solution, oversaturated with the elements of interest will be pumped through a cylindrical monolith of NRVB. The solution at the outlet of the column will be recirculated to a reservoir where it will be saturated again with the metals and pumped into the column. Measurement of the concentration of the elements in the reservoir and at the column outlet will be performed regularly. At the end of the experiment (4 years), the concentration profile along the cement specimen will be determined by ICP-MS after grinding off thin slices of the column. Complementary, non-destructive techniques such as SEM and XRD will be used to assess the radial distribution of the metals in the column as well as to provide information on the mineralogy. In another set of experiments, the solution recirculated through the column will be spiked with CDPs.

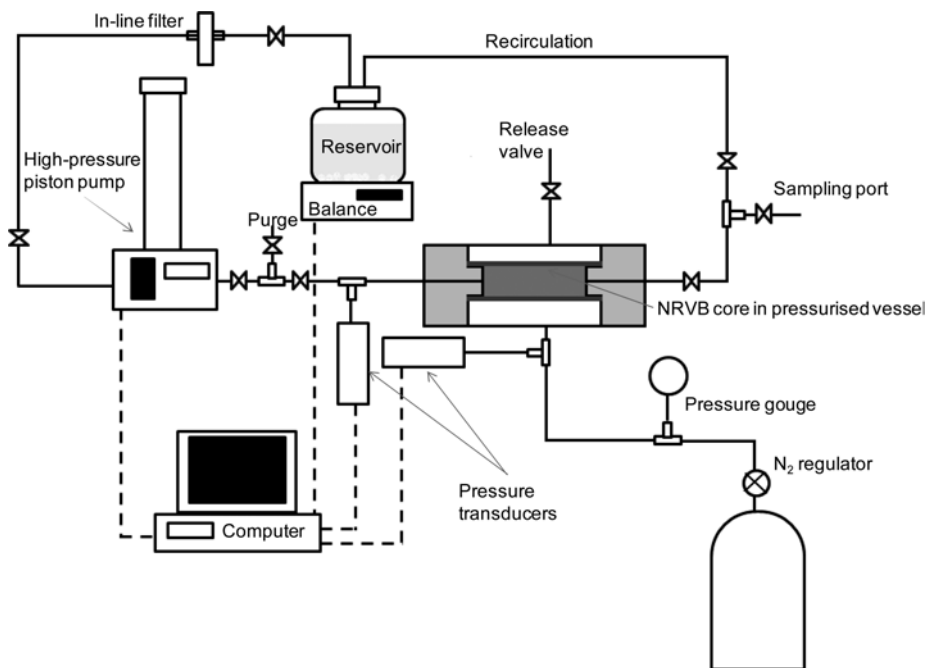


Figure 2 Schematic of the setting of the advection experiments

2.3 Solubility

Whereas in the advection and diffusion experiments the solution in contact with the cement is NRVB-equilibrated water, in the solubility experiments a range of solutions will be used. Solubility will be studied in saturated $\text{Ca}(\text{OH})_2$, NaOH $\text{pH}=12.3$, NRVB-equilibrated water and NRVB-equilibrated water with added CDPs. The aim is to assess the solubility of the elements and to understand the mechanisms and phases controlling the concentration in solution from very simple systems to more complex (more realistic) solutions. This project proposes to adopt a rigorous approach to the solubility limits and the demonstration of the chemical containments concept. In equilibrium experiments, the attainment of equilibrium is proved by showing that the solubility is reversible. Therefore, the equilibrium will be approached from undersaturation and oversaturation directions. In the first case an excess of the element of interest in its solid form as oxide or hydroxide is contacted with a solution and let to dissolve up to saturation. Using oversaturation involves spiking the solution with an excess of the element and leaving it to precipitate. To establish the kinetics of the saturation, monthly samplings will be made of the liquid phase and the concentrations the elements of interest will be measured by ICP-MS. Moreover, the concentration of other components of the solution, such as, Na, Ca, and Al will be measured by ICP-MS and or ICP-OES to detect changes due to the formation of insoluble mixed phases. Additionally, structural techniques such as XRD and SEM in combination with EDS will be used not only to identify the new solid formed in the experiments, but also to assess any corrosion of the primary solids. The total duration of the experiment will be 4 years.

3 RESULTS OF THE TRIAL EXPERIMENTS AND DISCUSSION

Two main problems have been encountered during the trial tests of the advection and diffusion experiments; (i) shrinkage of the NRVB and (ii) changes in porosity and surface precipitation.

During the experiments, shrinkage of the cement monoliths was observed, which caused advective flows between the solid and the column container. In some other experiments, the experiment continued with no disturbances for a period of 2-3 months after which a drop in pressure was detected along the column which indicated either cracking or shrinkage of the monolith. A number of mechanisms have been described by Crossland⁵⁹ that can cause cement shrinkage and cracking. Causes of shrinkage such as plastic shrinkage originated by drying or settlement can be discarded because of the scale and conditions of the experiments, so our attention was focused on three other possible causes of shrinkage: (i) thermal changes, (ii) hydration and (iii) carbonation. The hydration of cement produces a pulse of heat that lasts only for a few days. Consequently the process of curing by immersion of the specimen in an excess of water would help to dissipate the heat, minimising the risk of cracks. The hydration itself can cause a reduction in the amount of water that is not fully compensated by the volume of the new solid. Even after the cement has set, it can carry on gaining strength by continued hydration using water from the pores. This leads to a further reduction in the volume called 'self-desiccation' and, depending on the water availability, there can be a further shrinkage known as autogenous. However, in cement pastes with a water:cement ratio higher than 0.5, such is the case of NRVB, autogenous shrinkage becomes insignificant.⁵⁹ The carbonation reaction causes shrinkage of the cement due to the preferential dissolution of crystals of calcium hydroxide under compressive stress and preferential precipitation of calcium

carbonate.⁵⁹ In the present work care was taken to avoid carbonation by using boiled and sparged solutions, preparing all solutions and performing all the experiments under N₂. Moreover, although carbonation requires water, if the solid is fully saturated with water it would become less permeable to gas and therefore less prone to carbonation,⁵⁹ which is the case in the present study. However, the risk of carbonation and therefore shrinkage persists, especially considering the duration of the experiment, and these problems have been taken into account when defining the experimental strategy.

The problem of the changes in volume can be overcome by selection of the curing conditions and by careful design of the experimental setup. To prevent shrinkage during the experiments, the cement must be fully hydrated as this will avoid or at least minimise hydration shrinkage during the experiment. Curing over a period of 28 of days is the accepted procedure and it has been observed that ca. 70% of alite (one of the calcium silicates of OPC) reacts within this period, whereas, in the same time, only 30% of other calcium silicate, belite, reacts to form calcium silicate gel and calcium hydroxide.⁵³ However, Jakob et al.³² observed that the permeability of high water:cement pastes strongly decreased during the first 2 months and then subsequently reached a constant value. Consequently they cured the cement for 2 months before performing through-diffusion experiments. Another aspect to take into account is the solution used for the curing of the cement specimens. It has been observed that cement pastes that have been cured in saturated Ca(OH)₂ showed two times lower diffusion coefficients than cement that was cured in 100% relative humidity.⁶⁰ Considering the above issues, the strategy adopted in the present study consists of curing NRVB over a period of at least 60 days in excess CO₂-free water in N₂ atmosphere. As the experiments themselves provide the cement with an unlimited amount of water that could potentially take hydration to further stages, the cement specimen will be covered with a shrinkable or flexible sleeve and the column will be placed in a pressurised vessel. This will prevent problems from further shrinkage. Examples can be found in the literature of advection experiments through non-porous soils⁶¹ or permeameter equipment^{62,63} which is suitable for the purposes of this project.

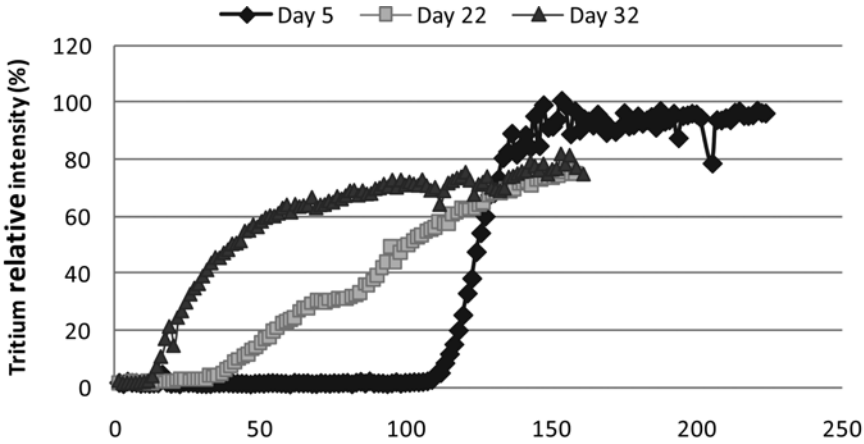
During the trial advection experiments a NRVB-equilibrated solution was pumped at a flow rate ranging from 0.025 cm³ min⁻¹ to 0.1 cm³ min⁻¹. The NRVB-equilibrated water was prepared under O₂- CO₂-free conditions, in a N₂-atmosphere glove box by constant shaking of DI water with NRVB at a liquid to solid ratio 50:1. After 7 days equilibration, the solution was pre-filtered and ultrafiltered before use. The composition of this NRVB-equilibrated water was determined by ICP-MS and ICP-OES and is shown in Table 1.

The experimental setup was kept in an inert atmosphere during operation. Consistently in all experiments, a decrease in porosity was observed during operation. The volume porosity of the cement column was determined by pumping HTO through the column (Figures 3.a and 3.b). At the end of the experiments, the examination of the column revealed the presence of a hard, crystalline white solid on the outlet surface of the column (Figure 4.a), whereas the inlet surface was free of precipitate and showed a smooth and soft appearance. The first suspicion was that calcite was precipitating but it was shown not to be the case by the use of scanning electron microscopy (SEM) analyses and the formation of calcium hydroxide, portlandite, was confirmed by X ray diffraction (XRD) (Figure 4.b).

Table 1 *Composition of the NRVB-equilibrated water used during the trial experiments*

Major components (mmol dm ⁻³)		Minor components (μmol dm ⁻³)	
Ca	60.4 ± 0.3	Ni	0.0712 ± 0.0005
Na	0.676 ± 0.0009	Fe	5.02 ± 0.05
K	1.42 ± 0.02	Co	0.0604 ± 0.0002
Li	3.60 ± 0.01	Cu	0.0233 ± 0.0005
Mg	0.0006 ± 0.0001	Zn	0.17 ± 0.004
TIC		Cd	0.0033 ± 0.00004
Total inorganic carbon (ppm as C)	5.75 ± 0.28	Cs	0.0927 ± 0.0004
		Cr	1.05 ± 0.03
		Th	0.00054 ± 0.00002
pH		Eu	0.0015 ± 0.0001
12.86 ± 0.02		Se	0.019 ± 0.005
		U	0.00015 ± 0.00002
		Pb	0.0119 ± 0.0007

(a)



(b)

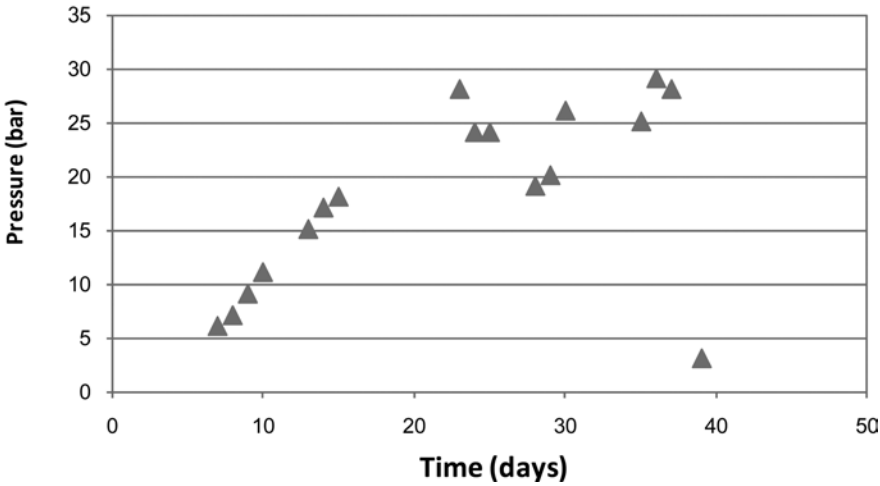


Figure 3 (a) Changes in the elution volume of HTO through the NRVB column ($V_{total} = 175 \text{ cm}^3$) with time, which indicate alteration of the porosity of the monolith and/or development of fractures and (b) evolution of the pressure through the NRVB columns during the advection experiments

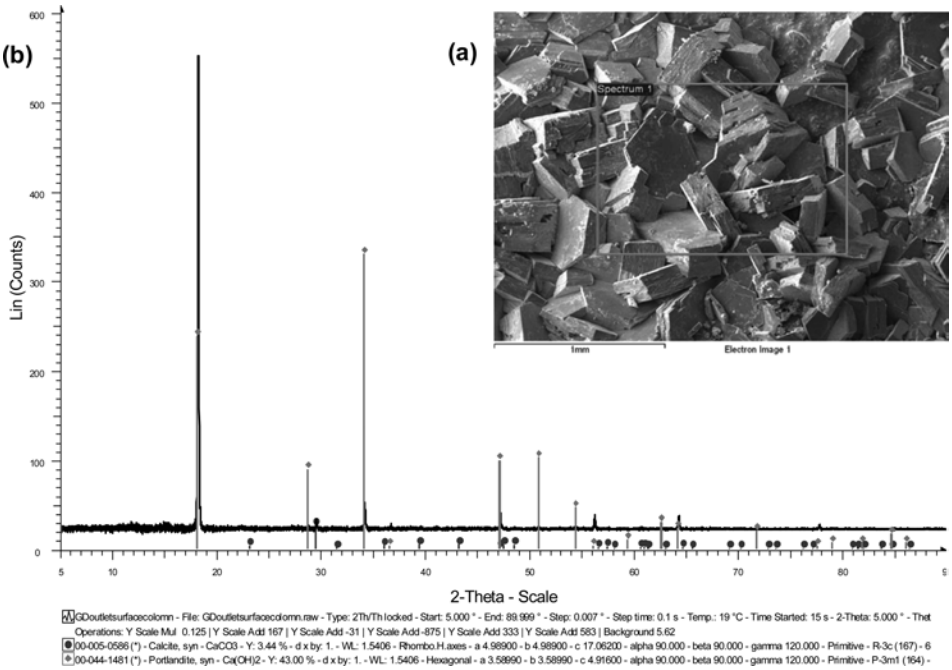


Figure 4 (a) SEM image of the precipitate on the outlet surface of the NRVB column and (b) XRD spectrum of the precipitate on the outlet surface of the NRVB column

An SEM image of an axial cut of one of the columns (Figure 5) shows that precipitation of portlandite occurred not only on the column outlet surface but also inside the column. Three different zones could be observed in the column; the inlet of the column (Figure 5.c) that showed signs of alteration and increases in microsporiocity, most likely due to leaching. The middle area of the column (Figure 5.b) did not show signs of leaching, but precipitation of portlandite was noticeable and finally, the top or outlet of the column (Figure 5.a), where the precipitation of portlandite was more severe. To investigate further the cause of the leaching and precipitation, a new series of experiments were performed in which NRVB-equilibrated water (solid:liquid 1:50) was pumped through the column and the composition of the outlet solution was determined by ICP-MS and ICP-OES (Figure 6).

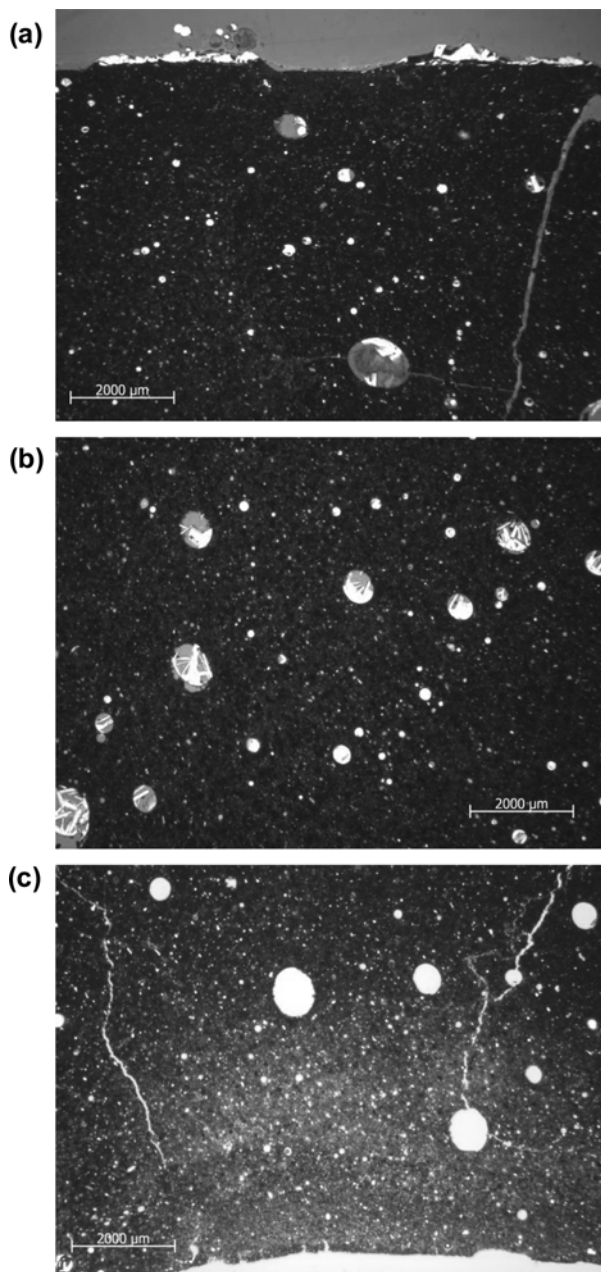


Figure 5 SEM images of axial cuts of one of the columns, **(a)** inlet of column, zone of leaching and alteration of cement matrix, with enhanced microporosity, loss of ettringite from gas bubbles, and no portlandite mineralisation in air bubbles, **(b)** middle section, lack of leaching and alteration of cement matrix, with no enhanced microporosity and Portlandite-lined gas bubbles and **(c)** outlet of column, lack of leaching and alteration of cement matrix, with no enhanced microporosity, Portlandite-lined gas bubbles and Portlandite-coated top face of column

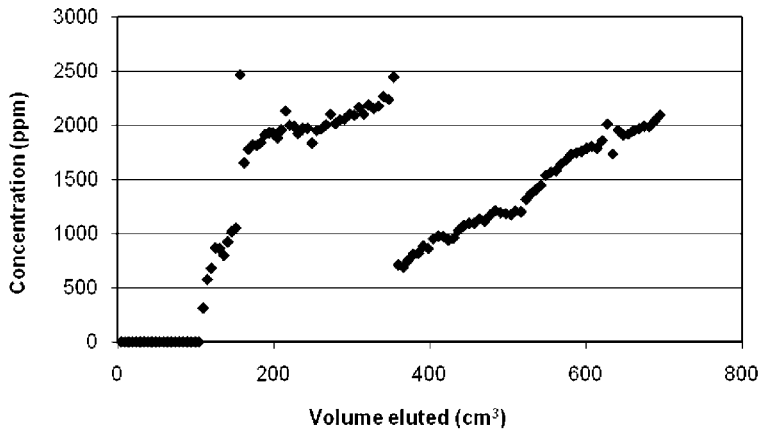


Figure 6 Concentration of Ca in solution at the outlet of the NRVB column

Figure 6 shows that after solution equivalent to the dead volume of the column (approx. 100 cm^3) had passed through the column, the concentration of Ca began to increase until it reached a concentration close to the solubility limit of $\text{Ca}(\text{OH})_2$. After ca. 375 cm^3 , the concentration of Ca suddenly dropped, and then increased again slowly. These changes in the composition of the outlet solution suggested a series of solubilisation and precipitation events. Therefore, the reasons for the precipitation along the column could be: (i) the NRVB-equilibrated water, liquid to solid ratio 50:1, is not fully saturated with the NRVB components, and this would cause leaching and precipitation on the outlet surface, and/or (ii) hydration of the NRVB clinker phase results in the formation of $\text{Ca}(\text{OH})_2$, from the lime aggregate and also as a product of calcium silicate hydration and, after the water in the system becomes saturated with $\text{Ca}(\text{OH})_2$, any further $\text{Ca}(\text{OH})_2$ generated is precipitated within the pore structure.⁵³ To test the first hypothesis a series of experiments were performed in which variable amounts of NRVB were contacted with water from 1:50 to 1:1 solid:liquid ratio, from 4 to 28 days and the composition of the leachate was determined. Results indicated that the solutions were fully equilibrated with Ca, but not with the other alkaline and alkaline-earth metals, not even at the highest liquid:solid ratio. This implies that it is not possible to obtain a solution similar to NRVB pore water simply by mixing NRVB and water. To avoid any leaching of the cement specimens during the advection and diffusion experiments it is necessary to use a solution equal to the pore water. To produce enough pore water, the pore water will be extracted⁶² and analysed, and an artificial pore water will be prepared of the same composition.

4 CONCLUSIONS: DEFINITION OF THE EXPERIMENTAL STRATEGY

Considering the initial objectives of the project are to demonstrate chemical containment and, given the results obtained during the trial experiments, the following experimental procedures have been defined:

- (a) Advection experiments: the column experiments will be performed using a pressurised vessel, a Hassler cell type, to minimise the effects of shrinkage. The NRVB specimens will be cured in water for a period of at least of 2 months before use. Waiting for the completion of the OPC hydration process as long as possible will minimise the precipitation of portlandite in the column. The use of (artificial) pore water will prevent leaching of alkaline and alkaline-earth metals, and the development of microfractures.
- (b) Diffusion experiments: through diffusion or steady state experiments will be performed. As in the case of advection experiments, the used of artificial pore water and well-cured monoliths will be crucial to avoid loss of structural strength and surface precipitation.
- (c) Solubility experiments: to demonstrate the concept of chemical containment it is important to prove the reversibility of the solubility process. For that reason both oversaturation and undersaturation will be performed. At the end of the experiments, not only the concentration in solution will be assessed but also the identity of the solid phase.

Moreover, all the experiments will be carried out in a controlled environment, a N₂-atmosphere free from O₂ and CO₂. This will avoid drifting of pH and prevent precipitation of CaCO₃.

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LEACHING OF $^{239,240}\text{Pu}$ AND ^{241}Am FROM THULE NUCLEAR BOMB PARTICLES INVESTIGATED BY SEQUENTIAL EXTRACTION

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1 INTRODUCTION

The radioactive particles investigated in this work originated from the so-called Thule accident, in which an aircraft carrying four thermonuclear weapons crashed on the sea ice close to Thule Air Base in NW Greenland in 1968. Radioactive materials were spread over the surrounding area because of a chemical explosion and fire. The accident was followed by clean-up, but the seabed under the point of impact was also contaminated as the impact broke up about 2500 m² of ice. The residual contamination in the area has been estimated to be about 10 TBq ^{239}Pu .¹ In addition to sea sediments, soil samples collected from the area have been shown to contain radioactive particles.²

The particle weathering rate depends on both particle characteristics and environmental conditions.³ Weathering of the particles will occur with time leading to the mobilization of radionuclides into the environment. Thule particles have been well characterized with respect to radionuclide activities, particle size, elemental distribution, morphology and oxidation state. U and Pu have been found to be distributed throughout the particles and present as mixed oxides: mostly U (IV) and Pu (III) and Pu (IV).^{4,5} Lind et al. reported that particle characteristics are more dependent on the source and release scenario than the environmental conditions to which they have been exposed.⁶

Even though the source term and characteristics of the Thule particles have been extensively studied, much less is known about their weathering and stability in nature. Sequential extraction, i.e. the selective dissolution of soil components with increasingly aggressive chemical treatments, can be used to obtain information on the partitioning of radionuclides in soils and sediments, useful for predicting the mobility and bioavailability of radionuclides. Each extraction is designed to attack a single geochemical phase, but complete specificity is seldom achieved. Nevertheless, a major advantage of sequential extraction procedures is that to some degree they simulate the various conditions to which the soil may be subjected in the environment.⁷

Our goal was firstly to test how feasible it is to carry out sequential extraction with isolated particles and secondly to obtain information on the weathering of Thule particles. This information can be useful in predicting the mobility and bioavailability of radionuclides associated with particles. Sequential extraction has previously been used for sediments/soils containing hot particles,^{8,9,10,11,12} but to our best knowledge it has not been carried out for single, isolated particles.

2 MATERIALS AND METHODS

2.1 Particles

Sampling and isolation of the nuclear bomb particles were performed by Risø National Laboratory, Denmark. The particles were sampled in 2007 approximately 10 km south of the impact point. Soil samples used in the present study were collected using both spades and tubes (10 cm diameter) to a depth of 3–15 cm depending on the presence of stones from an area of 50 × 50 metres having elevated activity of ^{241}Am as indicated by portable NaI(Tl) spectrometers. Particles were isolated from one of the soil samples using a sample splitting technique, where the sample was divided into two parts, and based on the gamma spectrometric measurements (^{241}Am), the part containing hot particles was identified and further divided. When the sample size was about 0.1 g, the soil was immersed in water and the splitting technique was continued with the help of a pipette. Using a low-volume (μL) pipette, the radioactive particles could be handled individually and safely. The use of water to manipulate the soil and particles facilitates the work and minimizes contamination, as the particle is secured with water and cannot be lost with dust. Isolated particles were then shipped in a few μL of water in a plastic vial to the Finnish Radiation and Nuclear Safety Authority (STUK), where the sequential extraction experiments were carried out. Two particles labelled here as A and B were studied. The particles were transferred from the vial with help of distilled water and isolated in a water droplet of 30 μL by the splitting technique.

2.2 Sequential Extraction Protocol

The sequential extraction method used here (Table 1) was developed by Tessier et al.⁷ and optimized by Outola et al.¹³ In the first fraction the sediment is treated with MgCl_2 to extract soluble species of elements that may be displaced from the solid phase by cation exchange. In the second fraction, ammonium acetate is used to attack easily acid soluble mineral phases. Acetic acid was used to buffer the solution at pH 4, as the release from carbonate phases is affected by changes in pH. In the third fraction, species that are associated with metal oxides and oxyhydroxides are expected to be released when targeted with $\text{NH}_2\text{OH}\cdot\text{HCl}$ in acetic acid. In the fourth fraction, hydrogen peroxide is used as a strong oxidizing agent to release elements associated with organic matter. In the fifth fraction, nitric acid is used to dissolve all but the most resistant phases, such as quartz or aluminosilicates, that remain in the residue.

Table 1 Summary of the sequential extraction protocol

Step	Reagent	Temperature (°C)	Concentration (M)	Duration (h)
I	MgCl_2 , pH 6	25	0.1	1
II	NH_4Ac in 25% HAc (v/v), pH 4	50	1.0	2
III	$\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% HAc (v/v), pH 2	70	0.1	6
IV	30% H_2O_2 in 0.02 M HNO_3 , pH 2	70		3
V	HNO_3	90	4.0	4

2.3 Sequential Extraction Experiments

Sequential extraction was carried out on two isolated particles. The activity of ^{241}Am in the particles isolated in 30 μL water droplets was first detected with a high purity Ge detector. Each particle was then transferred to 5 or 10 mL vials made of Teflon-PFA (Perfluoroalkoxy) that had a conical interior. Next, 1 mL of the appropriate reagent at the specified concentration was added to the samples as outlined in Table 1. The vials were placed in a water bath for the appropriate time and temperature. In fraction IV, two reagents were used, i.e. 0.05M HNO_3 (0.35 mL) and 30% H_2O_2 (0.55 mL). Dilute nitric acid was first added to the sample together with the first portion of H_2O_2 (0.2 mL). The second portion of H_2O_2 was added one hour later and the third H_2O_2 portion 2 hours later.

After each sequential extraction step was completed, the particle was isolated from the solution using the splitting technique. Care was taken to minimize the loss of material, e.g. the pipette tips, and vials were rinsed with water and dilute nitric acid. The rinsing solution was then combined with the extracted solutions. The water in which the particle had been shipped was combined with the first extracted solution. After the final extraction step (V) was completed, it became obvious that the Thule particles had disintegrated into several parts. In this case, the solution was filtered through a 0.45 μm cellulose nitrate membrane filter and the residual ^{241}Am activity on the filter paper was measured with a Ge detector. The extracted solutions from the first four steps (I–IV) were acidified with nitric acid and all the solutions were later filtered through 0.45 μm cellulose nitrate membrane filters before radiochemical separations were carried out. The filter papers were measured with a Ge detector and imaged with autoradiography to check whether they contained any residual radioactive material.

2.4 Gamma-ray Spectrometry

A high purity p-type Ge detector with 50 % relative efficiency was used to measure the ^{241}Am activities of the two particles prior to extraction, between each extraction step, and to determine the residual activity left in the particles. Measured samples were either a single water droplet of 30–50 μL on the bottom of the vial, or filter paper with a diameter of 2.5 cm containing residual material. Measurement times varied between 5 and 120 minutes depending on the ^{241}Am activity in the sample.

2.5 Liquid Scintillation Counting

The activity sum of alpha-particle-emitting radionuclides in extracted solutions was determined by liquid scintillation counting to estimate the size of the aliquot needed for radiochemical Pu and Am analysis. Two mL of the extracted solution (5% of the original amount) were mixed with 20 mL of scintillation cocktail solution and the sample was measured for 6 hours with a Quantulus liquid scintillation spectrometer.

2.6 Radiochemical Separation of Pu and Am from the Extracted Solutions

Depending on the activity concentration present, an aliquot was taken from the extracted solutions (0.4–95%). The aliquots were spiked with ^{242}Pu and ^{243}Am tracers. A blank sample was also run together with the real samples to rule out possible contamination coming from the reagents or glassware. Nitric acid and 0.5 mL of H_2O_2 was added to the extracted solutions, which were then heated on a hotplate. Solutions were evaporated to

dryness, dissolved into 10 mL 8 M HNO_3 and heated on the hotplate, where 0.2 g NaNO_2 was added to the sample and heating continued for 10 minutes. After the sample had cooled down, it was loaded into an anion exchange column (2 mL Dowex 1x4, 100-200 mesh) and the column was rinsed with 15 mL of 8 M HNO_3 . The load and rinse solutions were collected for Am determination. The column was then rinsed with 20 mL of 9M HCl and Pu eluted with a 15 mL mixture of NH_4I and 9 M HCl.

Solutions containing Am and Pu were evaporated and dissolved into 4 mL of 1 M HNO_3 . Am and Pu isotopes were co-precipitated by adding 50 μg Ce and 0.5 mL HF. The precipitate was collected on a membrane filter (polypropylene, pore size of 0.1 μm). Co-precipitation of Am from the MgCl_2 fraction produced a large amount of precipitate so that alpha spectrometry could not be carried out. The samples were further purified prior to alpha counting. The membrane filters were dissolved in 3 mL concentrated nitric acid on a hot plate and 0.3 g boric acid was added to dissolve the CeF_3 precipitate. Separation of Am was carried out according to Eichrom method ACW04 followed by co-precipitation with CeF_3 .

2.7 Alpha Spectrometry

Co-precipitated Am and Pu sources were measured with a semiconductor detector (PIPS, Canberra) for 4 days. In one of the samples (step 3, particle A), Pu was present in the Am spectra. The oxidation step with NaNO_2 probably failed prior to anion exchange, and Pu as valence state III followed Am. Since the alpha peaks of $^{239,240}\text{Pu}$ and ^{242}Pu were separate from the peaks of ^{241}Am and ^{243}Am , the activity of these nuclides could be determined from the same spectrum. However, as the ^{238}Pu peak was very close to peak of ^{241}Am , ^{238}Pu activity could not be determined. The interference from ^{238}Pu in the ^{243}Am peak area was negligible.

Pu and Am in the residual material from particle B were directly measured with a semiconductor detector for four days without preceding radiochemical separation. ^{238}Pu activity could not be determined from the residue, as ^{238}Pu was under the much larger ^{241}Am peak. The interference from ^{238}Pu in the ^{243}Am peak area was corrected based on the $^{238}\text{Pu}/^{239,240}\text{Pu}$ ratio determined from the radiochemically purified solutions.

2.8 Autoradiographic Measurements

Imaging plates¹⁴ were used to verify the fragmentation of particles A and B after the sequential extraction was completed. The plates were placed in contact with the filters containing residual materials. The exposure time varied from 2 to 6 days.

2.9 Alpha-gamma Coincidence Setup

Residual material from particle A was measured with the alpha-gamma coincidence setup of the PANDA testbed.¹⁵ This setup consists of a broad-energy HPGe gamma detector and a position-sensitive alpha detector connected to a time-stamping event-mode data acquisition system. The alpha detector is a $64 \times 64 \text{ mm}^2$ double-sided silicon strip detector with a pixel size of $2 \times 2 \text{ mm}^2$. During the measurement, the distance between the detectors facing each other was $8.0 \pm 0.5 \text{ mm}$, and the sample was set between them at $3.5 \pm 0.5 \text{ mm}$ distance from the alpha detector. The sample was measured for four days. In this study, the coincidence technique was used to reduce the inaccuracy of the alpha detection efficiency. In addition, the coincidence technique allows generating a low-background gamma spectrum of the alpha emitters only.

Table 2 The activity of ^{241}Am (Bq) in particles A and B originally and after each extraction step as determined by gamma-ray spectrometry. Uncertainties refer to 1σ .

Step	Particle A	Particle B
Original activity	7.6 ± 0.5	13.4 ± 0.9
I	7.3 ± 0.4	12.8 ± 0.9
II	6.5 ± 0.5	11.5 ± 0.8
III	6.7 ± 0.5	12.0 ± 0.8
IV	6.5 ± 0.5	5.9 ± 0.4
V	3.9 ± 0.3	<0.02

3 RESULTS AND DISCUSSION

3.1 Leaching of Pu and Am from the Thule Particles

The two radioactive particles (A and B) respectively contained 7.6 ± 0.5 Bq and 13.4 ± 0.9 Bq of ^{241}Am as determined by gamma-ray spectrometry prior to sequential extraction experiments (Table 2). The measurements of particles after each sequential extraction step revealed that ^{241}Am was totally released from particle B during the 5-step sequential extraction protocol, whereas for particle A only half of the ^{241}Am was released. Gamma-ray spectrometry could not reveal detailed information about the amounts released among the first extraction steps, as they were smaller than the uncertainty of gamma spectrometric determination.

More detailed information on the release of Am as well as that of Pu was obtained from alpha spectrometry following the radiochemical purification of the extracted solutions (Tables 3 and 4). To compare the leaching behaviour of Pu and Am with each other, as well as the weathering of the two particles, the released amounts of Pu and Am in each step are also given as percentages in Tables 3 and 4. Pu and Am behaved similarly, but the two Thule particles behaved somewhat differently as compared to each other. Particle A started to dissolve significantly in the last step of the extraction protocol, where it was treated with hot nitric acid, and the residue contained about half of the original activity. Particle B started to dissolve earlier, i.e. when treated with the oxidizing agent, H_2O_2 . Most of the Pu (56%) and a considerable amount of the Am (44%) were released when particle B was treated with nitric acid. In this case, the residue only contained 0.1% of the original Pu and Am activities. In both particles, very small amounts of Pu and Am were found in the easily exchangeable fraction where the sample was treated with MgCl_2 .

Hamilton et al. carried out sequential extraction on marine sediments from Thule, and similarly to our study they found very little Pu released in the first two steps of the extraction.¹⁰ However, they reported the majority of Pu to be associated with Fe/Mn oxides (fraction III), while we found that fraction to be of less importance. Torrao et al. studied Pu-contaminated soil from the Nevada test site, and reported that significant amounts of Pu were soluble in H_2O_2 .¹¹ They found this somewhat surprising, as Pu was known to be present as a dioxide and should only have been released with more resistant phases. Pu in Thule particles is known to be present as oxides, but in particle B we also determined a relatively high amount of Pu and Am released with the peroxide/nitric acid fraction that targets organic-bound elements. Vlasova et al. applied sequential extraction to sediment samples and reported that ^{238}Pu originating from hot particles was mostly in the residual fraction, whereas $^{239,240}\text{Pu}$ of a different origin was also found in the organically bound fraction.¹⁶

Table 3 Particle A: Activities of Pu and Am isotopes released (Bq and percentages) in each extraction step and left in the residue as determined by alpha spectrometry. Uncertainties refer to 1 σ .

Step	^{238}Pu	$^{239,240}\text{Pu}$		^{241}Am	
	Bq	Bq	%	Bq	%
I	<0.001	0.0039 ± 0.0007	0.010 ± 0.002	0.0021 ± 0.0001	0.028 ± 0.002
II	<0.0007	0.031 ± 0.002	0.079 ± 0.004	0.0078 ± 0.0005	0.10 ± 0.01
III	0.0013 ± 0.0002	0.086 ± 0.004	0.22 ± 0.01	0.019 ± 0.001	0.26 ± 0.02
IV	-	1.4 ± 0.1	3.6 ± 0.2	0.41 ± 0.02	5.4 ± 0.3
V	0.23 ± 0.04	17.5 ± 0.7	45 ± 2	3.5 ± 0.2	47 ± 3
Residue	-	20.3 ± 0.4	52 ± 1	3.6 ± 0.3	48 ± 4

- not determined

Table 4 Particle B: Activities of Pu and Am isotopes released (Bq and percentages) in each extraction step and left in the residue as determined by alpha spectrometry. Uncertainties refer to 1 σ .

Step	^{238}Pu	$^{239,240}\text{Pu}$		^{241}Am	
	Bq	Bq	%	Bq	%
I	0.0086 ± 0.0021	0.055 ± 0.003	0.072 ± 0.004	0.024 ± 0.001	0.17 ± 0.01
II	0.017 ± 0.003	1.2 ± 0.05	1.6 ± 0.1	0.15 ± 0.01	1.1 ± 0.1
III	0.083 ± 0.013	6.5 ± 0.3	8.6 ± 0.4	1.3 ± 0.1	9.0 ± 0.6
IV	0.28 ± 0.04	26 ± 1	34 ± 1	6.3 ± 0.4	45 ± 3
V	0.53 ± 0.08	42 ± 2	56 ± 2	6.2 ± 0.4	44 ± 3
Residue	-	0.074 ± 0.003	0.098 ± 0.004	0.011 ± 0.001	0.089 ± 0.006

- not determined

3.2 Isotopic Ratios in Extracted solutions and in the Residuals

The $^{241}\text{Am}/^{239,240}\text{Pu}$ ratio was twice as high in the first fraction as that in the other fractions for both particles (Fig. 1a). This indicates that ^{241}Am is more soluble than $^{239,240}\text{Pu}$. However, the activities of Am and Pu released in the first step, where each particle was leached with MgCl_2 , accounted for only less than 0.2% of the total activity of Am and Pu. The more soluble nature of Am as compared to Pu in Thule particles has also been reported by other authors.^{5,12} Lee et al. applied sequential extraction to contaminated soil and also concluded that Am was more effectively removed from the soil.¹⁷

$^{241}\text{Am}/^{239,240}\text{Pu}$ activity ratios in particle A were consistently higher than in particle B in all extracted solutions and in the residue. A paired t-test confirmed that the difference in $^{241}\text{Am}/^{239,240}\text{Pu}$ ratios between the two particles was statistically significant (t-stat = 4.33, df = 5).

The integrated $^{241}\text{Am}/^{239}\text{Pu}$ ratio was determined for both particles by summing the ^{241}Am activities released in each step with the amount remaining in the residual and dividing this by the summed $^{239,240}\text{Pu}$ activities. The integrated $^{241}\text{Am}/^{239,240}\text{Pu}$ ratio was found to be 0.192 ± 0.011 for particle A and 0.185 ± 0.009 for particle B (reference date December 2009). The ratios reported for Thule particles in the literature include 0.169 ± 0.005 , 0.14 ± 0.02 and 0.13 ± 0.01 .^{1,4,18} Thus, our results are somewhat higher than the values reported by other investigators, but they agree with the literature values when taking into consideration the still ongoing ingrowth of ^{241}Am .

The $^{238}\text{Pu}/^{239,240}\text{Pu}$ activity ratio in extracted solutions varied from 0.011 to 0.015. As expected, no significant difference could be detected between the two particles or between different fractions (Fig. 1b). The ratios were in good agreement with literature values.¹⁹

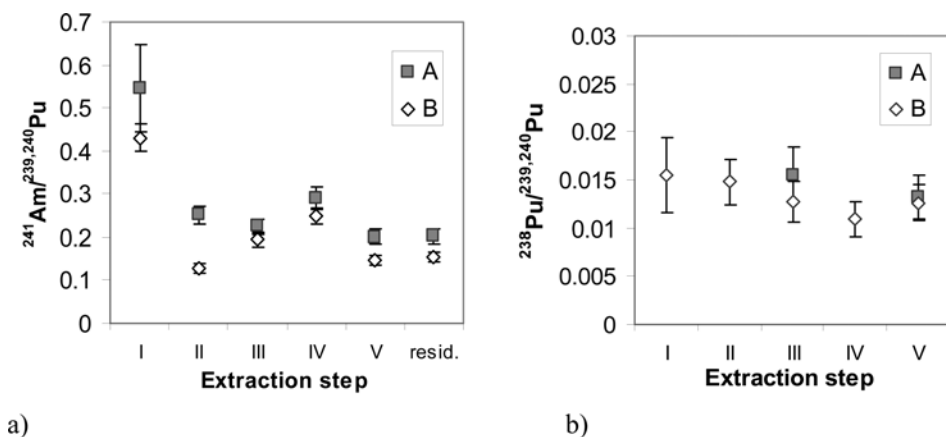


Figure 1 Activity ratios of a) $^{241}\text{Am}/^{239,240}\text{Pu}$ and b) $^{238}\text{Pu}/^{239,240}\text{Pu}$ in solutions extracted from Thule particles A and B and in the remaining residuals

3.3 Weathering of the Particles

Weathering of the particles may occur through dissolution and fragmentation. Fragmentation of particles A and B was investigated by imaging the residual material. Figure 2 indicates that particle A had broken into a few fragments that contained about half of the original ^{241}Am activity. Particle B had also broken into several fragments that, however, only contained 0.1% of the original ^{241}Am activity. All solutions collected during the extraction were filtered before radiochemical separation and the filter papers were also imaged to check the presence of radioactive particles. In two filters (particle B, steps II and IV), a few hot spots were discovered that, however, contained less than 0.1% of the original ^{241}Am activity.

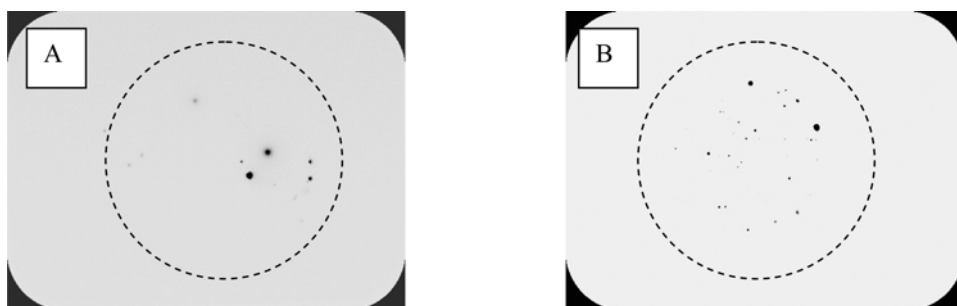


Figure 2 Imaging plate pictures of the filter papers containing residual from Thule particles A and B. The size of the membrane filters is illustrated by the dashed circles

Table 5 Activity sum of alpha-particle emitting radionuclides (Bq) in each extracted solution determined by liquid scintillation counting. Uncertainties refer to 1 σ .

Extraction step	Particle A (Bq)	Particle B (Bq)
I	<0.003	0.08 $\pm$ 0.01
II	0.05 $\pm$ 0.01	1.27 $\pm$ 0.06
III	0.13 $\pm$ 0.01	7.58 $\pm$ 0.38
IV	1.87 $\pm$ 0.09	31.3 $\pm$ 1.6
V	21.2 $\pm$ 1.1	47.2 $\pm$ 2.4

3.4 Quality Control

3.4.1 Liquid Scintillation vs. Alpha Spectrometry. Before the extracted solutions were radiochemically purified, they were measured with a liquid scintillation counter (LSC) to determine the activity sum of alpha-particle-emitting radionuclides in each solution (Table 5). LSC measurements could be used as a quality control tool by comparing the activity sum of alpha-particle-emitting radionuclides determined by LSC with those determined by alpha spectrometry. These two methods are independent and the analyses were carried out from separate aliquots. Results from both methods were in good agreement within their reported uncertainties (Fig. 3). The differences were less than 5%, except for the samples with very low activity, where higher differences (20–30%) were observed. In the case of alpha spectrometry, the activity sum was calculated by summing the activities of Am and Pu isotopes, whereas LSC results included all alpha-particle-emitting radionuclides. ^{235}U and ^{238}U are known to be present in these particles,¹⁹ but they were not determined with alpha spectrometry. However, the contribution of U is negligible to the activity sum, as ^{235}U activity is expected to account for less than 0.01% of the $^{239,240}\text{Pu}$ activity. The contribution of ^{238}U to the activity sum is even smaller.

3.4.2 Activity budget. To determine possible material losses during the sequential extraction, the activity budget for ^{241}Am was calculated by summing the activities of ^{241}Am released in each extraction step with those remaining in the residual, as determined by alpha spectrometry. The activity budget of ^{241}Am derived in this way for particles A and B was 7.6 ± 0.4 Bq and 14.0 ± 0.6 Bq respectively. Taking into consideration the uncertainty of the measurements, the results are in close agreement with those obtained from gamma-ray spectrometry prior to the sequential extraction (Table 2) and do not indicate material losses during the extraction. The $^{239,240}\text{Pu}$ activity budget (the amount released in each step + that left in the residual) was 39 ± 1 Bq and 75 ± 2 Bq for particles A and B, respectively. The $^{239,240}\text{Pu}$ activity of the particles prior to the extraction procedure was not determined.

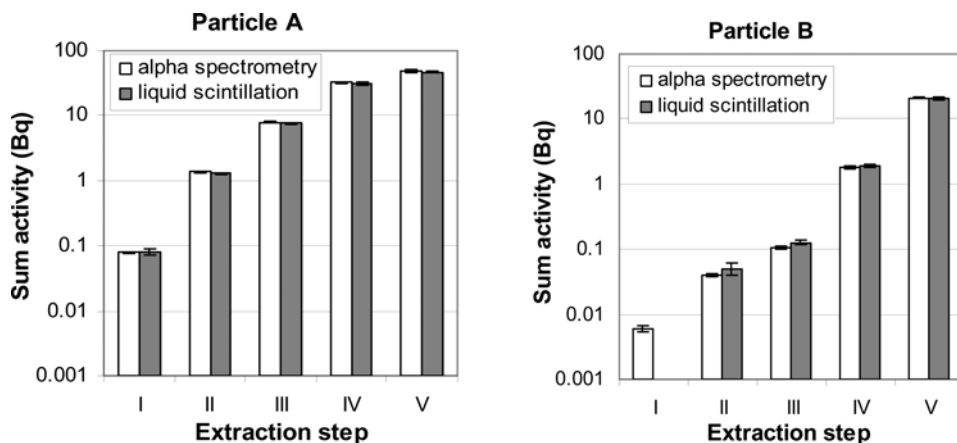


Figure 3 Comparison of the activity sum of alpha-particle-emitting radionuclides released from particles A and B in each extraction step as determined by alpha spectrometry and liquid scintillation counting.

4 CONCLUSIONS

Sequential extraction was carried out separately for two isolated nuclear bomb particles originating from the Thule accident in 1968 to gain information about the solubility of particle-bound Pu and Am in the environment. Experiments demonstrated that sequential extraction is feasible to carry out with individual particles. Most of the Pu and Am were released with the most aggressive treatments or remained in the residual. Leaching of Pu and Am was found to differ somewhat between the two particles. While the Am and Pu were completely released from one of the particles during the five-step sequential extraction procedure, the other particle had half of the original activity still associated with the residual when the extraction protocol was finished. Am was found to be slightly more soluble than Pu, indicated by twice as high $^{241}\text{Am}/^{239,240}\text{Pu}$ ratios in the easily soluble fraction as in the other fractions. However, only a small amount of both Am and Pu were easily soluble.

Acknowledgements

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CAESIUM-137 IN NORWEGIAN COASTAL AREAS

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1 INTRODUCTION

The fission product Cs-137 is present in all parts of the Norwegian environment, brought here atmospherically or by ocean currents. The most important sources are fallout from atmospheric nuclear weapons tests, discharges from nuclear fuel repossessing plants and fallout from the Chernobyl accident, all of which have caused the presence of this radionuclide in the marine environment.

The presence of this radionuclide is monitored in annual investigations, and the activity concentrations in the Norwegian marine environment are found to be relatively low. However, results from monitoring the contents of Cs-137 in surface sediments in Norwegian fjords in the period 1999 to 2008 are from $< 0,7$ Bq/kg (d.w.) up to 415 Bq/kg (d.w.) (1, 2, 3, 4, 5, 6, 7, 8); Figure 1.

Some of the fjords monitored have high activity concentrations of Cs-137 in surface sediments. These are all connected to land areas which received relatively large amounts of fallout from the Chernobyl accident in 1986 (9). The activity concentrations in some Norwegian fjords are 10-20 times higher than in open marine areas, and are comparable with the activity concentrations in the Irish Sea and the Baltic Sea (10).

2 MATERIALS AND RESULTS

In this work the Cs-137 activity concentrations in 14 sediment cores from the outlet and the head of Laksefjord and Sognefjord (Figure 2), have been investigated. Using the lead-210 dating method with correction of supported lead-210 (11), each centimeter-thick layer in 11 of the cores has been dated.

The Cs-137 activity concentrations in the upper sediment-layer from all 14 cores show Cs-137 content of three different levels (Figure 3). In the outlet of Sognefjord the Cs-137 level (approximately 33 Bq/kg (d.w.)) is about 6 times higher than the level (approximately 5.8 Bq/kg (d.w.)) in Laksefjord. In the head of Sognefjord the Cs-137 level (approximately 293 Bq/kg (d.w.)) is about 10 times higher than the level in the outlet of Sognefjord (10).

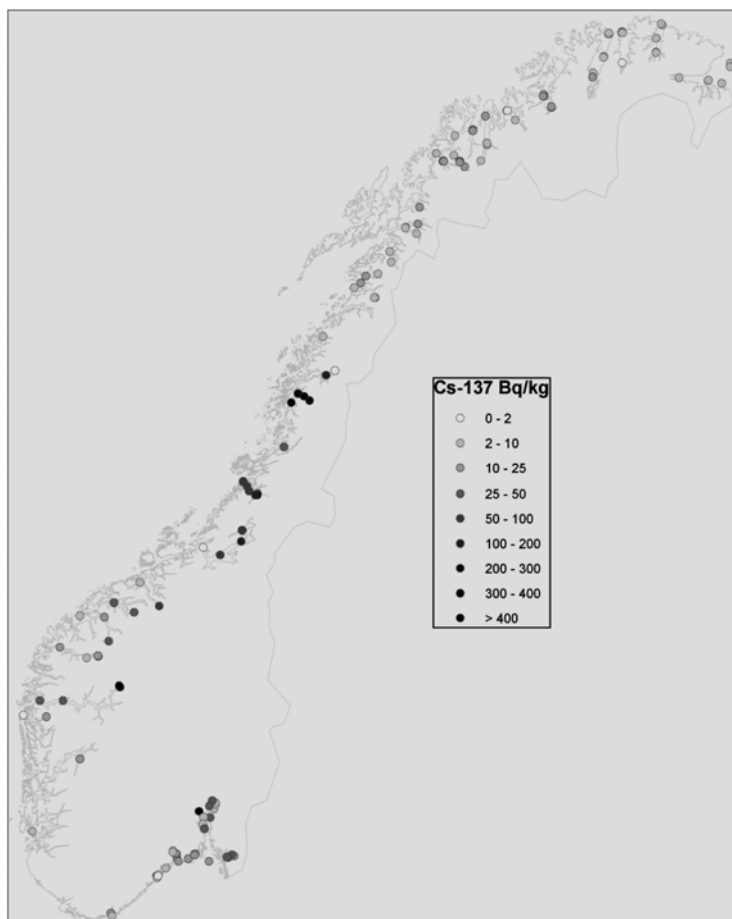


Figure 1 *Cs-137 in surface sediments, Bq/kg (d.w.)(10).*

3 DISCUSSION

In all cores analyzed, the maximum Cs-137 activity concentrations are found in the upper layers (Figure 4). This indicates a continuous supply of Cs-137 from ocean currents and run-off from land.

There are no specific signals in the dated sediment layers to indicate which of the main sources are the dominating ones. It is likely that Sognefjord, which is much deeper than the areas outside the fjord (Figure 5), can accumulate Cs-137 from both ocean currents and run-off.

Chernobyl fallout on the land area surrounding the head of Sognefjord is most likely the source of the elevated contents of Cs-137 there. It can be focused in the head of fjords due to the ratio between the drain-off area and the area receiving the drain-off. The catchment area delivering the drain-off is 1 134 km², while the sea area initially receiving this drain-off is only 61 km²(12).

There are also elevated contents of Cs-137 in some other Norwegian fjords (Figure 1). These fjords are all located in areas which received large amounts of Chernobyl fallout.

Fjords located in areas which received moderate amounts of Chernobyl fallout do not show such elevated levels.

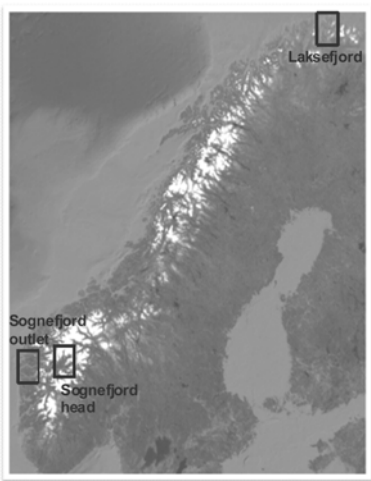


Figure 2 *Sampling sites*

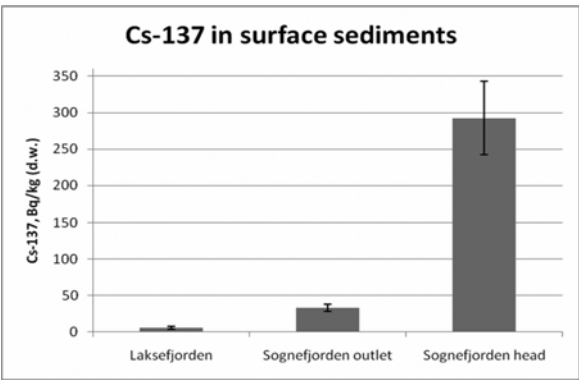


Figure 3 *Cs-137 in surface sediments from the three sampling sites, Bq/kg (d.w.).*

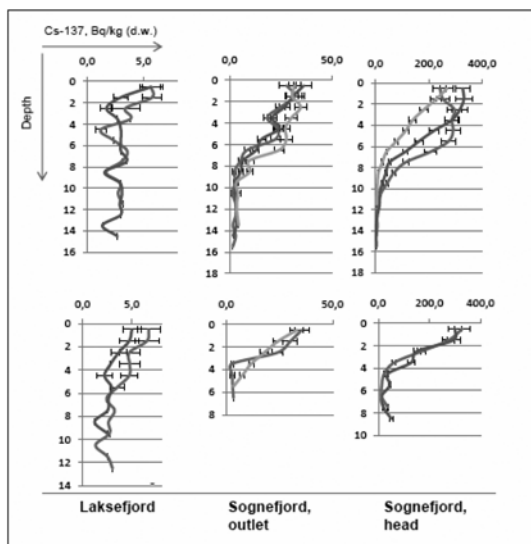


Figure 4 Cs-137 in sediment cores from the three sampling sites, Bq/kg (d.w.)(10).

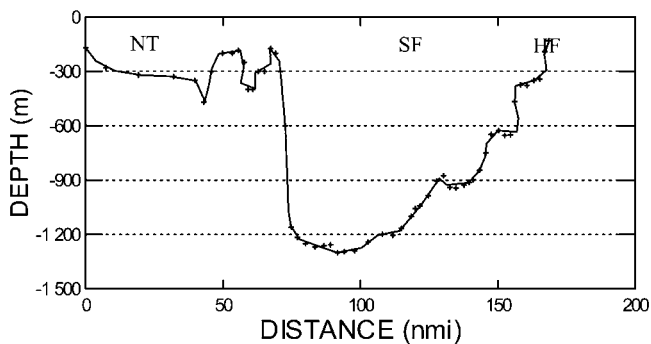


Figure 5 Depth profile across the Norwegian trench (NT), Sognefjord (SF) and into head of fjord (HF) (10).

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MARINE RADIOACTIVITY IN THE CHANNEL ISLANDS, 1990 - 2009

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1 INTRODUCTION

Since the mid-1960s, samples of marine environmental materials collected from Alderney, Guernsey and Jersey have been analysed to determine the concentrations of artificial radionuclides in the vicinity of these Channel Islands. The three surveillance programmes now primarily monitor the effects of radioactive discharges from the French reprocessing plant at La Hague and the power station at Flamanville; they also serve to monitor any effects of historical disposals of radioactive waste in the Hurd Deep, a natural trough in the western English Channel. Fish and shellfish are monitored in order to determine exposure from the internal irradiation pathway; sediment is analysed with relevance to external exposures. Seawater and seaweeds are sampled as environmental indicator materials and, in the latter case, because of their use as fertilisers. Milk and crop samples from the Channel Islands have also been analysed and reported in recent years, but these will not be discussed here.

Regular reporting of environmental surveillance data, providing radionuclide concentrations in surface and coastal waters of the British Isles began in 1967,¹ reports generally being published annually. Channel Islands data were also included in this report series, but were limited to a few samples (mostly seaweed) for the analyses of gross beta, caesium-137 and ruthenium-106. By the 1970s the transport and behaviour of transuranic elements plutonium and americium in the Irish Sea from Sellafield (then Windscale) had been extensively studied and reported - a few examples are cited.²⁻⁵ At this time, information on the environmental fate of La Hague discharges was more sparse in comparison to Sellafield discharges, however it was shown that plutonium and americium could be detected in the waters of the English Channel (and southern North Sea).^{6,7} The Channel Islands surveillance programmes also contained a few measurements showing low level uptake of these radionuclides in shellfish, reported in the then ongoing MAFF annual monitoring report series.⁵ In 1981, a study to determine the occurrence of transuranic elements in the marine environment of the Channel Islands concluded that plutonium and americium was present at concentrations much higher than those apportioned to fallout from atmospheric weapons testing.⁸

A thorough review of the adequacy of arrangements for the monitoring for the Channel Islands was carried out in 1989, which provided information of possible changes in radiological exposure pathways which may affect dose to people, interpretation of the 1989 monitoring data, assessment of doses to people who consumed large amounts of seafood and were exposed to external radiation for long periods, and time trend analysis of gross beta and ruthenium-106 in seaweed (*Porphra*).⁹ The report concluded that the environmental concentrations of radionuclides, from wastes disposed to sea, from the mid-1960s to 1989, showed there had been no major trends in concentrations.

The Channel Islands surveillance programmes have continued throughout the intervening years to the present time and although the monitoring requirements are reviewed annually, any changes to the programme mostly reflect observations from the previous one or two years and/or future requirements based on likely seafood consumption. The Channel Island monitoring data are presently reported annually in the joint UK regulators' annual Radioactivity in Food and the Environment (RIFE) series of reports. The most recent report is RIFE 15, which provides information for all the monitoring carried out in 2009.¹⁰

The objective of this paper is to provide concentrations of certain radionuclides in selected indicators (seafood, seaweed, and sediment) over a long time period to assess the impact upon the surrounding environment of the Channel Islands. The concentration data have been compiled to assess the time trends from 1990 (after the last published review of 1989 data) until the present time. These data give a clearer and broader picture of radionuclide trends in the environment which are not obvious from the annually published technical reports.

2 SOURCES OF ARTIFICIAL RADIONUCLIDES

There are three main sources of artificial radionuclides that could impact the marine environment of the Channel Islands.

- i) Authorised discharges from the French reprocessing plant at la Hague;
This site is a nuclear fuel reprocessing plant of AREVA on the Cotentin Peninsula. It has been in operation since 1976 and produces plutonium which is then recycled into MOX fuel at the Marcoule site.
- ii) Authorised discharges from the French nuclear power station at Flamanville;
This power station site is also located on the Cotentin Peninsula. It is powered by two pressurised water reactors (PWRs) and began commercial operation in 1986. Construction began on a new reactor (Flamanville 3) in 2007.
- iii) Releases from historical disposals of radioactive waste in the Hurd Deep.
The disposal of packaged radioactive wastes at the eastern end of the Hurd Deep occurred on fourteen occasions between 1950 and 1963. The disposals were authorised by the UK Government. The waste consisted of small amounts of radioactivity¹¹ originating from various laboratory processes.

Of minor significance to the Channel Islands are the discharges from the UK nuclear site at Winfrith; the main source of discharge was the Steam Generating Heavy Water Reactor (SGHWR) which was shut down in 1995 and is currently undergoing decommissioning, and from sites with operational nuclear reactors at Dungeness (in the

UK), Paluel, Penly and Gravelines (in France). The locations of these sources are shown in Figure 1. Contributions from Chernobyl and weapon test fallout are also negligible.

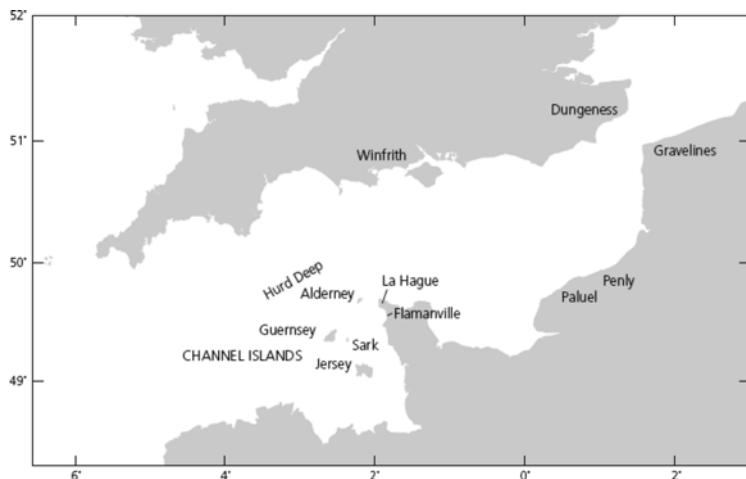


Figure 1 Sources of artificial radionuclides near the Channel Islands

3 RADIONUCLIDE MONITORING DATA

The data in this paper have all been published in the annual Radioactivity in Food and the Environment Report (RIFE) reports and the earlier MAFF annual monitoring report series. Most recent data, for the Channel Islands surveillance programme in 2009, is located in Table 8.3 in RIFE 15,¹⁰ with supporting text in Section 8.2. In the RIFE data tables, if more than one sample is collected and analysed, the value of the radionuclide concentration is reported as the mean of the individual concentrations for that sample. These mean values have also been used in the compilation of the datasets reported here.

From the concentration data available, three indicators types (seafood, seaweed, and sediment) were chosen to investigate radionuclide trends around Alderney, Guernsey and Jersey. Many measurements of radionuclide concentrations were at or below the analytical limits of detection. Therefore, comment on the data collated here has focused on the using positively detected values. Further description of the 3 indicators types are given in Table 1, together with a list of the determinand radionuclides for which data have been analysed and annually reported over the last two decades.

Table 1 Sample details and available determinands

LOCATION	SAMPLE TYPE	DETERMINANDS
ALDERNEY (Little Crabbe Harbour)	Sand	Cs-137, Ru-106
JERSEY (St Helier)	Mud	Cs-137, Ru-106, Pu-239+240, Am-241
GUERNSEY (St Sampson's Harbour)	Mud	Cs-137, Ru-106, Pu-239+240, Am-241
ALDERNEY (Quenard Point)	<i>Fucus</i> seaweed	Cs-137, Ru-106, Tc-99, Pu-239+240, Am-241
JERSEY (La Rozel)	<i>Fucus</i> seaweed	Cs-137, Ru-106, Tc-99, Pu-239+240, Am-241
GUERNSEY (Fermain Bay)	<i>Fucus</i> seaweed	Cs-137, Ru-106, Tc-99, Pu-239+240, Am-241
ALDERNEY	Toothed Winkles	Cs-137, Ru-106, Pu-239+240, Am-241
JERSEY (La Rozel)	Limpets	Cs-137, Ru-106, Pu-239+240, Am-241
GUERNSEY	Limpets	Cs-137, Ru-106

4 RESULTS AND DISCUSSION

Figures 2, 3 and 4 provide the trends of radionuclide concentrations in sediments, seaweed and seafood over the period, 1990–2009. Overall, low concentrations of radionuclides were detected in the marine environment around all the Channel Islands. There was evidence of routine releases from the nuclear industry in some samples for ruthenium-106 in all substrates (in the early 1990's), and for technetium-99 in seaweed for the last decade. These were most likely due to discharges from the nuclear fuel reprocessing plant at La Hague in France. With the available data, apportionment of the other radionuclides to the possible different sources, including weapon test fallout, is difficult in view of the low concentrations detected. There was no detectable effect in Channel Islands waters of any releases of radioactivity from the Hurd Deep site.

Figure 2 provides Channel Islands data for caesium-137, ruthenium-106, plutonium-239+240 and americium-241 in sediments. All trend data, with the exception of ruthenium-106, were above the analytical level of detection (i.e. values positively detected). Ruthenium-106 concentrations were all below the level of detection at all sites from 1997 onwards. Overall, radionuclide concentrations were slightly higher at Jersey (in comparison to Guernsey and Alderney), and this was most likely due to the differences in the type and mineralogy of the sediments sampled. Between 1990 and 1996, ruthenium-106 concentrations declined with time. Although there were some data scatter observed within years for caesium-137 concentrations, the trend in sediments generally decreased over the whole study period generally reflecting the changes in liquid discharges from La Hague, especially with the decreases in these discharges in the early 1990s.¹² At Guernsey, one higher caesium-137 result was observed in 1998. This is also consistent with a small caesium-137 peaks (in the same year) in the *fucus* seaweed result, but not observed in the limpet result (Figures 3 and 4). Trends in plutonium-239+240 and americium-241 also show some scatter in concentrations between individual years, but the trends for the same radionuclides are remarkably similar for both Guernsey and Jersey, with a suggestion that both transuranic concentrations have decreased over time at Jersey.

Figure 3 provides Channel Islands data for caesium-137, ruthenium-106, technetium-99, plutonium-239+240 and americium-241 in *fucus* seaweed (*fucus vesiculosus* or *fucus*

serratus). Technetium-99 data are only available from 1998 onwards. All trend data were positively detected values except for caesium-137 and ruthenium-106 concentrations which were below the level of detection from 1997 onwards for Alderney and Guernsey, and from 2000 onwards for Jersey. With the exception of ruthenium-106 data, radionuclide concentrations were also slightly higher at Jersey (in comparison to Guernsey and Alderney) in the earlier of the two decades. However in the more recent decade, with the exception of technetium-99, there is no noticeable difference in the concentrations observed between the Channel Islands. The reasons for these observations are not clear but the differences could be related to water dispersion mechanisms following discharge from La Hague, which become more apparent during relatively higher discharges (during the 1990s) or for the most conservative radionuclides such as technetium-99. Indeed, it has been reported that a small percentage (5%) of the La Hague discharge is swept southwest towards the Channel Islands.¹³ The results from the monitoring data presented here tend to support the schematic transport map reporting that the water transport flows southwards along the west Cotentin Peninsula coastline, before being swept southwest.¹²

Between 1990 and 2009, caesium-137, ruthenium-106, plutonium-239+240 and americium-241 concentrations in *fucus* seaweed declined with time. The trends in technetium-99 show some scatter in concentrations between individual years, probably due to a variety of environmental reasons (e.g. differences in uptake due to seasonality) and differences in sampling procedures (e.g. different *fucus* species). Overall concentrations are shown to be relatively constant with time, particularly at Alderney and Guernsey.

Figure 4 provides Channel Islands data for caesium-137, ruthenium-106, plutonium-239+240 and americium-241 in seafood (mollusc). Trend data for caesium-137 and ruthenium-106 were at or below the analytical level of detection from 1997 onwards, together with all radionuclide data obtained in 1998. Radionuclide concentrations in mollusc samples were significantly lower than their corresponding determinands in sediments. From the available data, caesium-137 and ruthenium-106 concentrations declined in the early 1990s, reflecting decreasing La Hague discharges,¹² thereafter concentrations were at or below the analytical level of detection. Trends in plutonium-239+240 and americium-241 show some scatter in concentrations between individual years, particularly for the wrinkle samples collected from Alderney. This scatter in wrinkle concentrations is to be expected since it has been previously reported that variation (including seasonal changes) is due to varying amounts of sediment being ingested, and that 90-95% of the activity within the wrinkle is present in the sediment in the alimentary tract.¹⁴

Assessments of the dose to people who consume high-rates of fish and shellfish are undertaken annually and published in the RIFE report series. In 2009, they were estimated to receive less than 0.005 mSv, which is less than 0.5 per cent of the dose limit for members of the public.¹⁰ The assessment included a contribution from external exposure. In 1989, the survey on the Channel Islands confirmed that doses due to discharges from the French reprocessing plant at La Hague and other local sources were less than 1 per cent of the limit.⁹ The concentrations of artificial radionuclides in the marine environment of the Channel Islands and the effects of discharges from local sources, therefore, continued to be of negligible radiological significance.

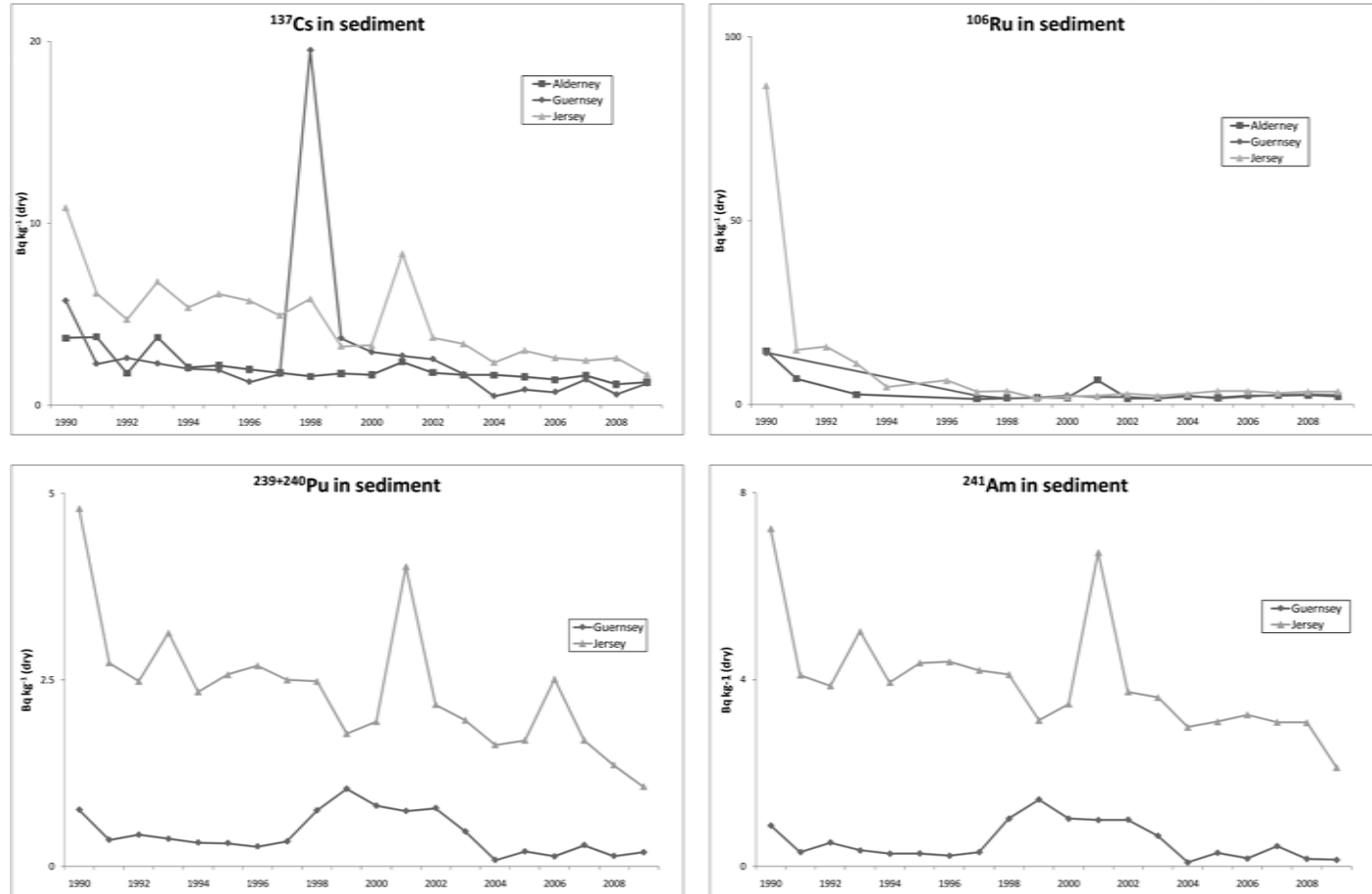


Figure 2 Trends of radionuclide concentrations in Channel Islands sediments (data below the level of detection are indicated in the text)

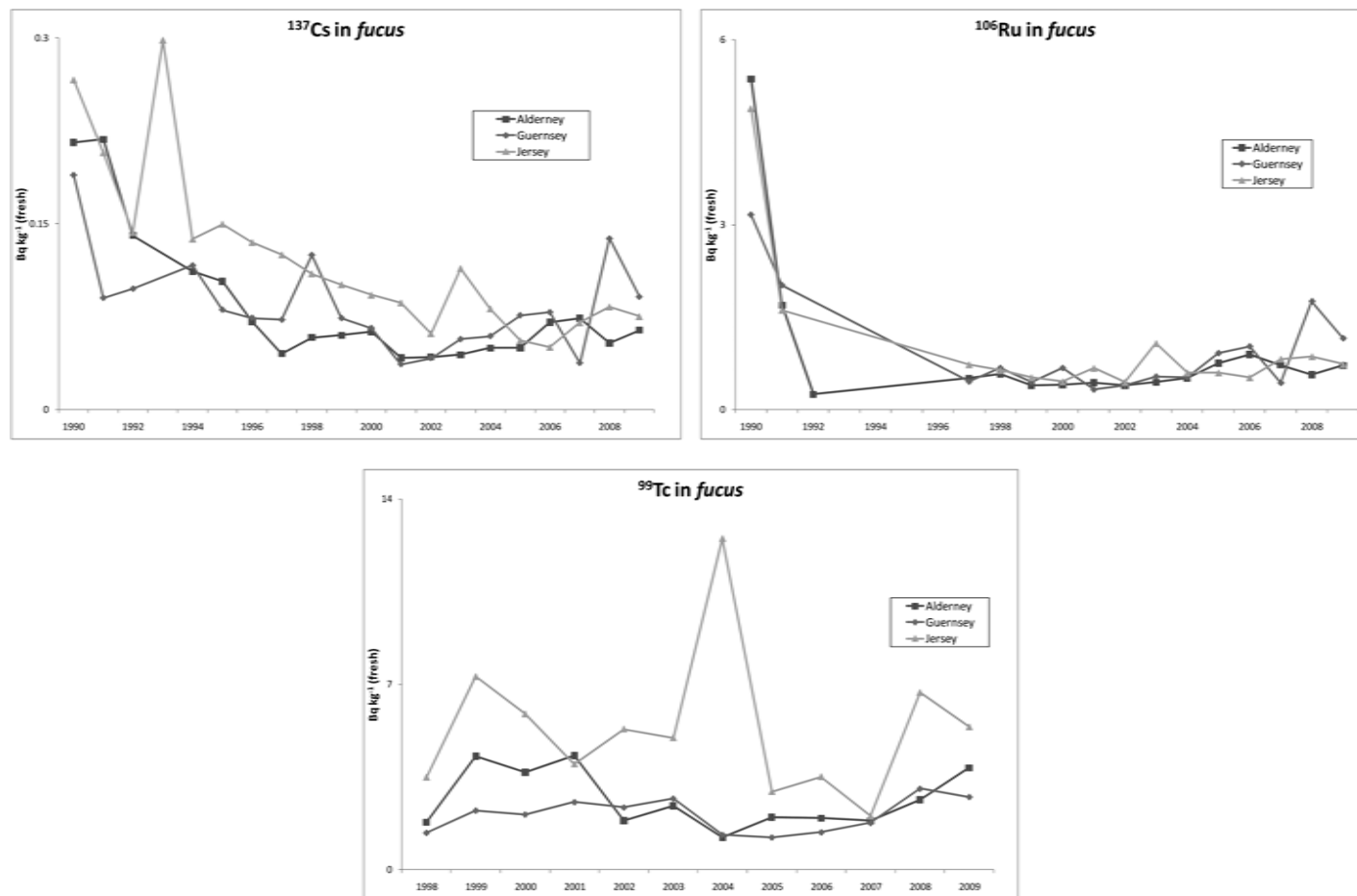


Figure 3 Trends of radionuclide concentrations in Channel Islands seaweeds (data below the level of detection are indicated in the text)

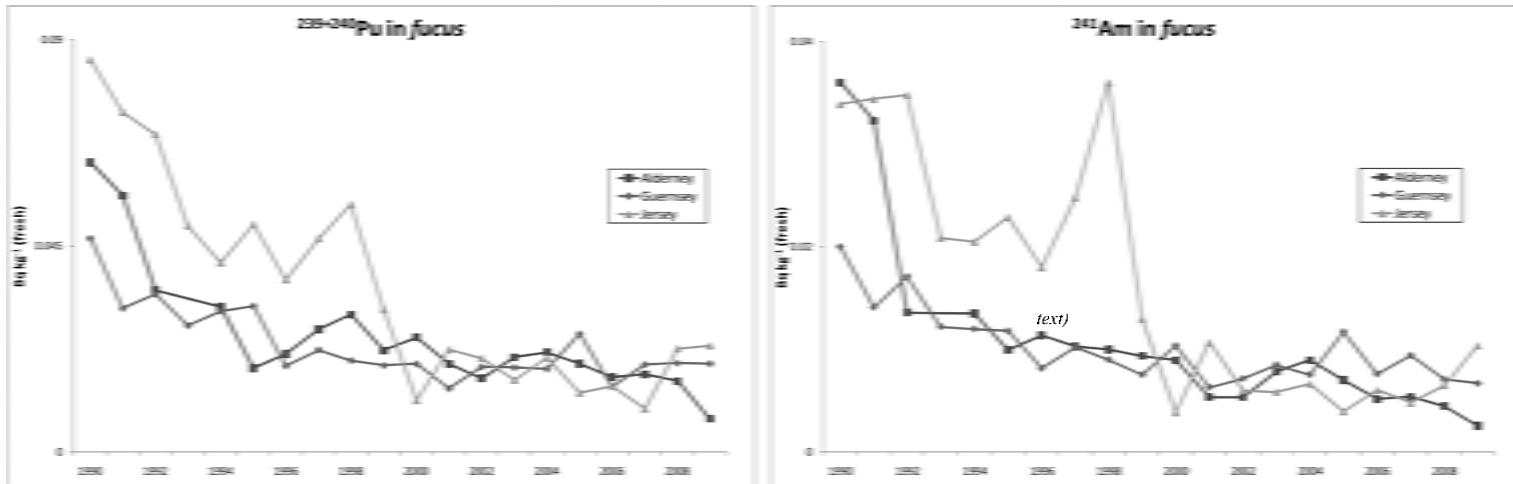


Figure 3 (continued) Trends of radionuclide concentrations in Channel Islands seaweeds (data below the level of detection are indicated in the

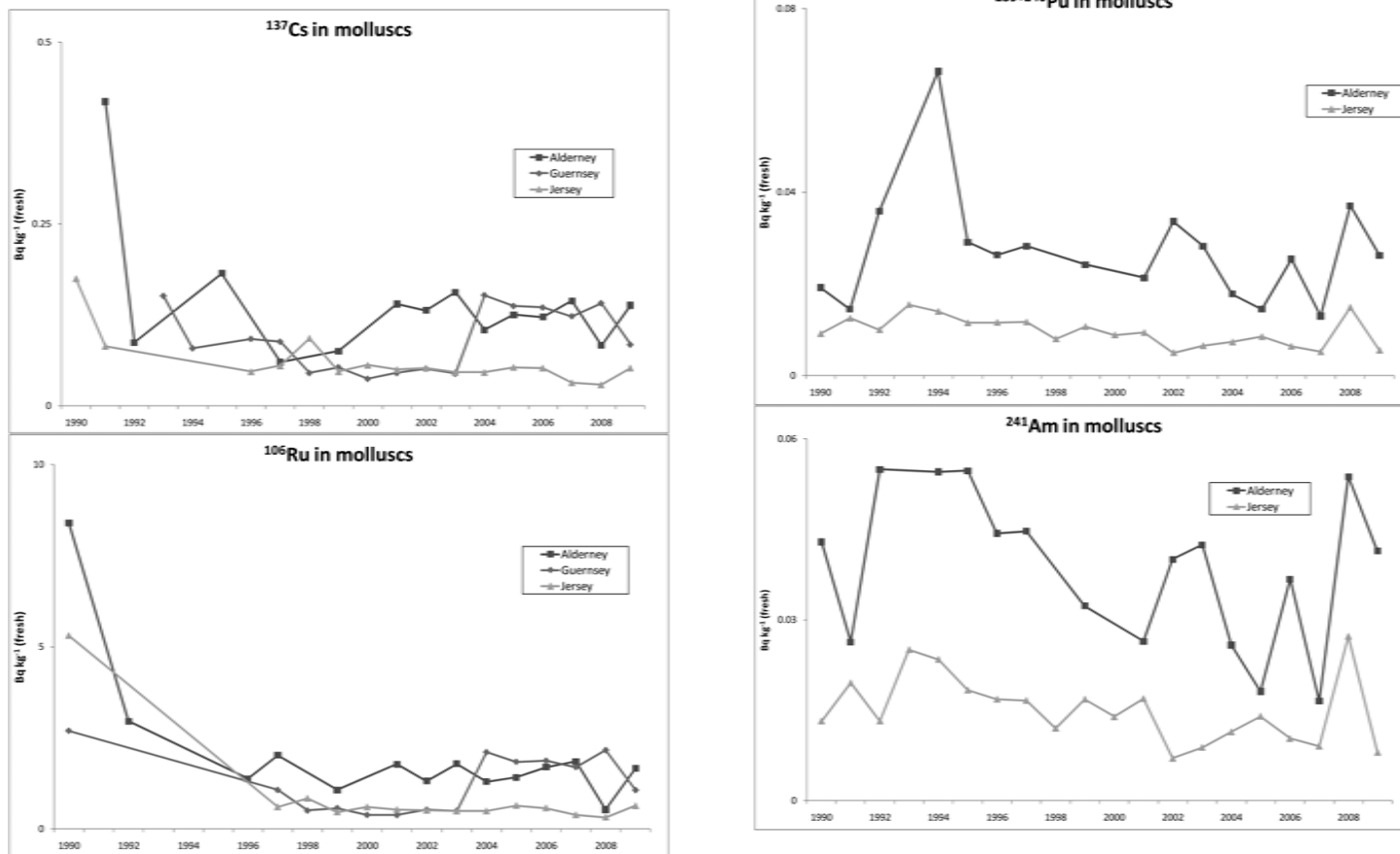


Figure 4 Trends of radionuclide concentrations in Channel Islands molluscs (data below the level of detection are indicated in the text)

5 CONCLUSIONS

The conclusions are summarised as follows

- Relatively low concentrations of radionuclides were detected in the marine environment around all the Channel Islands.
- Most non-transuranic radionuclide concentrations reported here (caesium-137 and ruthenium-106) have declined since the last review in 1998.
- Transuranic radionuclide concentrations reported here (plutonium-239+240 and americium-241) and have either declined since the last review in 1998, or there has been no significant change in concentrations (albeit with some environmental scatter between individual years).
- The effects of discharges from local sources have continued to be of negligible radiological significance.
- There was no detectable effect in Channel Islands waters of any releases of radioactivity from the Hurd Deep site.

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DEVELOPMENT OF A SMALL MOBILE UNIT FOR EMERGENCY RADIOLOGICAL MONITORING OF THE FOODCHAIN

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1 INTRODUCTION

In the event of an emergency involving the release of radioactivity to the environment, such as at a nuclear establishment or as a result of a radiological/nuclear (R/N) incident, protection of the public is a first priority. Short-term countermeasures of shelter, evacuation and application of stable iodine can all reduce the risk to the public if applied effectively. Further, the Food Standards Agency has the responsibility to rapidly assess the potential impact on the food chain and to expedite a response, which may involve restrictions on particular types of food under the provisions of the Food and Environment Protection Act 1985. Avoidance of unnecessary restrictions would be important on grounds of continuance of essential supplies, cost, and the need for disposal of unusable food. Appropriate calculational models can predict likely areas for food restrictions but validation would be needed in terms of ground deposition of radionuclides and concentrations in relevant environmental materials and foods. Therefore, appropriate monitoring facilities would need to be available to support such model assessments.

Historically (e.g. post - Chernobyl), Food Standards Agency and its predecessors carried out such monitoring by field sampling and transport to fixed laboratories, often distant, for analysis. More recently, Cefas has developed a small Mobile Monitoring Unit (MMU) based on modular equipment transported by fleet or hire vehicles which can be deployed rapidly in the event of an emergency to provide early field support and data transmission to headquarters decision making teams. The arrangements for monitoring food chains in the UK in the event of a nuclear/radiological emergency are briefly reviewed here, with particular reference to the need for mobile monitoring facilities. The development of the MMU is described and its capabilities summarised. The unit has been successfully deployed during emergency exercises, and experience of this deployment is related.

2 FEASIBILITY STUDY

Initially, a study was carried out to assess the feasibility of developing a small mobile monitoring unit.¹ Existing mobile facilities of all types available to nuclear site operators

and other organisations in the UK and abroad (particularly in Europe), were reviewed to survey experience and availability. Based on this, a number of options were set out, ranging from: no action (i.e. minimal use of existing systems); collaboration with other organisations; a modular system for transport by vans or estate cars; to small and large dedicated vehicles. Advantages and disadvantages were considered.

As a result, the study excluded the “do nothing” option. The options with dedicated vehicles were ruled out on grounds of capital cost and that such vehicles need permanent parking/garaging, regular maintenance and are subject to depreciation. Collaboration was investigated and found to be costly, with the added risk that in an emergency affecting more than one organisation there could be competition for use of facilities. Hence the recommendation from the feasibility study was for a small, modular, transportable detector system.

Equipment requirements were also considered, and it was recommended to employ mainly gamma spectrometry in view of its ability to provide relatively rapid radionuclide identification and measurement with minimal sample preparation. Other systems, such as alpha and beta contamination monitors, could be added, and inclusion of gamma dose rate instruments would be prudent. It was recommended to employ High Purity Ge (HpGe) spectrometry systems for radionuclide identification and measurement, with NaI(Tl) scintillation detectors for cost-effective analysis of known gamma emitters. The study made a number of other recommendations on data transfer, power supplies, communications and radiological safety.

3 DEVELOPMENT OF THE MOBILE MONITORING UNIT (MMU)

3.1 Ge detectors

The MMU employs two HpGe detectors with modular shielding that can be assembled easily.² The first system constructed is shown in Figure 1. It is based on a cost-effective p-type detector of 50% efficiency relative to 3"x 3"NaI, with Al end cap and good energy resolution. It has a 5 l liquid nitrogen Dewar vessel giving a holding time of about 3 days; it was envisaged that this would be long enough to obtain further liquid nitrogen more locally to the point of use. This detector uses the Canberra “Inspector” analysis system. For the second detector, shown in Figure 2, the specification included a request for improved efficiency at photon energies 30-60 keV, thus uses a n-type detector of 60% efficiency with carbon fibre end-cap. It has a lighter, 3 l Dewar with holding time of 2 days. It uses the ORTEC “nomad plus” analysis system.

In order to obtain a low limit of detection, shielding was provided, but to control the weight and allow portability the thickness was limited to 1" of aged lead. This was machined in rings with a lid to allow easy carriage and assembly. Both detectors were provided with a modular table for mounting the detector in an upward configuration for easy placement of the shielding and samples. The maximum size that can be accommodated is a standard laboratory 1 l plastic bottle, but the normal sample is a standard 287 ml tub.

3.2 NaI(Tl) detectors

Considerations of cost and efficiency pointed towards the popular 3"x 3" size of detector. Three detectors were acquired, including high voltage supplies and pulse-height analysis systems. The latter eliminated traditional analogue-to-digital converters in favour of sound

cards (which use an identical principle) incorporated into the laptops used to accumulate the spectral data.

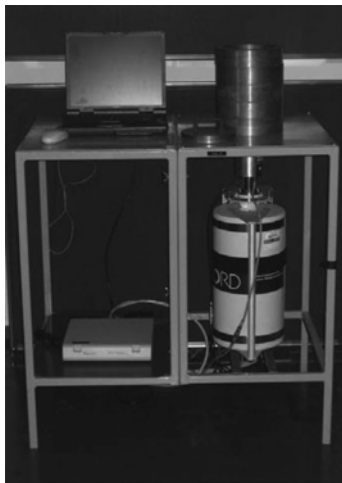


Figure 1 *p-type HpGe system*

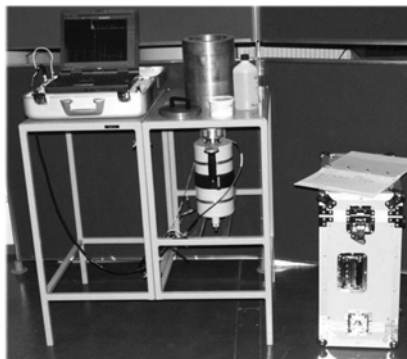


Figure 2 *n-type HpGe system*

Simple stands were designed to hold the detectors in use. The efficiency of the NaI detectors is such that an adequate detection limit can be obtained for nuclides emitting high-energy photons (say >500 keV) and where there is minimal interference with natural background peaks, but at lower energies and in the presence of interference, minimal shielding is advantageous. The need for minimal shielding helped to keep the design light and simple, and easy to accommodate different sizes of sample. As for the HpGe detectors, the system was calibrated for the standard 287 ml tub source. This may be extended to a 1 l bottle for measurement of liquids.

The system in operation in the field is shown in Figure 3.

3.3 Additional Equipment

The detectors described above are supported by further equipment. First, there are three 'milk monitors' consisting of 3" x 3" NaI detectors with 35 mm diameter wells operating in single channel mode with digital rate meters; these provide an output in counts per second and can be used to rapidly screen samples of milk which are inserted into the detector in 28 ml vials. There is a pool of mini-681 environmental survey meters with MC71 energy-compensated GM tubes to measure gamma air kerma rates; these can be used both for radiological safety of staff (personal dosimeters are also carried) and also to screen areas of land for dose rate which can be related to surface deposition. To monitor surface contamination there is a Berthold LB122 contamination monitor for beta activity and Electra Ratemeter with AP5 probe for alpha contamination.

In addition to radiological items there is communications equipment, such as mobile phones and additional laptops for e-mail communication of data. A supply of maps, both hard copy and digital, is included, as well as GPS equipment.

A supply of monitoring implements such as quadrats to demarcate areas of grass, trowels, shears, polythene bags, ties, marker pens, etc. accompanies the equipment.



Figure 3 *Operation of the NaI system*

Electrical supplies to the detectors and other equipment are at 240V, supplied by either inverters operating from 12V leisure batteries or from petrol driven inverter generators. These are maintained in a state of readiness. The timescale of independent operation is of the order of 2-3 days, after which it is envisaged that more permanent accommodation would be found, eg in a local government building or village hall.

The equipment packed ready for transport is shown in Figure 4.



Figure 4 *MMU ready for shipment*

4 TESTING, MAINTENANCE, AND QUALITY CONTROL

Following set-up of the counting equipment it was progressively tested, both in the laboratory and in the field, in order to optimise performance. The limits of detection were investigated, and these are shown in Table 1.

Table 1 *Approximate Minimum Detectable Activities* (Bq kg⁻¹, wet weight)*

<i>System</i>	<i>Radionuclide</i>			
	¹³¹ I	¹³⁴ Cs	¹³⁷ Cs	²⁴¹ Am
3"x3" NaI unshielded	110	40	36	-
3"x3" NaI 4mm Pb shield	58	36	33	-
p-type HPGe	27	26	28	-
n-type HPGe	16	17	15	36

*Based on a count time of 10 minutes for a 287 ml tub under normal background conditions. For comparison, the reference level for Cs in sheep following the 1986 Chernobyl accident was 1000 Bq kg⁻¹.

The counting equipment is supported, calibrated and maintained by Cefas. Minor repairs may be carried out by in-house electronics staff. Major components are covered by an annual manufacturers support contract. To maintain a consistent level of quality, Standard Operating Procedures have been developed covering both the counting equipment used in the MMU and sampling techniques. SOPs are reviewed annually and modified following feedback from the users and requirements of the customer.

Calibration of the detectors is carried out, following normal Cefas practice, against traceable certified standard solutions. Different density materials in a range of geometries represent the different types of environmental samples analysed. Equipment is tested on a quarterly basis with performance and corrective action recorded. All dose monitoring instruments are tested and calibrated annually by an approved testing laboratory.

Training and refreshment of MMU operating staff is vital to effective operation, and this is accomplished both by training in the laboratory and in the field on simulated emergency exercises. As part of the continued MMU team laboratory training, quality control samples are passed through the counting equipment on a regular basis. Each detector has its own quality control sample consisting of a sealed 287 ml tub containing known amounts of Am-241, Cs-137 and Co-60; these have been chosen to give a test over the full energy range. In the analysis they are treated as samples and the results reported are compared to the known activities. If the activities are within the upper and lower limits set for the equipment then it is passed ready for use. Peak positions are also checked and if necessary adjustments made. Other test samples can be used for general diagnostics or demonstrations. Equipment is tested and charged on a regular basis to maintain a state of readiness in case of an incident. Feedback obtained from exercises and training sessions is reviewed and, where practicable, suggestions are incorporated into the MMU systems and procedures thus maintaining a level of self-improvement and quality of service.

Simulated emergency exercises are carried out in the field approximately annually. Figure 6 shows the MMU in use during a field exercise. These are either held as part of the national exercise programme set by the Nuclear Emergency Planning Liaison Group or arranged independently by Cefas in liaison with customers. These exercises test the equipment itself and also the MMU staff both in operating it and also in taking appropriate samples.



Figure 6 *MMU staff operating from a van in the field.*

5 FIELD EXPERIENCE AND SAMPLING

Putting the MMU to practical use both in terms of field trials and in operating under simulated emergency conditions has been vital to successful development of the unit. Initial field trials helped establish some of the basic parameters and practical issues.

In the early stages of monitoring, it is important to the Food Standards Agency to confirm the results of modelling of the source of the release, the direction of the plume and resultant deposition, thus grass and soil are monitored. Initial modelling and plotting of the plume identifies potential first areas to monitor, and, in the field, quadrats are used to outline areas of grass which is sheared and placed in plastic bags. On return to the counting vehicle, the measured activity is converted to activity per unit area which is then used to confirm or adjust the results of initial modelling. Soil is also sampled by taking surface scrapes using a trowel and placing it in a sample pot; at the vehicle the soil is weighed and the measured activity converted to activity per unit area, with the same objective as for grass. At a later stage, when the extent of deposition is better characterised, food samples are begun to be analysed for protection purposes. The initial emphasis is on leafy vegetables which are counted directly by gamma spectrometry, and milk, which is sampled from local farms and measured using the milk monitors.

Simulated emergency operation continues to provide experience and opportunities to optimise the system. After each exercise there is a post-mortem to try to learn from the experience. Coordination of: the field sampling; the analysis of samples; and data communication requires considerable judgement. For example, after setting up, pressure is on obtaining early results, thus initial sample delivery should be timed so that samples are ready when detectors are able to begin counting. This dictates the number of locations which can first be sampled. Further, the initial base for the MMU needs to be both fairly

central to the source of samples; basic facilities to provide creature comforts are also desirable. Assistance with sample collection by staff based in the vicinity with local road knowledge would be advantageous, as would a move after a few days operation to more practical accommodation with more space and fixed power supplies.

6 LIMITATIONS

Being a mobile unit, the MMU is subject to a number of limitations. First, the sample throughput rate for the main Ge and NaI detectors is about 4 samples per hour per detector, giving a maximum of 20 per hour with all detectors in operation. Thus the MMU would not be expected to have as large a sample throughput capacity and accuracy as an established, fixed laboratory, and in a real situation samples are also likely to be transported to established laboratories, particularly for analysis of alpha-emitting radionuclides. Other limitations relate to: the cooling-down time of the Ge detectors before analyses can begin, though this may be achieved whilst the MMU is en route; the limited availability of sample preparation which might give errors due to non-homogeneity of samples; temperature fluctuations which affect, particularly, the NaI(Tl) detectors; and the short counting times available under emergency conditions. Nevertheless these disadvantages need to be balanced against the MMU's speed of analysis for provision of rapid advice, and the reassurance this can offer in the local context.

7 CONCLUSIONS

A small mobile monitoring unit has been developed for assistance of the Food Standards Agency in a nuclear or radiological emergency. It can provide rapid measurements of radioactivity in grass, soil, milk and foodstuffs, mainly for gamma-emitting radionuclides. The unit is regularly tested in emergency exercise conditions. Experience suggests that, whilst the unit has a limited sample throughput capability, the results could provide useful initial information to validate dispersion models and to monitor radioactivity in foods.

Acknowledgement

We are grateful to the Food Standards Agency for funding this ongoing work.
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COMPARISON OF ANALYTICAL METHODS AND ICP-MS CORRECTION SCHEMES

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1 INTRODUCTION

Technetium is a second row transition element located in group 7 (IUPAC) of the periodic table and it shares much of its chemistry with its superior homologue, rhenium. The element has no stable, non-radioactive isotopes, and only trace amounts of technetium are found naturally.¹ The only occurrences in nature are due to spontaneous fission or neutron capture in uranium and molybdenum ores. The bulk of the technetium in the environment is of anthropogenic origin: a by-product of nuclear weapons testing, medical applications and nuclear power generation.²

There are three long-lived isotopes of the element ($t_{1/2} > 10^5$ years), but of these only ^{99}Tc is produced in macroscopic quantities. It is generated in high yield (6 atom%) from fission of ^{235}U or ^{239}Pu in nuclear reactors, and terabecquerel (kilogram) quantities are produced each year.³

The predominant chemical form of technetium in the environment under aerobic conditions is the pertechnetate ion (TcO_4^-) which is highly mobile in surface and ground waters.^{2,4,5} Furthermore, technetium is readily accumulated in plants,^{4,5} providing a route for ingestion and contribution to the committed radiation dose to the human population.

The greatest potential for the release of ^{99}Tc to the environment is in the reprocessing of spent nuclear fuel.⁶ Historically, nuclear reprocessing facilities have been unable to immobilise technetium from waste streams and technetium has been discharged in aqueous waste. In the last decade, tighter regulatory discharge limits for Tc have been imposed, and waste streams are treated routinely to minimize ^{99}Tc discharge.⁷ However, ^{99}Tc continues to be discharged to the environment³ and there remains a requirement to monitor levels of ^{99}Tc in groundwaters around such sites.

Technetium-99 is a pure beta emitter ($E_{\text{max}} = 294$ keV), and the main methods used for its determination in environmental samples have been radiometric: for example, liquid scintillation counting,⁸ and beta gas flow proportional counting,⁹ have been employed but these require lengthy chemical separation procedures to isolate ^{99}Tc from sample matrix and other beta emitters before measurement.

Inductively coupled plasma mass spectrometry (ICP-MS) has become well established for the determination of long-lived radionuclides in environmental samples,^{10,11} and this technique has been utilised extensively for the determination of ^{99}Tc ¹²⁻¹⁸ supplanting more traditional radiometric procedures. Although ICP-MS has many advantages over

radiometric determinations, many of the reported analytical methods for the analysis of environmental samples are still protracted by lengthy clean-up procedures to remove interfering elements prior to measurement, as spectroscopic interference at low activity concentrations is a significant issue.

The principal interferences in the determination of ^{99}Tc by ICP-MS are well documented.¹⁵⁻¹⁹ The presence of both natural ruthenium and molybdenum are known to give rise to elevated signals at $m/z = 99$. Natural ruthenium contains the direct isobar ^{99}Ru (12.76%), and signal enhancement at $m/z = 99$ due to molybdenum has been observed and attributed to either $^{98}\text{Mo}^1\text{H}^+$ formation¹⁹ or incomplete mass resolution from adjacent $^{98}\text{Mo}^+$ and $^{100}\text{Mo}^+$ peaks.¹⁷ Where levels of interfering elements are low, mathematical corrections¹⁹ can be applied to raw data to account for the interference effect. This is generally achieved by monitoring alternative isotopes of the interfering elements and relating those signals to the effect upon the analytical signal at $m/z = 99$. Such corrections are accomplished using either an assumed isotopic abundance (in the case of Ru), or an empirical factor derived from observed signals (in the case of Mo). The possibility of isobaric interference at $m/z = 99$ arising from other elements has also been described,¹⁵⁻¹⁷ although these effects have been reported to be minimised or eliminated by the use of ultrasonic nebulisation,¹⁵ or by specific tuning of analytical instruments.¹⁷

Although much has been reported about isobaric and abundance sensitivity interference upon analyte signals, the present literature pays little attention to the effects of interferences upon the isotopes monitored for the purpose of interference correction. We report here the significance of high levels of strontium upon the corrections applied for ruthenium and molybdenum interference, and present a simple, direct method for the rapid screening of borehole waters as applied to samples originating on and around the Sellafield site in Cumbria.

3 EXPERIMENTAL

3.1 Instrumentation

A PerkinElmer Sciex Elan DRC II ICP mass spectrometer with a Meinhard quartz nebuliser and cyclonic quartz spray chamber was used. Typical operating conditions and instrumental parameters are given in Table 1. Operating conditions were initially optimised using a multi-element solution containing Mg, Al, Cr, Mn, Cu, Cd, In, Ba, Ce, Pb, Th, and U at $1\ \mu\text{g L}^{-1}$. Conditions were adjusted to achieve adequate precision ($\text{RSD} \leq 2\%$) across the mass range and the Ce and Ba signals were used to adjust plasma conditions to minimise oxide and doubly charged ion formation. The signal at $m/z = 101$ was monitored to minimise the background. The instrument was further tuned using a solution containing ^{99}Tc at $2\ \text{ng L}^{-1}$ and In at $50\ \text{ng L}^{-1}$ to achieve the required stability and sensitivity for the determination of ^{99}Tc . The instrument was calibrated for ^{99}Tc over the range $0.1 - 20\ \text{ng L}^{-1}$.

3.2 Reagents and Materials

Ultra pure water ($18\ \text{M}\Omega\ \text{cm}$, ELGA PURELAB classic water purification system, Marlow International Parkway, Marlow, UK) and high purity nitric acid (Aristar grade, Fisher Chemicals, Loughborough, Leicestershire, UK) were used throughout. Stock ^{99}Tc standards were supplied by Sellafield Standards Laboratory, Sellafield Ltd., Cumbria, UK. Working solutions were prepared by serial dilution of the stock standards. Individual and

multi-element solutions of stable elements were prepared by dilution of commercially available, 1000 mg L⁻¹, single element standard solutions (SPEX Certiprep Group, Stanmore, Middlesex, UK).

3.3 Sample Processing

Aliquots of samples, 10 mL, were analysed directly after the addition of a fixed volume of indium internal standard solution in nitric acid to give an In concentration of 10 µg L⁻¹ and a nitric acid concentration of 1% v/v. Individual working standards containing Mo and Sr were run with each batch of samples to determine appropriate correction factors.

Table 1 *Typical ICP-MS operating parameters*

ICP RF Power (W)	1200
Plasma gas Flow (L/min)	15
Auxiliary Gas Flow (L/min)	0.8
Nebuliser Gas Flow (L/min)	0.97
Sweeps/readings	250
Number of Replicates	3
Scan mode	Peak Jumping
MCA channels	1
m/z monitored	88, 99, 100, 101, 115
Dwell Time ⁹⁹ Tc (ms)	150

3.4 Performance Assessment

The performance of the method was assessed using an 11 x 2 approach in keeping with the MCERTS performance standard for the chemical testing of water.²⁰

Eight groups of synthetic samples were prepared into which the interfering elements, Ru, Mo and Sr were spiked at varying concentrations spanning the ranges expected within borehole samples (Table 2). Within each of these matrix groups samples containing three levels of ⁹⁹Tc activity concentration were prepared: zero, 1.0 ng L⁻¹ (0.63 Bq L⁻¹) and 10.0 ng L⁻¹ (6.3 Bq L⁻¹).

Samples were analysed in duplicate on 11 occasions and data were analysed according to the MCERTS standard²⁰ to evaluate accuracy and precision.

Table 2 *Sample matrix element concentrations*

Matrix Group	Ru / ng L ⁻¹	Mo / µg L ⁻¹	Sr / mg L ⁻¹
1	-	-	-
2	5	-	-
3	20	-	-
4	-	5	-
5	-	30	-
6	-	-	0.5
7	-	-	2.0
8	10	10	1.0

4 RESULTS AND DISCUSSION

4.1 Assessment of Interfering Elements

A systematic study of the interference effects of 31 metallic elements¹⁷ considered the spectral overlap at $m/z = 99$ of direct isobars, doubly charged isobars, dimeric isobars and polyatomic argides, oxides and halides of the elements in nitric acid solutions. The study concluded that with appropriate tuning only ruthenium and molybdenum showed appreciable levels of interference at $m/z = 99$.

It is clear from the literature that correction for molybdenum and ruthenium is essential in the determination of ⁹⁹Tc and that this is achieved by monitoring alternative isotopes of these elements and relating this signal to the effect upon the signal at $m/z = 99$. However, such corrections require reliable measurement at the alternative isotope masses of the interfering elements. There are few references in the literature to the interference effects upon these signals.

Table 3 shows potential isobaric overlap from a range of elements in the region of Ru, Mo and ⁹⁹Tc measurement. It is evident that if $m/z = 98$ or 100 is selected to monitor and correct for Mo interference, and $m/z = 101$ or 102 is used to correct for Ru interference, there is potential for error in the measurement of these signals due to interference originating from Sr, Pt and Hg.

Table 3 Potential isobaric overlap in the m/z 98 – 102 region

Species	m/z						
Tc ⁺	99						
Sr ⁺	84 (0.56%)	86 (9.86%)	87 (7.0%)	88 (82.58%)			
SrN ⁺	98	100	101	102			
SrO ⁺	100	102					
Pt ⁺	190 (0.014%)	192 (0.78%)	194 (32.97%)	195 (33.83%)	196 (25.24%)	198 (7.16%)	
Pt ²⁺					98	99	
Mo ⁺	92 (14.84%)	94 (9.25%)	95 (15.92%)	96 (16.68%)	97 (9.55%)	98 (24.13%)	100 (9.63%)
MoH ⁺					98	99	101
Hg ⁺	196 (0.15%)	198 (9.97%)	199 (16.87%)	200 (23.10%)	201 (13.18%)	202 (29.86%)	204 (6.87%)
Hg ²⁺	98	99	100		101		
Ru ⁺	96 (5.54%)	98 (1.87%)	99 (12.76%)	100 (12.60%)	101 (17.06%)	102 (31.55%)	104 (18.62%)

Interference arising from Pt and Hg is unlikely. The elements are not abundant in nature and the probability of formation of doubly charged ions from these elements in the plasma is low. The second ionisation potentials of Pt and Hg are higher than the first ionisation potential of Ar²¹ and since the degree of ionisation of Ar in the plasma is expected to be less than 0.1%¹⁷ the formation of Pt²⁺ and Hg²⁺ will be negligible, and correction for these elements can be disregarded.

Our work suggests, however, that strontium derived polyatomic ions are significant. A series of strontium solutions in dilute nitric acid (1% v/v) containing Sr in the range 0 - 4.0 mg L⁻¹ were analysed under the conditions used for the determination of ⁹⁹Tc. The signals

at $m/z = 98, 100$ and 101 were recorded. Results (Figure 1) showed a linear increase in the observed signal with Sr concentration at each of the monitored m/z values. We attribute this to the formation of SrN^+ and SrO^+ in the plasma since the order of the effect observed for a given m/z value follows the natural abundance of the isotope from which the polyatomic ion is formed: the effect at $m/z = 98$ being least since it is derived from ^{84}Sr (0.56%) and the effect at $m/z = 100$ the greatest since it is derived from ^{86}Sr (9.86%).

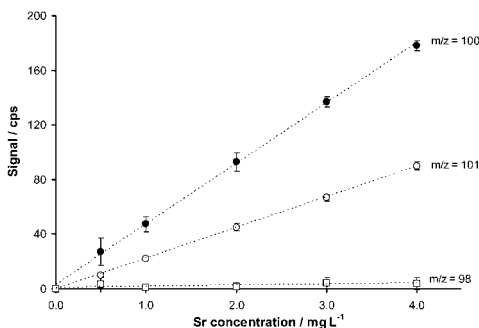


Figure 1 The influence of Sr concentration upon Ru and Mo signals

This effect is substantial. The instrument response to ^{99}Tc is typically $40 \text{ cps ng}^{-1} \text{ L}$. If signals are corrected for ^{99}Ru by subtraction of a fraction of the observed ^{101}Ru signal (isotopic ratio $^{99}\text{Ru}:^{101}\text{Ru} = 0.748$), then the assumption that the signal at $m/z = 101$ is wholly attributable to ^{101}Ru could lead to a significant bias. The presence of Sr at 1 mg L^{-1} (giving a signal of approx 20 cps at $m/z = 101$) could lead to a negative bias in the measurement of ^{99}Tc at 1 ng L^{-1} by as much as 40%. The strontium-derived interference will also have an effect upon corrections for Mo interference compounding the error.

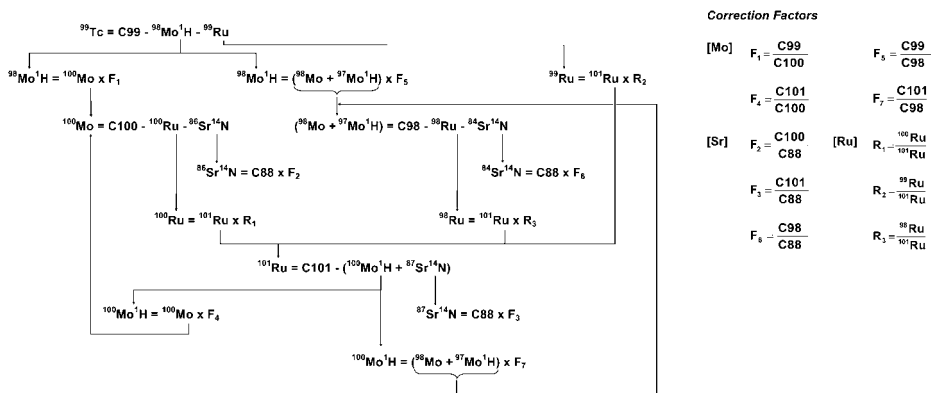


Figure 2 Theoretical correction scheme for Ru, Mo and Sr interference

A correction scheme to account for Sr interference is given in Figure 2. The scheme uses ^{101}Ru to correct for interference by ^{99}Ru since, although ^{102}Ru is more abundant, potential interference by Sr is likely to be significantly greater. An isobar at $m/z = 102$ can be

derived from the most abundant Sr isotope, ^{88}Sr (82.58%). The scheme presents two options for Mo interference correction: the use of the ^{98}Mo or ^{100}Mo signals. Either approach has merit. It may be possible to simplify the ^{98}Mo scheme because of the low abundance of ^{84}Sr giving minimal interference at $m/z = 98$, however, we illustrate the approach to correction here using the ^{100}Mo scheme.

The scheme is complicated by the cyclic nature of the Mo/Ru correction: theoretically, the signal attributed to ^{101}Ru requires correction for $^{100}\text{Mo}^1\text{H}$, for which the correction is derived from ^{100}Mo , and the ^{100}Mo signal requires correction for ^{101}Ru for which the correction is derived from ^{101}Ru . In practice, this was not a significant issue as the observed signal at $m/z = 101$ was found to be independent of Mo concentration.

A series of molybdenum solutions containing Mo in the range 0 – 40 $\mu\text{g L}^{-1}$ were analysed under the conditions used for the determination of ^{99}Tc . The signals at $m/z = 99$ and 101 were recorded. Results (Figure 3) showed a linear increase in the observed signal at $m/z = 99$ with Mo concentration as expected and reported elsewhere,¹⁹ but no such relationship was observed at $m/z = 101$. This observation is consistent with the findings of Más *et al.*¹⁷, wherein the concept of Mo hydride formation is discounted and the interference effect at $m/z = 99$ is attributed to abundance sensitivity.

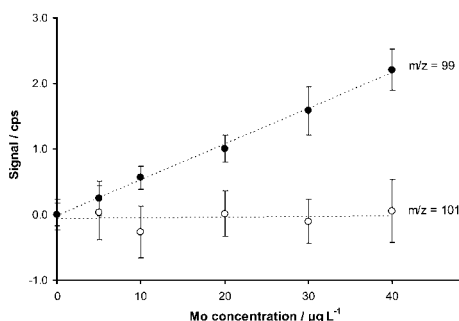


Figure 3 The influence of Sr concentration upon Ru and Mo signals

The absence of a Mo-derived signal at $m/z = 101$ simplifies the overall correction scheme such that the ^{101}Ru signal need only be corrected for Sr interference. The correction scheme can thus be summarised by a single equation:

$$^{99}\text{Tc} = \text{C99} - \left[\left(\text{C100} - \left\{ \left(\text{C101} - \langle \text{C88} \times \text{F}_3 \rangle \right) \times \text{R}_1 \right\} - \left\{ \text{C88} \times \text{F}_2 \right\} \right) \times \text{F}_1 \right] - \left[\left(\text{C101} - \langle \text{C88} \times \text{F}_3 \rangle \right) \times \text{R}_2 \right]$$

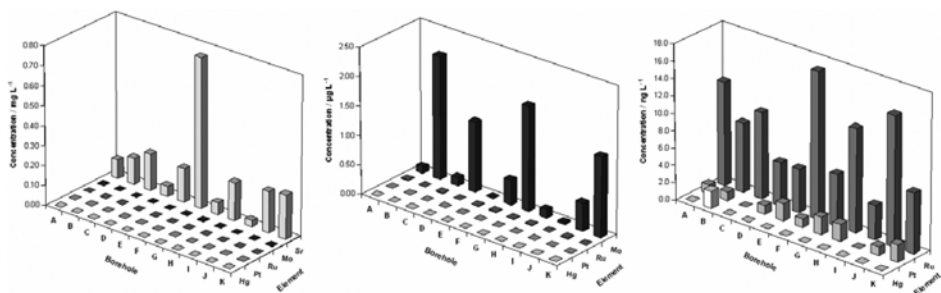
Where C88, C99, C100, and C101 represent the normalised, blank-corrected signals at the indicated m/z values for the sample being processed. The correction factors, F_1 , F_2 and F_3 , were determined by running Sr and Mo standard solutions with the analytical batch and deriving ratios (Figure 2) from the observed signals. Fixed values were used for the Ru isotopic ratios, R_1 and R_2 . These values were initially derived experimentally and then used in subsequent analyses. The values used (Table 4) were lower than the ratios derived from published isotopic compositional data.²² This is to be expected because of mass bias effects in the ICP-MS.²³ The values obtained were consistent with mass bias in the type of ICP-MS used: mass fractionation factors (f_{MD}) and mass discrimination values (MD) calculated from the data were typical.²⁴

Table 4 Ruthenium isotopic ratio data

	Isotopes	Natural isotopic ratio	Observed isotopic ratio	f_{MD}	MD (%)
R ₁	^{100}Ru : ^{101}Ru	0.739	0.718	1.03	2.9
R ₂	^{99}Ru : ^{101}Ru	0.748	0.721	1.04	1.8
R ₃	^{98}Ru : ^{101}Ru	0.110	0.094	1.16	5.5

4.2 Analysis of borehole samples

Analysis of borehole waters from a range of sampling points around the Sellafield site (Figure 4) showed insignificant, low ng L^{-1} , levels of Pt and Hg. Ru concentrations were also in the low ng L^{-1} range but, as there is a direct Ru isobar to ^{99}Tc , these levels are significant with regard to interference in the measurement of ^{99}Tc . Mo concentrations were in the low $\mu\text{g L}^{-1}$ range, which, for our operating parameters, is on the borderline of interference with ^{99}Tc . Strontium concentrations were in the low mg L^{-1} range – sufficient to bring about an observable negative bias in ^{99}Tc results corrected for Ru and Mo interference.

**Figure 4** Selected element concentrations in typical borehole samples

The ^{99}Tc content of 42 borehole samples was determined using the proposed ICP-MS procedure and data were processed to generate three sets of results: uncorrected; corrected for Mo and Ru only; and corrected for Mo, Ru and Sr. Each data set was compared with the results of the analysis of the same samples using a conventional radiochemical procedure²⁵ based upon isolation of pertechnetate using extraction chromatographic resin (TEVA[®], Eichrom) and measurement of beta activity by gas flow proportional counting.

The samples selected were those with ^{99}Tc activity concentrations of $< 1 \text{ Bq L}^{-1}$ as this is the region where the spectroscopic interference effects are most marked.

The comparison (Figure 5) illustrates the requirement for correction. Uncorrected results, (a), are very sporadic, Mo and Ru corrected results, (b), show better correlation but there is a noticeable negative bias, particularly significant around zero ^{99}Tc activity concentration. The inclusion of a Sr correction, (c), improves correlation and eliminates the negative bias.

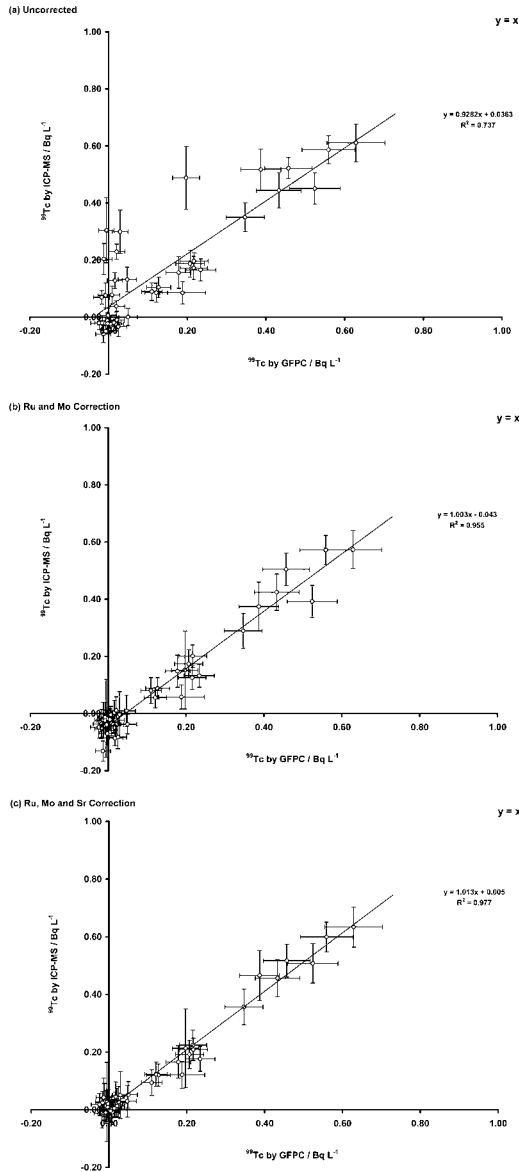


Figure 5 Comparison of analytical methods and ICP-MS correction schemes

4.3 Performance characteristics

Statistical analysis of the data from the determination of ^{99}Tc in the spiked synthetic samples was carried out according to the MCERTS performance standard for the chemical testing of water.²⁰

Samples from all matrix groups showed acceptable precision and bias with the exception of the low-level technetium sample from group 2 where, although the mean

recovery was shown to be acceptable, within-batch precision was 17% (RSD). Subsequent re-analysis of the synthetic sample revealed incorrect spiking, or contamination, with Ru. The Ru content of this sample was found to be $35 \mu\text{g L}^{-1}$, emphasising that there is an upper limit to the levels of interfering elements for which the correction can be applied if acceptable precision is to be achieved.

Limits of detection were dependent upon the degree of correction applied to the results. The worst-case value, with the levels of interfering elements assessed, was 0.1 Bq L^{-1} . The detection limit in the absence of interfering elements was 0.03 Bq L^{-1} , and the mean value across all groups, 0.06 Bq L^{-1} .

Table 5 *Method performance data*

Group	Within batch RSD / %		Between batch RSD / %		Accuracy / %		LOD / Bq L^{-1}
	^{99}Tc Low [†]	^{99}Tc High [‡]	^{99}Tc Low	^{99}Tc High	^{99}Tc Low	^{99}Tc High	
1	7.8	1.3	5.4	2.6	90.0	100.6	0.03
2	17.3 *	2.0	6.8	3.0	97.0	98.7	0.05
3	4.0	2.6	2.5	2.9	95.0	100.9	0.09
4	3.0	1.5	3.5	2.6	96.3	100.9	0.07
5	1.7	3.0	4.1	3.2	95.5	100.3	0.04
6	3.6	1.7	2.5	2.7	97.1	100.4	0.04
7	2.9	0.8	6.4	3.1	102.3	99.7	0.1
8	2.7	1.7	6.1	2.7	93.0	101.4	0.09

[†] Low ^{99}Tc spiked at 0.6 Bq L^{-1}

* Solution contaminated - found to contain Ru at 35 pg mL^{-1}

[‡] High ^{99}Tc spiked at 6 Bq L^{-1}

5 CONCLUSIONS

Analysis of waters for ^{99}Tc by quadrupole ICP-MS will always require an in-depth assessment of interferences in order to successfully quantify the low levels required by environmental monitoring programmes around nuclear sites. In many cases this will necessitate sample clean-up before measurement. Where levels of ruthenium and molybdenum are known to be low, it is possible to measure ^{99}Tc directly. However, even when levels of ruthenium and molybdenum in samples are low, if there is no sample clean-up prior to analysis it is apparent that correcting for molybdenum and ruthenium is not enough. Account must be taken of gross levels of elements that can interfere with not only $m/z = 99$, but also m/z values monitored for the purpose of Ru and Mo interference correction: in the case of the Sellafield borehole waters, strontium must be accounted for.

This study has demonstrated that rapid, cost effective screening of non-saline samples can be achieved by direct measurement without sample pre-treatment, and that results comparable to those of more traditional radiometric determinations can be achieved.

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ULTRA-TRACE DETERMINATION OF PLUTONIUM IN CORAL SAMPLES USING MULTI-COLLECTOR ICP-MS

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1 INTRODUCTION

Sources of plutonium isotopes to the marine environment are well defined, both spatially and temporally. Due to the physical and chemical properties of Pu and the long half-lives of its most abundant isotopes, ^{239}Pu ($T_{1/2} = 24\,100$ years) and ^{240}Pu ($T_{1/2} = 6\,561$ years), Pu is a potential tracer for oceanic processes.¹ The main sources of Pu to the World Ocean are fallout from the atmospheric nuclear tests and liquid discharges from the nuclear industry.² In the Pacific Ocean, the two main sources of Pu are global fallout and close-in fallout from the former US Pacific Proving Grounds (PPG) in the Marshall Islands.

The isotopic composition of Pu in the marine environment is characteristic of the source of contamination. The $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio in integrated worldwide global fallout is characterised by a ratio of about 0.18 while PPG-derived Pu is characterised by ratios higher than 0.25.^{3,4} Remobilised Pu from the lagoon sediments around PPG still act as a significant Pu source to the Pacific Ocean with an annual $^{239+240}\text{Pu}$ export of about 0.2 TBq to the open ocean.⁵ The common hypothesis is that PPG-derived Pu is transported long distances by the prevailing surface currents, North Equatorial Current and Kuroshio Current, in the Northwest Pacific. The Kuroshio Current plays an important role in energy balance and may have an impact on regional and global climate. Retrospective studies of the isotopic composition of Pu may therefore provide valuable information on past changes in the Kuroshio Current and further the development of ocean circulation models.

Coral bands contain elemental and isotopic information relating to the past ocean chemistry at the time of growth and are therefore an excellent proxy for the historical Pu signal in the surrounding seawater. The main advantage of using coral bands to retrieve the historical record of Pu isotopes is the absence of mixing processes between the annual/seasonal growth bands that may occur in ocean sediments.

Determination of Pu in environmental samples has usually been carried out by conventional alpha-spectrometry with the disadvantage of not resolving ^{239}Pu and ^{240}Pu due to their similar alpha energies. Recent developments of more sophisticated analytical techniques, such as ICP-MS, have made the determination the two Pu isotopes more reliable and accessible.⁶ Due to the excellent precision and accuracy of multi-collector ICP-MS for determine isotope ratios, it is a suitable technique for Pu isotope ratio analyses in low-level environmental samples.⁷

The separation of Pu prior to ICP-MS analysis required several steps to purify the samples from potential interferences. The most significant interference in Pu ICP-MS analysis is ^{238}U , with the formation isobaric hydrides ($^{238}\text{UH}^+$) and peak tailing from the ^{238}U peak, which may cause overestimation of the ^{239}Pu signal. Due to the limited sample mass of high temporal-resolution coral annual bands it is important that the analytical procedure is optimised for high Pu chemical yield and effective removal of U.

An analytical method for ultra-trace determination of Pu in small size coral samples using MC-ICP-MS is reported. The aim of the study was to optimise and validate an analytical method for measuring Pu isotopes in annual/seasonal coral band samples as part of a project using the historical Pu signature for studying past changes in ocean currents in the Northwest Pacific. The resulting analytical method is based on total digestion using high-pressure acid digestion, chemical separation by a combination of anion exchange and extraction chromatography and Pu analysis by MC-ICP-MS. The suitability of the method is demonstrated by application to a short coral core from the Chuuk Lagoon in the tropical Northwest Pacific.

2 METHODS AND RESULTS

2.1 ICP-MS Measurements

The Pu isotopes, ^{239}Pu and ^{240}Pu , were measured by a NEPTUNE high-resolution MC-ICP-MS equipped with an Apex HF high efficiency sample introduction system. The measurements were performed in low-resolution mode with a sample flow rate of $\sim 0.1\text{ ml min}^{-1}$ using a microflow PFA-100 nebuliser coupled to a SC-Micro Autosampler. The Pu isotopes and ^{238}U were measured simultaneously using multiple ion counting detectors and a Faraday cup, respectively. Tuning was performed daily by analysing a ^{242}Pu standard solution until maximal ion signal intensity was achieved. The ^{242}Pu sensitivity was usually around $1.8 \times 10^7\text{ cps (ng ml}^{-1}\text{)}^{-1}$ during normal operating conditions.

Standard solutions of ^{238}U were analysed to determine the contribution from ^{238}U (UH^+ and peak tailing) at masses 239 and 240. The signal ratios of masses 239 and 240 to mass 238 were usually in the ranges $1.3\text{--}2.1 \times 10^{-5}$ and $1.4\text{--}3.1 \times 10^{-7}$, respectively.

Estimations of limit of detection (LOD) and limit of quantification (LOQ) are based on IUPAC recommendations.⁸ The LOD was estimated to 0.02 fg ml^{-1} for Pu, corresponding to an absolute LOQ of $0.2\text{ }\mu\text{Bq}$ and $0.9\text{ }\mu\text{Bq}$ for ^{239}Pu and ^{240}Pu , respectively, for sample volumes of $\sim 2\text{ ml}$.

2.2 Analytical Method

The analytical method for the determination of Pu in coral samples is based on a total digestion of the samples followed by a combination of anion exchange and extraction chromatography (Figure 1).⁹ Briefly, the coral samples were dried and spiked with a known amount of ^{242}Pu and digested on a hot plate using tightly sealed Teflon bombs containing a mixture of HCl and HNO_3 , followed by Pu co-precipitation with $\text{Fe}(\text{OH})_3$. The precipitate was dissolved in 8 M HNO_3 and treated with NaNO_3 to control the Pu oxidation state (Pu(IV)) and passed through a preconditioned AG 1-X8 anion exchange column. The column was washed with 8 M HNO_3 and 10 M HCl before Pu was eluted with $9\text{ M HCl-}0.1\text{ M NH}_4\text{I}$. The eluent was evaporated to dryness and treated with HNO_3 and H_2O_2 to destroy any organic material and remove iodine. The samples were dissolved in $3\text{ M HNO}_3\text{--}1\text{ M Al}(\text{NO}_3)_3$, treated with iron(II) sulfamate and ascorbic acid to reduce all Pu

to Pu(III), and loaded onto a preconditioned two-column series of UTEVA and TRU resins. The samples passed through the UTEVA column directly onto the TRU column. After washing with 3 M HNO₃ the UTEVA was disconnected and Pu was eluted from the TRU column with 0.1 ammonium oxalate. The eluent was evaporated and treated with HNO₃ on a hot plate and transferred to ~2 ml 1% HNO₃ for the MC-ICP-MS analysis.

The overall average radiochemical Pu yield for the entire procedure was $86.5 \pm 2.7\%$ with the majority of Pu losses recorded in the anion exchange step. The average Pu yield for the extraction chromatography step was close to 100 %.

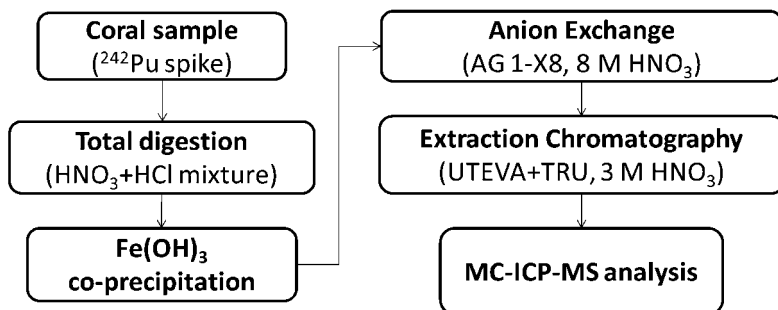


Figure 1 Flow chart of the analytical method for Pu determination in coral samples.

The U decontamination factor (DF) for the entire procedure was about 1.2×10^4 with DF after the initial anion-exchange step of only ~140. This emphasises the need for additional purification steps for the determination of Pu in low-level coral samples using MC-ICP-MS.

The analytical method was validated by analyses of IAEA-367 (Marshall Islands sediment) and IAEA-384 (Fangataufa Atoll sediment) reference materials (Table 1). The matrix of the reference materials contained almost 100 % calcium carbonate (CaCO₃) and is therefore representative of coral samples. The results in Table 1 represent the average of different samples with sample sizes ranging from 1 to 200 mg. The accuracy of the ²³⁹⁺²⁴⁰Pu activity concentrations was in good agreement (within 95 % confidence interval) with the IAEA recommended values, based on the method of comparing the certified and measured values with their combined uncertainties.¹⁰

The ²⁴⁰Pu/²³⁹Pu atom ratios in the IAEA-367 and IAEA-384 reference materials are heavily influenced by local fallout from the nuclear test sites in the Marshall Islands (PPG) and French Polynesia, respectively. There is no certified value for the ²⁴⁰Pu/²³⁹Pu atom ratio in the IAEA-367 sample. However, the obtained ratio agrees well with other reported values in the literature.^{11,12} The IAEA-384 ²⁴⁰Pu/²³⁹Pu atom ratio agrees well (within the 95 % confidence level) with the IAEA information value of 0.048 ± 0.012 ($k = 2$).

Table 1 ²³⁹⁺²⁴⁰Pu activity concentrations and ²⁴⁰Pu/²³⁹Pu atom ratios in IAEA certified marine reference materials obtained by MC-ICP-MS.

Reference material	²³⁹⁺²⁴⁰ Pu (Bq kg ⁻¹) ^a	²³⁹⁺²⁴⁰ Pu IAEA value (Bq kg ⁻¹) ^a	²⁴⁰ Pu/ ²³⁹ Pu (Atom ratio) ^a
IAEA-367 ($n = 5$)	36 ± 4	37 ± 13	0.306 ± 0.010
IAEA-384 ($n = 7$)	108 ± 14	108 ± 19	0.051 ± 0.004

^a Uncertainties are expressed as the expanded standard uncertainty ($k = 2$).

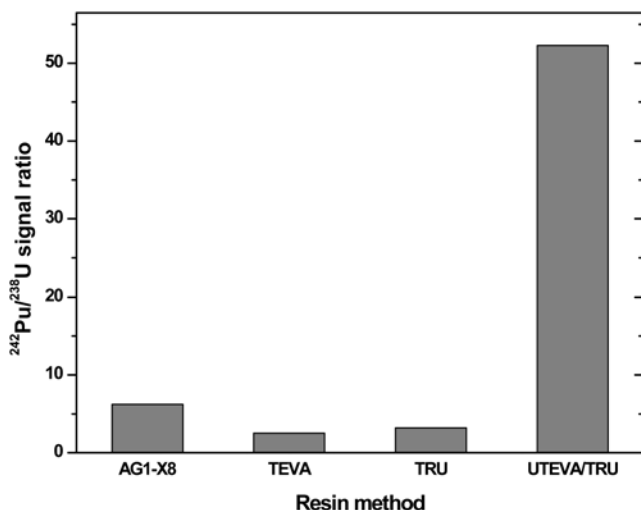


Figure 2 $^{242}\text{Pu}/^{238}\text{U}$ signal ratio (kcps mV^{-1}) in 0.1 g of IAEA-384 reference sample prepared using different resins.

A good indicator of method performance is the $^{242}\text{Pu}/^{238}\text{U}$ signal ratio in the MC-ICP-MS measurements, combining the Pu yield and U removal rate. Figure 2 shows the $^{242}\text{Pu}/^{238}\text{U}$ signal ratio for the reported analytical method compared with other methods (resins) from the literature.¹³⁻¹⁵ The observed Pu yields were similar (>80 %) for all the tested methods.

2.3 Determination of Pu Isotopes in Coral Samples

Plutonium is incorporated in the coral bands during growth with a constant relationship between the Pu concentration in the coral and the Pu concentration in the surrounding seawater.¹⁶ The analytical method was applied to the determination of ^{239}Pu and ^{240}Pu in a coral collected from the tropical Northwest Pacific.

The coral (*Porites*) sample was collected from Weno Island in the Chuuk Lagoon (7.45 °N, 151.90 °E) during the summer of 2008. The most recent ~40 cm (from the top) of the core was cut vertically to give a 5 mm thick slab and annual growth bands were estimated visually from X-radiograph images, corresponding to growth over approximately 25 years. Annual sub-samples (0.6–2.0 g) were retrieved by cutting the slab perpendicular to the growth axis.

The ^{239}Pu activity concentrations (Figure 3) showed a slight decrease along the annual coral growth bands corresponding to a reduced input of Pu into the lagoon in recent years. However, the ^{239}Pu trend does not reflect the Pu deposition pattern from global fallout, indicating an additional Pu source such as the remobilised Pu from the Marshall Islands (PPG).

The $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios (Figure 4) showed a similar trend with decreasing ratios in the more recent coral bands. The elevated $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios seen, compared with the global fallout ratio of 0.18, supports the hypothesis that Pu-laden seawater is transported by surface currents from the Marshall Islands (distance $\approx$ 2 100 km) to this lagoon.

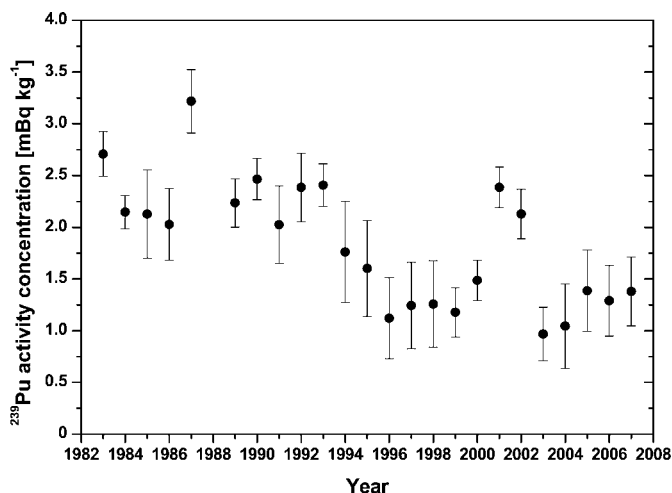


Figure 3 ^{239}Pu activity concentrations in annual growth bands of a Chuuk Lagoon coral. The error bars represent ± 1 standard deviation

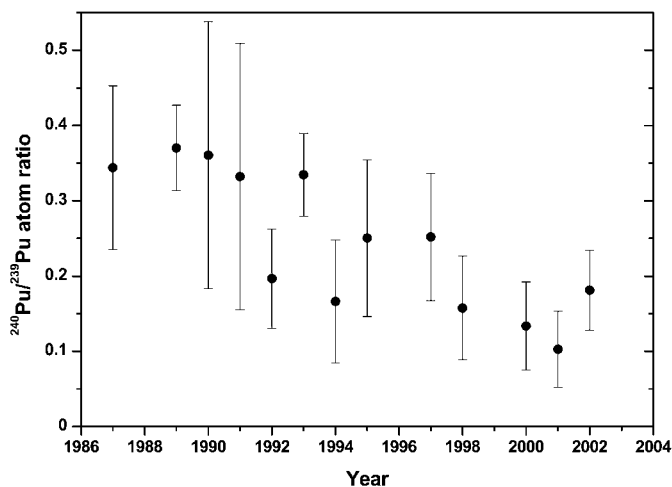


Figure 4 $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios in annual growth bands of a Chuuk Lagoon coral. The error bars represent ± 1 standard deviation

3 CONCLUSIONS

The overall Pu yield of the analytical method and the improved removal of U suggest that the method is suitable for the determination of ultra-trace Pu concentrations in small sized coral samples.

The analytical method was validated by analyses of certified reference materials with similar matrices to the coral samples. The $^{239+240}\text{Pu}$ results showed agreement with IAEA

values within the 95 % confidence interval and the $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios agreed well with previously reported ratios.

The method was applied to the determination of ^{239}Pu concentrations and $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios in small size coral samples collected at Chuuk Lagoon in the tropical Northwest Pacific. The results indicated transport by ocean surface currents of remobilised Pu from the contaminated marine sediments surrounding the former nuclear testing grounds on the Marshall Islands.

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²⁴⁸Cm, 31

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