IAEA/AQ/65

IAEA Analytical Quality in Nuclear Applications Series No. 65

Certification of Activity Concentration of Radionuclides in IAEA-465 Baltic Sea Sediment

IAEA
International Atomic Energy Agency

CERTIFICATION OF ACTIVITY CONCENTRATION OF RADIONUCLIDES IN IAEA-465 BALTIC SEA SEDIMENT

The following States are Members of the International Atomic Energy Agency:

AFGHANISTAN
ALBANIA
ALGERIA
ANGOLA
ANTIGUA AND BARBUDA
ARGENTINA
ARMENIA
AUSTRALIA
AUSTRIA
AZERBAIJAN
BAHAMAS
BAHRAIN
BANGLADESH
BARBADOS
BELARUS
BELGIUM
BELIZE
BENIN
BOLIVIA, PLURINATIONAL STATE OF
BOSNIA AND HERZEGOVINA
BOTSWANA
BRAZIL
BRUNEI DARUSSALAM
BULGARIA
BURKINA FASO
BURUNDI
CAMBODIA
CAMEROON
CANADA
CENTRAL AFRICAN REPUBLIC
CHAD
CHILE
CHINA
COLOMBIA
COMOROS
CONGO
COSTA RICA
CÔTE D'IVOIRE
CROATIA
CUBA
CYPRUS
CZECH REPUBLIC
DEMOCRATIC REPUBLIC OF THE CONGO
DENMARK
DJIBOUTI
DOMINICA
DOMINICAN REPUBLIC
ECUADOR
EGYPT
EL SALVADOR
ERITREA
ESTONIA
ESWATINI
ETHIOPIA
FIJI
FINLAND
FRANCE
GABON
GEORGIA
GERMANY
GHANA
GREECE
GRENADA
GUATEMALA
GUYANA
HAITI
HOLY SEE
HONDURAS
HUNGARY
ICELAND
INDIA
INDONESIA
IRAN, ISLAMIC REPUBLIC OF
IRAQ
IRELAND
ISRAEL
ITALY
JAMAICA
JAPAN
JORDAN
KAZAKHSTAN
KENYA
KOREA, REPUBLIC OF
KUWAIT
KYRGYZSTAN
LAO PEOPLE'S DEMOCRATIC REPUBLIC
LATVIA
LEBANON
LESOTHO
LIBERIA
LIBYA
LIECHTENSTEIN
LITHUANIA
LUXEMBOURG
MADAGASCAR
MALAWI
MALAYSIA
MALI
MALTA
MARSHALL ISLANDS
MAURITANIA
MAURITIUS
MEXICO
MONACO
MONGOLIA
MONTENEGRO
MOROCCO
MOZAMBIQUE
MYANMAR
NAMIBIA
NEPAL
NETHERLANDS
NEW ZEALAND
NICARAGUA
NIGER
NIGERIA
NORTH MACEDONIA
NORWAY
OMAN
PAKISTAN
PALAU
PANAMA
PAPUA NEW GUINEA
PARAGUAY
PERU
PHILIPPINES
POLAND
PORTUGAL
QATAR
REPUBLIC OF MOLDOVA
ROMANIA
RUSSIAN FEDERATION
RWANDA
SAINT LUCIA
SAINT VINCENT AND THE GRENADINES
SAMOA
SAN MARINO
SAUDI ARABIA
SENEGAL
SERBIA
SEYCHELLES
SIERRA LEONE
SINGAPORE
SLOVAKIA
SLOVENIA
SOUTH AFRICA
SPAIN
SRI LANKA
SUDAN
SWEDEN
SWITZERLAND
SYRIAN ARAB REPUBLIC
TAJIKISTAN
THAILAND
TOGO
TRINIDAD AND TOBAGO
TUNISIA
TURKEY
TURKMENISTAN
UGANDA
UKRAINE
UNITED ARAB EMIRATES
UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND
UNITED REPUBLIC OF TANZANIA
UNITED STATES OF AMERICA
URUGUAY
UZBEKISTAN
VANUATU
VENEZUELA, BOLIVARIAN REPUBLIC OF
VIET NAM
YEMEN
ZAMBIA
ZIMBABWE

The Agency's Statute was approved on 23 October 1956 by the Conference on the Statute of the IAEA held at United Nations Headquarters, New York; it entered into force on 29 July 1957. The Headquarters of the Agency are situated in Vienna. Its principal objective is "to accelerate and enlarge the contribution of atomic energy to peace, health and prosperity throughout the world''.

IAEA/AQ/65

IAEA Analytical Quality in Nuclear Applications Series No. 65

CERTIFICATION OF ACTIVITY CONCENTRATION OF RADIONUCLIDES IN IAEA-465 BALTIC SEA SEDIMENT

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 2021

COPYRIGHT NOTICE

For further information on this publication, please contact:

IAEA Environment Laboratories, Monaco
Radiometrics Laboratory
International Atomic Energy Agency
4a Quai Antoine 1er, 98000
Principality of Monaco

CERTIFICATION OF ACTIVITY CONCENTRATION OF RADIONUCLIDES
IN IAEA-465 BALTIC SEA SEDIMENT
IAEA, VIENNA, 2021
IAEA/AQ/65
ISSN 2074–7659

Printed by the IAEA in Austria
September 2021

FOREWORD

For more than 50 years the IAEA, through its Environment Laboratories, has been providing quality products and services for the study of radionuclides in marine samples, including the organization of interlaboratory comparisons, the production of reference materials and certified reference materials, and training. Producing a new reference material is a long process, covering the identification of needs, sample collection, pretreatment, physical homogenization, bottling, homogeneity testing, distribution to laboratories, data evaluation, preliminary reporting, additional analyses by expert laboratories, certification of material (including the determination of property values and their uncertainties), and finally issuing the reference materials and certified reference materials. More than 45 reference materials and certified reference materials have been produced, including a wide range of marine sample matrices and radionuclides.

As part of these activities, a sediment sample with elevated radionuclide levels due to a historical nuclear accident in the Baltic Sea region has been selected for a characterization study. This study aims to provide sufficient data using several different analytical methods to develop a new reference material. It is expected that the sample, after certification, will be issued as a certified reference material that can be used for the analysis of anthropogenic and natural radionuclides in sediment.

The IAEA wishes to thank the participants and laboratories that took part in this characterization study and the Helsinki Commission expert group on monitoring of radioactive substances in the Baltic Sea (HELCOM MORS EG) for providing the Baltic Sea sediment. The IAEA officers responsible for this publication were Mai Khanh Pham and S. Tarjan of the Division of IAEA Environment Laboratories.

EDITORIAL NOTE

This publication has been prepared from the original material as submitted by the contributors and has not been edited by the editorial staff of the IAEA. The views expressed remain the responsibility of the contributors and do not necessarily reflect those of the IAEA or the governments of its Member States.

This publication has not been edited by the editorial staff of the IAEA. It does not address questions of responsibility, legal or otherwise, for acts or omissions on the part of any person.

The use of particular designations of countries or territories does not imply any judgement by the publisher, the IAEA, as to the legal status of such countries or territories, of their authorities and institutions or of the delimitation of their boundaries.

The mention of names of specific companies or products (whether or not indicated as registered) does not imply any intention to infringe proprietary rights, nor should it be construed as an endorsement or recommendation on the part of the IAEA.

The contributors are responsible for having obtained the necessary permission for the IAEA to reproduce, translate or use material from sources already protected by copyrights.

The IAEA has no responsibility for the persistence or accuracy of URLs for external or third party Internet web sites referred to in this publication and does not guarantee that any content on such web sites is, or will remain, accurate or appropriate.

CONTENTS

1. INTRODUCTION

The accurate and precise determination of radionuclide concentrations in marine samples is an important aspect of marine radioactivity assessment and in the use of radionuclides in studies of oceanographic processes. To support and improve data quality, the IAEA Environment Laboratories (IAEA-EL) in Monaco regularly conduct characterization studies aimed to assign values to reference materials for radionuclides and other components in different matrices of marine samples as an integral part of the Sub-programme IAEA Reference Products for Science and Trade [1, 2].

In collaboration with HELCOM-MORS, sediment was sampled by the RV Aranda August 2012 cruise on 26 August 2012, at 82 m depth in the Baltic Sea (59° 34.91' N, 23° 37.61' E) at the station JML.

As the sample was collected in the Baltic Sea, elevated levels of long-lived anthropogenic radionuclides (such as caesium, plutonium isotopes) were expected due to the contamination caused by the Chernobyl nuclear accident. Participants were informed that the expected activities for natural and anthropogenic radionuclides would be in the ranges:

- γ-ray emitting radionuclides 0.1–1.5 kBq kg^{-1}
- α-particle emitting radionuclides 0.5–5 Bq kg^{-1}

The results of anthropogenic and natural radionuclides from 27 laboratories were used by the IAEA-EL to calculate the certified and information values of the new certified reference material (CRM). This report includes all details on the production of IAEA-465, complying the relevant standard ISO 17034 and ISO Guide 35 [3,4].

2. METHODOLOGY

2.1. SAMPLING AND PREPARATION OF THE MATERIAL

A total mass of 225 kg wet sediment was sampled by box corer (20 cm × 20 cm) on 26 August 2012, at 82 m depth in the Baltic Sea (at 59° 34.91' N, 23° 37.61' E; station JML of the RV Aranda August 2012 cruise for the HELCOM COMBINE program (HELCOM Contracting Parties within the COMBINE monitoring program).

The sediment sample was first air-dried to 108 kg and subsequently freeze-dried yielding 60 kg of dry sediment. The sample was then ground into powder using a micronisation technique (air-jet mill). The powder was then homogenised by mixing in a nitrogen atmosphere, then bottled and sealed in polyethylene flasks (50 g units) and coded as IAEA-465. A total of 960 bottles were produced. All bottles of sediment powder were sterilised with a 28 kGy gamma-ray dose (^{60}Co) at an irradiation facility (Synergy Health, France).

The density of sediment is 0.5 kg·dm^{-3}. The particle size distribution is shown in Fig. 1. The dominant particle size (approx. 80%) is between 1 and 10 microns.

The major elemental composition (excluding carbon and oxygen) of the sediment is 1.7% of Al, 12.9% of Si, 3.25% of K, 0.76% of Ca and 4.6% of Fe determined by XRF technique.

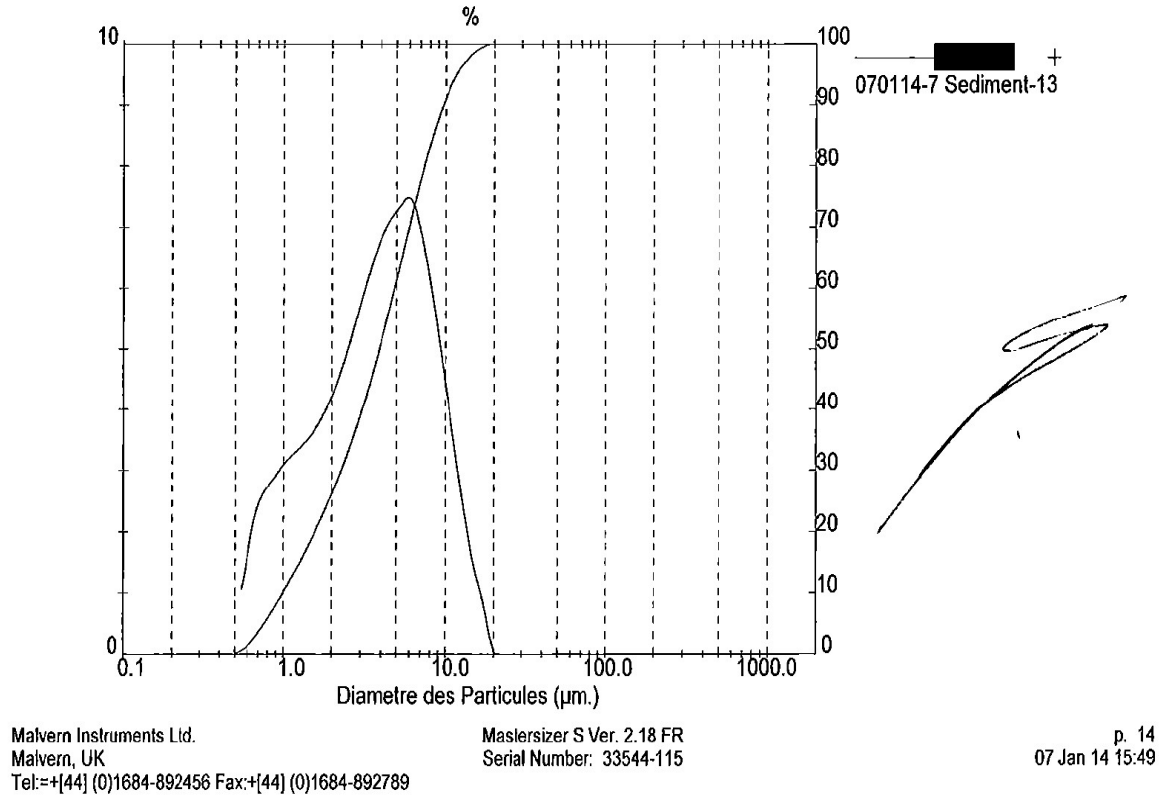

FIG.1. Particle size distribution of the IAEA-465 CRM.

2.2. HOMOGENEITY STUDY

Sample homogeneity was checked via three different ways:

1. the basic sediment elements were analysed by XRF technique from 16 packing bottles randomly selected (bottles number 120, 137, 229, 250, 3, 346, 371, 446, 489, 561, 611, 690, 721, 801, 841, 921), taking three 4 g aliquots, the results evaluated for Al, Si, S, Cl, K and Fe as main components, and for Zn, Br, Rb and Sr as minor elements,
2. gamma-ray spectrometry analysis from 15 packing bottles randomly selected (bottles number 5, 250, 611, 921, 120, 841, 446, 561, 137, 90, 371, 489, 801, 781, 229) and 3 subsamples of 40 g sample size, and the second was performed on 20 randomly selected bottles (bottles number 665, 682, 501, 505, 524, 537, 539, 546, 547, 553, 555, 720, 625, 504, 517, 687, 575, 491, 681, 606) taking 20 g of sample.
3. alpha emitting natural and transuranic radionuclides were determined by AMS (for Pu isotopes) and triple quadrupole ICP-MS (for U and Th isotopes) and by alpha particle spectrometry. Both between and within packing unit homogeneity was assessed.

The results were evaluated by basic statistical methods using the decomposition of standard deviation type measurement uncertainties, assuming that the remaining uncertainty is due to the heterogeneity only, as a conservative approach. The heterogeneity markers were selected according to the origin of the radionuclides. ^{40}K represents a macro component of the raw matrix (sediment, 3.25% K), and the ^{232}Th-series (^{228}Ac, ^{208}Tl) gives some information about the natural origin minor components. The Pu isotopes and ^{137}Cs are considered as anthropogenic origin pollutants, and the U isotopes can be a mixture of natural and anthropogenic pollution.

From these three separate sets of analytical results obtained from homogeneity tests, only one typical heterogeneity parameter was assessed and used in the final uncertainty budget.

2.3. STABILITY STUDIES

Both long-term and short-term stability of the IAEA-465 are demonstrated. Considering the long preparation process (from 2012 to 2020), the long-term stability can be assessed, via measurements performed during this period.

The conditions of the short-term stability test simulate the expected harsh transport situations with high variation of ambient temperature and exposure to direct heat radiation.

Activity concentrations of selected representative radionuclides (^{40}K, ^{137}Cs, ^{210}Pb, ^{228}Ra and ^{238}U) from IAEA-465 samples stored at ambient temperature (AT, approx. 22 °C), at -25 °C and at 70 °C for two weeks have been determined by gamma-ray spectrometry to assess stability under simulated varying environmental conditions.

TABLE 1. IAEA-464 GAMMA-RAY SPECTROMETRY MEASUREMENT FOR SHORT-TERM STAILITY CHECK STATISTICAL EVALUATION OF THE XRF MEASUREMENTS

Radionuclide	Temperature	Bottle number (number aliquots)	Confirmation measurement (Y/N)	Number of measurements
^{40}K, ^{137}Cs, ^{210}Pb	AT (22°C)	953 (2), 954 (2)	Y	4
^{228}Ra, ^{238}U	AT (22°C)	953 (2), 954 (2)	Y	4
^{40}K, ^{137}Cs, ^{210}Pb	-25°C	404 (2), 863 (2), 631 (1)	Y	5
^{228}Ra, ^{238}U	-25°C	404 (2), 863 (2), 631 (1)	Y	5
^{40}K, ^{137}Cs, ^{210}Pb	70°C	448 (2), 880 (2), 568 (1)	Y	5
^{228}Ra, ^{238}U	70°C	448 (2), 880 (2), 568 (1)	Y	5

2.3.1. Short-term stability study

The radionuclides were selected to keep the measurement uncertainty components as low as possible, by using fewer complex spectra evaluation gamma-ray spectrometry. Radionuclides with simple gamma-ray spectrometry spectra evaluations were selected to keep the measurement uncertainty components as low as possible. Precise repeatability parameters for each radionuclide were determined with a series of repeated measurements. The spectra were evaluated correcting for the sample mass and radioactive decay, and the gamma results were directly compared using zeta-score evaluation [6].

2.3.2. Long-term stability study

The results obtained from the short-term stability check, performed in 2020 (see above 2.3.1) were also used for long-term stability (or monitoring), as they were performed more than 5 years after the first homogeneity study by gamma-ray spectrometry at RML in 2012.

The results of the confirmation measurements were compared with the original Certified and Information Values by statistical evaluation using zeta-score calculation. Once the stability of the material was confirmed, all assigned values and their uncertainties of the activity concentrations were decay corrected to a new reference date of the 1st January 2020, while updated the reporting format of the uncertainties.

2.4. CHARACTERISATION

This characterisation study was organised to obtain sufficient data using different analytical methods on a sediment sample with elevated radionuclide levels in the Baltic Sea region due to the influence of the Chernobyl nuclear accident.

The characterisation study was designed to include the analysis of anthropogenic and natural radionuclides. Participating laboratories were requested to determine as many radionuclides as possible from the following: ^{40}K,^{137}Cs, ^{210}Pb,^{210}Po, ^{226}Ra, ^{228}Ra, U, Th and Pu isotopes. Any additional radionuclide measurements were included in the report as information values, unless sufficient data was available to justify statistical evaluation. The participating laboratories were chosen for both radiometric (γ-ray spectrometry, α-particle spectrometry and β-particle counting) and mass spectrometry measurement techniques (e.g., ICP-MS and AMS).

The samples were distributed to the selected 26 laboratories in May 2016. Each participant received 50 g of the sediment sample.

For each radionuclide analysed, the following information was requested:

- Average mass of sample,
- Number of analyses,
- Mass activity concentration calculated in net values (i.e., corrected for blank, background, moisture content, etc.), expressed in Bq kg^{-1},
- Estimate of whole budget uncertainty contribution,
- Description of chemical procedures and counting equipment,
- Reference standard solutions used; and
- Chemical recoveries, counting time, half-life (using data base for decay correction: http://www.lnhb.fr/nuclear-data/module-lara/).

Results not statistically significant were reported as “less than” values.

The reference date for decay correction purposes was set at 26 August 2012.

The selection of participants for this characterisation study was based on the measurement performances demonstrated by their laboratories in the previous IAEA inter-laboratory comparisons and certification campaigns on marine sediments. Only results from laboratories with a quality system, using validated methods, applying uncertainty and traceability concepts, and having provided good results in previous IAEA interlaboratory comparisons were accepted for the calculation of certified values and their uncertainties.
The deadline for reporting data was set for 30 September 2016. A reminder was sent to participants who did not submit the results in time extending the deadline to March 2017. A total of 26 laboratories sent their reports. The list of reported radionuclides is given in Table 9, Appendix I.

2.5. MOISTURE CONTENT DETERMINATION

The moisture content of the freeze-dried material, determined by drying a 1 g aliquot to a constant mass at 105°C, was found to be approximately 3.3 % at the time of the preparation of this sample. However, as the moisture content may change with the ambient humidity and temperature, it was recommended that it be determined again by the analyzing laboratories by drying at 105°C to a constant mass at the time of analysis in the laboratory and to correct the results accordingly.

3. RESULTS AND DISCUSSION

3.1. RESULTS OF HOMOGENEITY STUDY

3.1.1. Overall homogeneity study

The results obtained from XRF analysis provide a comprehensive and statistically strong picture about the homogeneity of the basic elemental composition of the material. The grain size is between 1–10-micron meter, and it was assumed that it will be similar for all radioactive analytes. The evaluation of the XRF measurement results from three 4 g aliquots from 16 packing bottles are presented in TABLE 2.

TABLE 2. STATISTICAL EVALUATION OF THE XRF MEASUREMENTS

Analyte	Average concentration	unc.	(s_{wb}), within units*	(s_{bb}), between bottle	u_h heterogeneity (relative value)
Al, %	1.676	0.091	0.117	0.121	0.097 (5.80%)
Si, %	12.821	0.086	0.171	0.240	0.170 (1.33%)
S, %	0.636	0.006	0.018	0.018	0.015 (2.31%)
Cl, %	0.943	0.004	0.008	0.017	0.011 (1.15%)
K, %	3.246	0.014	0.016	0.037	0.023 (0.72%)
Fe, %	4.609	0.008	0.013	0.047	0.028 (0.61%)
Zn, $mg \cdot kg^{-1}$	177.56	1.94	1.58	3.59	2.26 (1.28%)
Br, $mg \cdot kg^{-1}$	156.06	0.91	0.78	2.29	1.40 (0.89%)
Rb, $mg \cdot kg^{-1}$	154.69	0.81	0.62	2.54	1.51 (0.98%)
Sr, $mg \cdot kg^{-1}$	132.51	0.60	0.58	1.69	1.03 (0.78%)

*Calculated from three replicates

Where the

- S_{wb}, % standard deviation due to the within unit of bottle, estimated from the three replicates
- S_{bb}, % standard deviation due to the between units of bottles, estimated from the averages of each bottle

The typical value for material heterogeneity, based on a conservative approach is 1.58%.

Using gamma-ray spectrometry, two homogeneity tests were carried out, the first was performed on 15 randomly selected bottles taking three 40 g of sample aliquots of each, and the second was performed on 20 randomly selected bottles taking 20 g of sample. For the former case of γ-emitters measurements, the sediment sample was sealed in a tin-can geometry for three weeks to obtain the ^{226}Ra–^{222}Rn equilibrium (and its progenies) before gamma-ray spectrometry measurement. For the latter case the direct gamma measurement was performed for ^{40}K and ^{137}Cs. The calculation of normalized count numbers and uncertainties were done following ISO 18589-3 [5] and procedures set up by the Radiometrics Laboratory. The method repeatability was determined by repeated measurement (under repeatability conditions for 10 times) of one selected sample (sample number 606, see detail in 2.2 for homogeneity study). For the assessment of the heterogeneity, the residual parts of the peak area variances were used according to ISO Guide 35:2017 [4]. The results of the statistical evaluation are summarized in TABLE 3.

TABLE 3. STATISTICAL EVALUATION OF HOMOGENEITY TEST BY GAMMA-SPECTROMETRY FOR 40 G SAMPLE SIZE

Nuclide	Energy KeV	Counts	u, count	Min, %	Max, %	s_{wb}, %	s_{bb}, %	$s_{rep.lim}$, %	$u_{het(max)}$, %	$u_{het(min)}$, %
^{40}K	1460	11157	106	-2.41	3.03	0.93	0.65	2.69	1.14	0.63
^{137}Cs	661.7	13265	115	-2.01	2.88	0.74	1.09	2.14	1.32	1.0
^{214}Pb	351.9	3627	60	-8.96	15.26	1.56	4.48	4.77	4.77	4.48
^{214}Bi	609.3	2614	51	-6.41	16.54	2.52	4.76	7.25	5.39	5.02
$^{226}Ra_{(sum)}$	185/ 186	8848	94	-7.53	16.0	0.97	4.58	2.79	4.68	4.56
^{226}Ra ($-^{235}U$)	186	1309	36	-14.4	19.2	1.15	3.45	3.31	3.64	2.36
^{228}Ac	911.1	2082	46	-3.48	4.63	2.10	0.81	6.06	2.25	0.53
^{228}Ac	338.3	1547	39	-6.55	6.0	2.13	1.50	6.13	2.60	0.55
^{208}Tl	583.2	2455	50	-7.56	4.4	1.97	1.47	5.67	2.46	1.40

Where the

- Counts the normalized counts for uniform counting time (60000 s) and for sample weight
- u, counts the uncertainty of count numbers
- Min, % the lowest relative deviation from 3x15 measurement
- Max, % the highest relative deviation from 3x15 measurement
- s_{wb}, % standard deviation due to the within unit of one bottle, estimated from the three replicates

- s_{bb}, % standard deviation due to the between bottles, estimated from the averages of each bottle
- $s_{rep.lim}$, % repeatability limit estimated from the replicates
- $u_{het(max)}$, % estimated uncertainty due to the heterogeneity based on conservative approach
- $u_{het(min)}$, % estimated uncertainty due to the heterogeneity without the statistical variation of the radioactive decay

The estimated heterogeneity parameters from the radon progenies are much higher than others, almost independent from the detected counts numbers. The likely reason is the variation of the ^{222}Rn concentration in the air of the laboratory. In cases of relatively low counts numbers from the analyzed sample, a small change may have a visible effect in the peak area. The distribution of these results is skewed towards high count numbers.

Decreasing the sample quantity to 20 g, the ^{40}K and ^{137}Cs (natural and anthropogenic representatives) were tested by gamma-ray spectrometry, with the same results. The evaluation of the measurement results is summarized in TABLE 4.

TABLE 4. HOMOGENEITY TEST RESULTS ON 20 G SAMPLE SIZE*

Parameter	^{40}K	^{137}Cs
Number of results	20	20
Normalized average count numbers	5110	6223
Standard deviation	68	155
Minimum, %	-2,62	-5.05
Maximum, %	2,67	5.59
s_{bb}, %	1.33	2.49
$s_{rep.lim}$, %	2.1	3.07
$u_{het(max)}$, %	1.33	2.49
$u_{het(min)}$, %	1.1	1.9

*Parameters are the same definitions as listed for TABLE 3.

For the 40 g aliquot size, the estimated typical uncertainty from the average variances (based on the conservative approach) is 1.61% for within and 1.76% for between packing units, while the combined value is 2.39%, excluding the ^{222}Rn progenies. Decreasing the aliquot size to 20 g had no significant change, as shown in TABLE 4.

These values are in the same order of magnitude to the XRF results, however the differences between the ^{40}K and ^{137}Cs indicate that the distribution of the radioactive contaminants might be slightly different compared to the basic rock element composition.

The between bottle homogeneity was tested for alpha emitting radionuclides using a 5 g sample size. Eight aliquots from one packing bottle were analyzed for Pu isotopes, a pure anthropogenic origin pollutant. The results are summarized in TABLE 5. Wet digestion, oxidation degree adjustment, separation by ion exchange chromatography and alpha particle spectrometry was the applied radioanalytical method.

TABLE 5. RESULTS OF THE BETWEEN BOTTLE HOMOGENEITY STUDY FOR PU ISOTOPES

Nuclide	a*, $Bq \cdot kg^{-1}$	u*, $Bq \cdot kg^{-1}$(%)	Min, %	Max, %
$^{239+240}Pu$	2.168	0.053 (2.45)	-3.10	4.61
^{238}Pu	0.0597	0.0053 (8.95)	-12.31	15.11

*a as activity concentration and u as standard deviation of 8 measurements.

3.1.2. Within-bottle homogeneity study/minimum sample intake

A third within bottles test was performed on ten 0.3 g aliquots for plutonium isotope analysis by mass spectrometry AMS by Centro Nacional de Aceleradores, Universidad de Sevilla, Spain and on ten 0.3 g aliquots for uranium isotope determination using ICP-MS QQQ triple quadrupole system by the Departamento de Fisica Applicada I, Universidad de Sevilla, Spain. The results of the statistical evaluation are summarized in TABLE 6.

TABLE 6. RESULTS OF THE SMALL QUANTITY (WITHIN BOTTLE) OF SAMPLE MEASUREMENTS FOR IAEA-465

Sample ID	Nuclide	a, $Bq \cdot kg^{-1}$	u, $Bq \cdot kg^{-1}$	Min, %	Max, %	Method
2	^{239}Pu	1.166	0.088	-9.7	14.6	AMS
	^{240}Pu	0.843	0.060	-9.3	14.8	
	^{236}U	$2.01 \cdot 10^{-10}$	$3.07 \cdot 10^{-11}$	-16.9	33.9	
11	^{238}U	110	2	-1.33	4.82	ICP-MS QQQ
	^{235}U	5.08	0.09	-1.34	4.34	
	^{234}U	117	2	-1.09	4.22	
	^{230}Th	79.2	5.9	-5.9	18.2	
	^{232}Th	64.9	3.3	-7.9	12.1	

*Parameters are the same definitions as listed for TABLE 5.

The range of the reported results demonstrate that the sample homogeneity acceptable for extremely low sample sizes of 0.3 g.

The conservative estimation of the uncertainty due to the sample heterogeneity of 2.39% is accepted for all analytes, considering that the minimum sample size for gamma-ray spectrometry is 20 g and 5 g for radiochemistry methods. For special analytical methods like AMS or ICP-MS, a smaller sample size of 0.3 g can be used, however the variation between results is expected to be higher.

Since the ISO Guide 35 recommends any statistical evaluation for the assessment of the material heterogeneity based on several repetitions and analyzing multiple packing bottles, the observed range (Min%, Max%) gives useful information about the expected result from single sample measurement for the user.

3.2. RESULTS OF STABILITY STUDY

The short-term stability test simulates the possible harsh transport conditions and gives some information about the behavior of the material. This short-term stability of the material was tested by keeping two bottles at -25ºC and two bottles at +70ºC (and for comparison, two other bottles were kept at the ambient temperature) for a period of two weeks. The samples detailed in TABLE 1 were treated accordingly and analyzed by gamma-ray spectrometry (in 2020), focusing on the

target radionuclides and method repeatability. The measurement results were evaluated by zeta-score. Since the reference values for the zeta-score calculation were determined 4 years ago (in 2016), this test will be considered as a long term-stability check as well.

The zeta-score test was defined as:

$$\zeta = \frac{a_{\mathrm{m}} - a_{\mathrm{c}}}{\sqrt{u_{\mathrm{m}}^2 + u_{\mathrm{c}}^2}} \quad (1)$$

where:
a_{m} is the measured value [Bq kg^{-1}]
a_{c} is the certified value [Bq kg^{-1}]
u_m is the standard uncertainty (k = 1) for the measured value [Bq kg^{-1}]
u_c is the standard uncertainty (k = 1) for the certified value [Bq kg^{-1}]

If the absolute value of the zeta-score test exceeded 2.58, the results were evaluated as being significantly different (at a 99% confidence level).

For IAEA-465, five radionuclides ^{40}K, ^{137}Cs, ^{210}Pb, ^{228}Ra and ^{238}U with an original certified value, were tested for stability at different temperatures. As shown in TABLE 7, all the zeta-scores returned (absolute) values below the critical value of 2.58 (representing a confidence level of 99%). This confirms the short-term and long-term stability of IAEA-465.

TABLE 7. RESULTS OF SHORT-TERM AND LONG-TERM STABILITY TEST MEASUREMENTS FOR IAEA-465

Nuclide	**^{40}K**			**^{137}Cs**			**^{210}Pb**		
Bottle/Aliquot	a, Bq kg^{-1}	u*, Bq kg^{-1}	zeta-score	a, Bq kg^{-1}	u*, Bq kg^{-1}	zeta-score	a, Bq kg^{-1}	u*, Bq kg^{-1}	zeta-score
Reference values	**1073**	**50**		**90.2**	**2.7**		**160**	**5.5**	
953/1[A]	1069.7	40.0	-0.07	89.6	2.9	-0.15	146	18	-0.73
953/2[A]	1087.7	40.6	0.21	90.7	2.9	0.13	135	41	-0.61
954/1[A]	1088.2	40.6	0.22	91.6	3.0	0.34	142	24	-0.74
954/2[A]	1069.9	40.0	-0.06	89.9	2.9	-0.07	136	15	-1.50
404/1[B]	1072.3	40.1	-0.03	90.8	3.0	0.15	158	18	-0.08
404/2[B]	1083.5	40.5	0.15	91.3	3.0	0.28	129	17	-1.77
863/1[B]	1081.2	40.4	0.11	90.9	3.0	0.17	149	17	-0.63
863/2[B]	1082.1	40.4	0.13	90.9	3.0	0.17	156	16	-0.22
448/1[C]	1024.3	46.5	-0.73	90.6	3.5	0.09	129	17	-2.12
448/2[C]	1050.2	47.6	-0.35	93.2	3.6	0.67	132	17	-1.95
880/1[C]	1068.6	39.9	-0.08	89.1	2.9	-0.28	183	21	0.76
880/2[C]	1034.1	38.7	-0.63	90.0	2.9	-0.06	131	16	-2.10
581/1[C]	1057.2	39.5	-0.26	89.8	2.91	-0.1	152	16	-0.73

*The uncertainty is calculated using the k=1 coverage factor
[A]Ambient Temperature (bottles number 953 and 954)
[B]Temperature at -25° C (bottles number 404 and 863)
[C]Temperature at +70°C (bottles number 448, 880 and 581)

TABLE 7. RESULTS OF SHORT-TERM AND LONG-TERM STABILITY TEST MEASUREMENTS FOR IAEA-465 (cont'd)

Nuclide	**^{228}Ra**			**^{238}U**		
Bottle/Aliquot	a, Bq kg^{-1}	u*, Bq kg^{-1}	zeta-score	a, Bq kg^{-1}	u*, Bq kg^{-1}	zeta-score
Reference values	**64.5**	**3.0**		**87.3**	**3.1**	
953/1[A]	63.7	3.5	-0.18	95.2	7.7	0.96
953/2[A]	64.9	3.5	0.08	76.0	6.8	-1.51
954/1[A]	62.4	3.4	-0.46	83.2	6.6	-0.56
954/2[A]	63.6	3.4	-0.20	81.4	7.2	-0.74
404/1[B]	64.1	3.4	-0.09	86.0	7.5	-0.16
404/2[B]	64.0	3.5	-0.10	99.6	7.7	1.47
863/1[B]	65.4	3.6	0.19	81.4	7.5	-0.72
863/2[B]	65.3	3.5	0.16	84.2	7.2	-0.40
448/1[C]	61.4	3.2	-0.69	82.8	7.2	-0.57
448/2[C]	62.9	3.4	-0.35	84.4	7.3	-0.36
880/1[C]	61.8	3.4	-0.60	82.1	6.4	-0.73
880/2[C]	61.1	3.2	-0.76	81.5	6.7	-0.78
581/1[C]	63.3	3.5	-0.26	93.3	6.8	0.81

*The uncertainty is calculated using the k=1 coverage factor
[A]Ambient Temperature (bottles number 953 and 954)
[B]Temperature at -25° C (bottles number 404 and 863)
[C]Temperature at +70°C (bottles number 448, 880 and 581)

3.3. DETERMINATION OF ASSIGNED VALUES AND UNCERTAINTIES

The characterisation campaign resulted in 29 reported radionuclides of interest. The obtained data was first checked for compliance with the certification requirements, and then for validity based on technical reasoning.

The property values were determined using robust statistics which, as described in ISO 13528 [6] were used for the determination of the assigned values. The robust mean and robust standard deviations were calculated as per Algorithm A as described in Annex C.21 of ISO 13528 [6]. The calculations are summarized in Appendix III.

The standard deviation of the robust mean was used as the uncertainty of the characterization for each radionuclide, and the uncertainty due to the heterogeneity (2.39 %) and the uncertainty of the short term and long-term stability check (0 %) were propagated to this component.

The activity concentrations for 29 radionuclides were reported and results are shown in Table 9, Appendix I, with the number of reporting laboratories for each radionuclide. The results for the most frequently measured radionuclides can be found in Tables 10 to 25, Appendix I, and Figures 2 to 9, 11 and 13 to 17, Appendix II, while the less frequently measured radionuclides are presented in Table 26, Appendix I. The certified values obtained after statistical treatment are presented in Appendix I, Table 27, and information values are presented in Appendix I, Table 28, with nuclide ratios for uranium and plutonium given in Table 29.

3.4. EXPLANATION OF TABLES

Tables 10–26 contain the original reported data with a reference date of 26-08-2012 and an expanded uncertainty (k=2). The robust mean was used for the assigned values. Tables 27–28

contain the derived property values corrected for radioactive decay (and in some cases ingrowth) to 01-01-2020 and reported with an expanded uncertainty (k=2).

3.4.1. Laboratory code

Each laboratory was assigned an individual code number to ensure anonymity.

3.4.2. Method code

The analytical techniques employed by participants are specified with following codes:

TABLE 8. CODE OF THE ANALYTICAL TECNIQUES APPLIED BY PARTICIPANTS

Method code	Method	Detailed procedure
A	α-particle spectrometry	Treatment, evaporation/precipitation, ion exchange and electrodeposition followed by α-particle spectrometry
G	γ-ray spectrometry	High resolution γ-ray spectrometry using HP-Ge (High Purity Germanium) detectors
LSC	Liquid Scintillation Counting	Treatment, evaporation/precipitation, Liquid Scintillation Counting
ICP-MS	Inductively Coupled Plasma Mass Spectrometry	Treatment, ion exchange, ICP-MS (Inductively Coupled Plasma Mass Spectrometry)
AMS	Accelerator Mass Spectrometry	Leaching, treatment, AMS (Accelerator Mass Spectrometry)

3.4.3 Number of results

The number of determinations corresponds to the number of individual results received from each laboratory.

3.4.4 Activity concentrations

The activity corresponds to the arithmetical or weighted mean computed from all the individual results obtained from the participants with the corresponding standard deviation or weighted uncertainty. They are calculated as activity concentrations for each radionuclide respectively and expressed in the derived SI unit Bq kg^{-1}. A robust mean is given for certification.

3.5. EXPLANATION OF FIGURES

The figures (*Figs*. 2 to 9, 11 and 13 to 17, Appendix II) present the data in order of ascending activity concentration. Data in Figures 2–9, 11 and 13–17 are the original reported data and standard uncertainty (k = 2) with a reporting date of 26-08-2012. Reported values are coloured green with a circular marker, vertical lines represent the standard uncertainties. The horizontal red line is the robust mean for each nuclide on the reference date and the red dot lines are the standard uncertainty (k = 2) of the robust mean. Figures 10 and 12 show the ingrowth and decay of ^{226}Ra and ^{210}Pb over time and are for information only.

3.6. CRITERIA FOR ASSIGNING CERTIFIED VALUES AND UNCERTAINTIES

A good agreement within the stated uncertainty was observed for results obtained with different methods. Therefore, all results were considered in deriving the certified values.

A certified value was assigned when at least 5 independent results were available and its relative expanded uncertainty at k = 2 was less than 15% (i.e., $u(\bar{x})/\bar{x} \leq 0.15$). These criteria were fulfilled for ^{40}K, ^{137}Cs, ^{210}Pb (with ^{210}Po daughter), ^{226}Ra (with ^{214}Bi and ^{214}Pb daughters), ^{228}Ra (with ^{228}Ac daughter), ^{228}Th (with ^{224}Ra, ^{212}Bi, ^{212}Pb and ^{208}Tl daughters), ^{230}Th, ^{232}Th, ^{234}U, ^{235}U, ^{238}U (with ^{234}Th and ^{234m}Pa daughters), and $^{239+240}$Pu. The certified values are presented in Table 27, together with their expanded uncertainty (k = 2).

3.7. RESULTS DISCUSSION

3.7.1. ANTHROPOGENIC RADIONUCLIDES

Results of the determination of ^{137}Cs, ^{238}Pu, $^{239+240}$Pu and ^{241}Am reported by participants are presented in Tables 10−12, Appendix I, and shown in Figures 2−5, Appendix II.

3.7.1.1. ^{137}Cs

Twenty-six data sets were reported by 24 laboratories (Table 10, Appendix I and *Fig*. 2, Appendix II); all data sets could be used for data evaluation. The laboratories mainly used direct γ-ray spectrometry for the ^{137}Cs determination.

3.7.1.2. Plutonium isotopes

The majority of participants used a conventional radiochemistry method including sample treatment, ion-exchange separation followed by electrodeposition and α-particle spectrometry. Some laboratories could separately determine ^{239}Pu and ^{240}Pu using ICP-MS and AMS, after radiochemical separation of plutonium isotopes.

***a)* ^{238}Pu**

Thirteen data sets were reported (Table 11, Appendix I and *Fig*. 3, Appendix II), which were used for data evaluation. This nuclide was measured by α-particle spectrometry.

***b)* $^{239+240}$Pu**

Twenty data sets were reported from 19 laboratories (Table 11, Appendix I and *Fig.* 4, Appendix II). Both α-particle spectrometry and mass spectrometry techniques were used for $^{239+240}$Pu determinations. Most analyses were performed using conventional α-particle spectrometry, while some results were combinations from ICP-MS and AMS methods.

3.7.1.3. ^{241}Am

Ten laboratories reported 12 data sets of ^{241}Am activity concentration with 7 using α-particle spectrometry with prior radiochemical purification from rare earth elements, and 5 laboratories using direct γ-ray spectrometry measurement (Table 12, Appendix I and *Fig*. 5, Appendix II). It is worth to noting that the ^{241}Am values given by α-particle spectrometry appear lower than those obtained by γ-ray spectrometry, however there is no significant difference between two α-particle spectrometry and γ-ray spectrometry measurement techniques.

3.7.2. NATURAL RADIONUCLIDES

3.7.2.1. ^{238}U Uranium series

***a)* ^{238}U**

Eighteen data sets were reported from 15 laboratories (Table 13, Appendix I and *Fig*.6, Appendix II). Six participants used a conventional method based on sample treatment, ion-exchange separation followed by electrodeposition and α-particle spectrometry. Seven other laboratories used direct γ-ray spectrometry technique. Five laboratories could determine the activities using ICP-MS method, with prior radiochemical separation of uranium isotopes. Since ^{234}Th (8 data sets from 7 laboratories) and ^{234m}Pa (3 data sets from one laboratory) are in secular equilibrium with ^{238}U, the data from all three radionuclides was used to calculate the ^{238}U value.

***b)* ^{234}U**

Eleven data sets were reported from 10 laboratories (Table 15, Appendix I and *Fig*. 7, Appendix II). Most participants used a conventional method based on sample treatment, ion-exchange separation followed by electrodeposition and α-particle spectrometry. Three laboratories could determine the activities using ICP-MS method, with prior radiochemical separation of the uranium isotopes.

***c)* ^{230}Th**

Five data sets were reported (Table 16, Appendix I and *Fig*.8, Appendix II). Most participants used a conventional method based on sample treatment, ion-exchange separation followed by electrodeposition and α-particle spectrometry. One laboratory could determine the activities using ICP-MS method, with prior radiochemical separation of the uranium isotopes.

***d)* ^{226}Ra**

Fifteen data sets were reported from thirteen laboratories (Table 17, Appendix I, and *Fig*.9, Appendix II), also 7 and 6 laboratories reported ^{214}Bi and ^{214}Pb results, respectively (Table 18, Appendix I). Most laboratories used direct γ-ray spectrometry to determine ^{226}Ra activity at 186 keV or through their progeny ^{214}Bi and ^{214}Pb peaks at 609 and 352 keV, respectively. One laboratory used α-particle spectrometry technique and another one used LSC measurement method. The difference in the ^{230}Th and ^{226}Ra results indicates that the two nuclides are not in secular equilibrium and deriving the ^{226}Ra value at some future date needs to take account of ingrowth from ^{230}Th as well as simple radioactive decay. The change in activity concentration of ^{226}Ra over time is done via the Bateman equations [8].

$$c_{Ra-226,t} = c_{Ra-2\ \ ,0} \cdot e^{-\left(\frac{\ln 2}{T_{Ra-2}}\right)\cdot t} + c_{Th-23\ ,0} \cdot \left[\left(\frac{T_{Th-23}}{T_{Th-230}-T_{Ra-2}}\right) \cdot e^{-\left(\frac{\ln 2}{T_{Th-230}}\right)\cdot t} + \left(\frac{T_{Th-23}}{T_{Ra-226}-T_{Th-230}}\right) \cdot e^{-\left(\frac{\ln 2}{T_{Ra-2}}\right)\cdot t}\right] \qquad (Eq.\ 1)$$

Where:

0 (or t_0): The reference time, in this case – 2012-08-26 00:00
t: Time between the reference time and the time of measurement
$c_{Th-23\ ,0}$: Concentration of ^{230}Th at the reference time
$c_{Ra-2\ \ ,0}$: Concentration of ^{226}Ra at the reference time
$c_{Ra-22\ ,t}$: Concentration of ^{226}Ra at the time of measurement
T_{Th-230}: Radioactive half-life of ^{230}Th
T_{Ra-226}: Radioactive half-life of ^{226}Ra
The change in activity concentration of ^{226}Ra over time is given in figure 10.

***e)* ^{210}Pb**

Twenty-four data sets were reported from 16 laboratories (Table 19, Appendix I and *Fig*.11, Appendix II). ^{210}Pb and ^{210}Po were considered to be in equilibrium at the characterisation study period (2016), as ten half-lives of ^{210}Po had passed since the sampling time (August 2012) and the ^{210}Pb values were decay corrected to the reference date on 26 August 2012. Results for ^{210}Po were divided by the activity ratio between ^{210}Pb and ^{210}Po (1.018), when these nuclides are in secular equilibrium:

$$\frac{c_{Po-210,eq}}{c_{Pb-210,eq}} = \frac{T_{Pb-2}}{T_{Pb-210} - T_{Po-21}} \qquad (Eq.\ 2)$$

Where:

$c_{Po-\ \ ,eq}$: Concentration of ^{210}Po when secular equilibrium has been reached
$c_{Pb-21\ ,eq}$: Concentration of ^{210}Pb when secular equilibrium has been reached
T_{Pb-21} : Radioactive half-life of ^{210}Pb
T_{Po-210}: Radioactive half-life of ^{210}Po

While most participants used direct γ-ray spectrometry to measure ^{210}Pb at 46.5 keV, nine participants used α-particle spectrometry with prior radiochemical purification of ^{210}Po, then auto-deposition on a silver disc.
The ^{226}Ra and ^{210}Pb are not in radioactive equilibrium; there is a relatively large ^{210}Pb excess in the material, requiring a more complex decay correction method. The supported ^{210}Pb is in secular equilibrium with ^{226}Ra, therefore it (together with its progenies) decays by the ^{226}Ra half-life, while the unsupported ^{210}Pb decays at its own half-life, as shown by the change in activity concentration of ^{226}Ra over time in the Bateman equations [8].

3.7.2.2 ^{235}U series

Fourteen data sets were reported from 12 laboratories (Table 20, Appendix I and *Fig*. 13, Appendix II). Five participants used a conventional method based on sample treatment, ion-exchange separation followed by electrodeposition and α-particle spectrometry. Five laboratories determined ^{235}U using direct γ-ray spectrometry at 186 keV peak/line by subtracting the ^{226}Ra contribution in the same peak/line; or by assuming that the uranium present was of natural isotopic composition (see Table 29) and thus the activity ratio of ^{235}U to ^{238}U was 0.04662 ± 0.00009, which allows the ^{235}U activity to be estimated by γ-ray spectrometry from the ^{234}Th activity (which is in secular equilibrium with ^{238}U) determined from 63.3 and 92.5 keV γ-rays of this nuclide. Three laboratories could determine the activities using ICP-MS method, with prior radiochemical separation of the uranium isotopes.

3.7.2.3. Thorium series

***a)* ^{232}Th**

Ten data sets were reported from 9 laboratories (Table 21, Appendix I and *Fig*.14, Appendix II). Three data sets were analysed by γ-ray spectrometry, four others used a conventional method based on sample treatment, ion-exchange separation followed by electro-deposition and α-particle spectrometry; and three data sets were determined by ICP-MS method.

***b)* ^{228}Ra**

Fourteen laboratories reported data for ^{228}Ra (Table 22, Appendix I and *Fig*. 15, Appendix II). All laboratories used direct γ-ray spectrometry to determine ^{228}Ra activity through progeny either ^{228}Ac at 911 keV or ^{228}Th at 238 keV or 583 keV. Since ^{228}Ac is always in secular equilibrium with ^{228}Ra, the results for ^{228}Ac are included in the calculation of ^{228}Ra (Table 23). Based on the reported results and control measurements there is no significant difference between the ^{232}Th, ^{228}Ra and ^{228}Th and progenies, so it can be assumed that the ^{232}Th series are in secular equilibrium.

***c)* ^{228}Th**

Eight data sets were reported (Table 24, Appendix I and *Fig*. 16 Appendix II). Most participants used direct γ-ray spectrometry to determine ^{228}Th at two peaks: 238 keV of the ^{212}Pb and 583 keV of the ^{208}Tl isotope. For the activity calculations it must be considered, that the ^{208}Tl is in the 35.93% probability branch after the ^{212}Bi isotope (Table 23).
Two laboratories used a conventional method based on sample treatment, ion-exchange separation followed by electrodeposition and α-particle spectrometry. As the decay chain between ^{224}Ra and ^{208}Tl is in secular equilibrium with ^{228}Th, results for ^{224}Ra, ^{212}Pb, ^{212}Bi and ^{208}Tl are included in the ^{228}Th dataset. It is assumed that the ^{220}Rn diffusion cannot influence the equilibrium because of its short half-life.

3.7.2.4. ^{40}K

Twenty-four data sets were reported from twenty-three laboratories (Table 25, Appendix I and *Fig*. 17, Appendix II). All participants determined potassium activities by gamma-spectrometry. The data showed good agreement between reported results.

3.7.3. LESS FREQUENTLY REPORTED RADIONUCLIDES

The results for the less frequently reported radionuclides are listed in Table 26, Appendix I.

3.7.3.1. ^{90}Sr

One laboratory reported two individual values for ^{90}Sr using liquid scintillation counting, giving an average value of 16.7 ± 2.4 Bq kg^{-1}.

3.7.3.2. ^{155}Eu

Two laboratories reported 6 individual values for ^{155}Eu using γ-ray spectrometry technique, which showed the different values between two laboratories (one laboratory reported the value of 1.87 ±0.13 Bq kg^{-1} and the other reported the value of 7.11±1.38 Bq kg^{-1})

3.7.3.4. ^{227}Ac

One laboratory reported ^{227}Ac (3.5 ± 0.6) Bq kg^{-1}, which is in the same range of ^{235}U mass activities (see above) showing that the ^{235}U and its progeny ^{227}Ac *might be* in equilibrium, but without further measurements, including determination of ^{231}Pa, a firm conclusion cannot be drawn. This radionuclide is frequently used to determine its parent ^{235}U activity concentration indirectly.

3.7.3.5. ^{236}U

One participant reported 9 individual values using AMS technique, give an average of 54 ±1 mBq kg^{-1}.

3.7.3.6. ^{239}Pu and ^{240}Pu

Two laboratories determined separately ^{239}Pu and ^{240}Pu mass activities using mass spectrometry (ICP-MS and AMS). It is worth noting that the sum of the ^{239}Pu and ^{240}Pu mass activities determined by these laboratories is in agreement with the $^{239+240}$Pu value determined by α-particle spectrometry (2.17 ± 0.04 Bq kg^{-1}).

4. METROLOGICAL TRACEABILITY

Only validated methods and calibrations applied within stated scope were used by participating laboratories in this characterisation study. All results obtained by different laboratories are checked if they are based on reliable measurement standards.

In the individual report form sent to the participants, they were asked to report the results in SI units (expressed as Bq kg^{-1} dry mass) at the reference date, and to provide the method determination of activity concentration, the details of tracers, and calibration solutions (metrological traceability). The individual results are therefore traceable to the SI. This is also confirmed by the agreement among the technically accepted datasets. As the assigned values are combinations of agreeing results individually traceable to the SI, the assigned quantity values are also traceable to the SI system of units.

5. CONCLUSIONS

In this characterisation study, the 27 selected laboratories (including IAEA-EL) reported results of natural and anthropogenic radionuclides in a sediment sample from Baltic Sea (IAEA-465).

The robust mean mass activities for the sets of individual data were chosen as the most reliable estimates of the true values and are reported as certified and information values. The certified radionuclides include ^{40}K, ^{137}Cs, ^{210}Pb, ^{210}Po, ^{226}Ra,^{228}Ra, ^{228}Th, ^{232}Th, ^{234}U, ^{235}U, ^{238}U, and $^{239+240}$Pu and the information values are given for other radionuclides ^{230}Th, ^{238}Pu, ^{239}Pu, ^{240}Pu and ^{241}Am. The agreement between the results confirms the absence of any significant method bias (if there is more than one method used) and demonstrates the identity of the radionuclides. Radionuclides are clearly defined as total radionuclide mass fractions and independent of the measurement method.

A summary of the certified and information values with expanded uncertainties for the most frequently reported anthropogenic and natural radionuclides can be found in Table 27 and Table 28, respectively in Appendix I

APPENDIX I.
TABLES OF MEASUREMENT RESULTS

Data in Tables 10–26 are the original reported data with a reference date of 26-08-2012 and an expanded uncertainty, where $k = 2$. The robust mean is included and used as certified values. Tables 27–28 are the derived property values corrected for radioactive decay (and in some cases ingrowth) to 01-01-2020 (using data base for decay correction: http://www.lnhb.fr/nuclear-data/module-lara/) and reported with an expanded uncertainty, where $k = 2$.

TABLE 9. RADIONUCLIDES REPORTED FOR IAEA-465

Radionuclide	Number of measurements	Number of results
^{40}K	66	24
^{90}Sr	2	1[1]
^{137}Cs	73	26
^{155}Eu	6	2
^{208}Tl[2]	21	7
^{212}Pb[6]	13	4
^{212}Bi[6]	6	1
^{224}Ra[6]	6	1
^{228}Th	19	8
^{228}Th (total)[3]	65	21
^{228}Ra	37	15
^{228}Ac[4]	17	5
^{228}Ra (total)	54	20
^{232}Th	34	10
^{210}Po[5]	22	7
^{210}Pb	44	17
^{210}Pb (total)[7]	66	24
^{214}Pb[6]	17	5
^{214}Bi[7]	20	7
^{226}Ra	42	15
^{226}Ra (total)[7]	79	27
^{230}Th	28	5
^{234}U	39	11
^{234}Th[7]	23	8
^{234m}Pa[8]	3	1
^{238}U	57	18
^{238}U (total)[7]	83	27
^{227}Ac	10	1[4]
^{235}U	45	14
^{236}U	9	1[4]
^{238}Pu	49	14
^{239}Pu	11	2
^{240}Pu	11	2
$^{239+240}$Pu	72	20
^{241}Am (α)	20	7
^{241}Am (γ)	10	5
^{241}Am (total)[8]	30	12

[1] One result only, no further analysis possible
[2] Included in the ^{228}Th dataset
[3] Total is for principal radionuclides and progeny radionuclides in secular equilibrium
[4] Included in the ^{228}Ra dataset
[5] Included in the ^{210}Pb dataset
[6] Included in the ^{226}Ra dataset
[7] Included in the ^{238}U dataset
[8] Total is for both measurement techniques (α-particle spectrometry and γ-ray spectrometry)

TABLE 10. RESULTS FOR ^{137}Cs IN IAEA-465
(Reference date: 26 August 2012, unit: Bq kg^{-1})

Lab code	Method code	No. of results	Mass (g)	^{137}Cs
1	G	2	23.69–48.55	132 ± 18
3	G	3	32–34	109 ± 4
4	G	3	49	123 ± 25
5	G	1	4.8735	112 ± 12
6	G	3	31.425	109 ± 10
7	G	4	27	105 ± 9
8	G	1	3.94	116 ± 1
9	G	3	33	95 ± 3
10	G	1	28.46	112 ± 7
11	G	1	11.819	104 ± 4
12	G	3	47.89	114 ± 4
13	G	3	48.9	102 ± 12
14	G	5	4.41–17.82	105 ± 7
15	G	6	44	112 ± 9
16	G	3	19.5–38.9	111 ± 15
17	G	4	49.89	102 ± 15
18	G	1	13.17	89 ± 8
18	G	1	3.81	108 ± 15
19	G	4	46.2	98 ± 7
20	G	4	45.22	101 ± 6
21	G	4	39	100 ± 12
22	G	3	10	102.5 ± 1.1
22	G	3	40	115 ± 2
23	G	2	4.6	104 ± 14
24	G	2	50	100.5 ± 1.5
25	G	3	49.39	108 ± 11

Number of reported laboratory means	26
Robust mean	106.8
Expanded uncertainty (k=2)	6.9

TABLE 11. RESULTS FOR ^{238}Pu AND $^{239+240}$Pu IN IAEA-465
(Reference date: 26 August 2012, unit: Bq kg^{-1})

Lab code	Method code	No. of results	Mass (g)	^{238}Pu	$^{239+240}$Pu
1	A	2	5.52–5.54	0.062 ± 0.014	2.29 ± 0.22
2	AMS	9	0.30	–	2.01 ± 0.04
4	A	3	4.9	0.069 ± 0.028	2.23 ± 0.15
5	A	3	5.0–5.3	–	2.13 ± 0.29
6	A	3	15.05– 6.48	0.058 ± 0.008	2.16 ± 0.10
9	A	3	33	0.081 ± 0.013	2.10 ± 0.09
10	A	3 – 5	5.4–5.9	0.206 ± 0.024	2.14 ± 0.18
12	A	3	5	0.057 ± 0.024	2.12 ± 0.36
13	A	2	0.51–0.523	<0.054	2.10 ± 0.70
16	A	3	4.9–9.6	–	2.43 ± 0.40
17	A	3	10.03– 0.06	0.082 ± 0.004	2.12 ± 0.03
18	A	1	14.16	0.074 ± 0.023	2.18 ± 0.27
20	A	4	11.01–11.03	0.079 ± 0.014	2.27 ± 0.15
21	ICP-MS	2	1	–	2.78 ± 0.10
22	A	8	5	0.059 ± 0.020	2.17 ± 0.03
22	A	2	5	0.054 ± 0.014	2.23 ± 0.07
23	A	4	3	0.053 ± 0.008	2.07 ± 0.12
25	A	3	1.07–1.12	–	2.54 ± 0.37
26	A	4	1–2	0.136 ± 0.042	1.84 ± 0.14
27	A	5	3	0.10 ± 0.01	2.69 ± 0.09
Number of reported laboratory means				14	20
Robust mean				0.073	2.19
Expanded uncertainty (k=2)				0.019	0.06

TABLE 12. RESULTS FOR ^{241}Am IN IAEA-465
(Reference date: 26 August 2012, unit: Bq kg^{-1})

Lab code	Method code	No. of results	Mass (g)	^{241}Am (ɤ-ray spectrometry)	^{241}Am (α-particle spectrometry)
1	A	2	4.2–4.4	–	0.77 ± 0.08
6	A	3	15.05–6.48	–	0.96 ± 0.06
8	G	1	3.94	1.90 ± 0.40	–
9	A	3	33	–	0.94 ± 0.09
10	G	1	28.46	1.38 ± 0.55	–
11	G	1	11.819	1.20 ± 0.30	–
12	A	3	5	–	0.98 ± 0.24
12	G	3	47.89	1.50 ± 0.58	–
17	A	3	10.03–10.06	–	0.61 ± 0.02
17	G	4	49.89	1.17 ± 0.30	–
20	A	4	11.01–11.03	–	0.99 ± 0.15
26	A	2	1–2	–	0.99 ± 0.05
Number of reported laboratory means				5	7
Robust mean				1.43	0.91
Expanded uncertainty (k=2)				0.33	0.13

TABLE 13. RESULTS FOR ^{238}U IN IAEA-465
(Reference date: 26 August 2012, unit: Bq kg^{-1})

Lab code	Method code	No. of results	Mass (g)	^{238}U
1	A	2	5.52–5.54	79.7 ± 8.2
4	A	3	4.9	76.6 ± 4.9
5	A	5	0.2875–0.3482	89.7 ± 5.1
6	ICP-MS	5	0.2–0.5	85.8 ± 8.7
8	G	1	3.94	97.7 ± 6.1
10	G	1	28.46	94.1 ± 7.5
10	A	3	5.9	85 ± 5
11	ICP-MS	10	0.26–0.29	109.9 ± 0.6
12	G	3	47.89	98.6 ± 7.6
13	G	3	48.9	84 ± 11
13	ICP-MS	1	0.523	85 ± 11
16	A	3	1.95	73.7 ± 5.5
19	G	4	46.2	84.6 ± 8.7
21	ICP-MS	2	1	54 ± 25
22	G	3	40	96 ± 25
25	ICP-MS	3	0.11–0.13	82.0 ± 3.9
25	A	3	1	81.1 ± 4.8
26	A	2	0.5	114 ± 13

Number of reported laboratory means	18
Robust mean	87
Expanded uncertainty (k=2)	10

TABLE 14. RESULTS FOR ^{234}Th IN IAEA-465
(Reference date: 26 August 2012, unit: Bq kg^{-1})

Lab code	Method code	No. of results	Mass (g)	^{234}Th*
3	G	3	32–34	84 ± 4
7	G	4	27	86 ± 19
8	G	1	3.94	98 ± 6
15	G	6	44	121 ± 24
17	G	4	49.89	93 ± 13
18	G	1	13.17	52 ± 9
18	G	1	3.81	81 ± 29
22	G	3	40	92 ± 21
Number of reported laboratory means				8
Robust mean				89
Expanded uncertainty (k=2)				14

*the values of ^{234}Th and ^{234m}Pa (Table 26) will be used for the final ^{238}U data evaluation (for a total of 27 data sets)

TABLE 15. RESULTS FOR ^{234}U IN IAEA-465
(Reference date: 26 August 2012, unit: Bq kg^{-1})

Lab code	Method code	No. of results	Mass (g)	^{234}U
1	A	2	5.52–5.54	83 ± 9
4	A	3	4.9	79 ± 5
5	A	5	0.2875–0.3482	92 ± 3
6	ICP-MS	5	0.2–0.5	89 ± 11
10	A	3	5.9	88 ± 5
11	ICP-MS	10	0.26–0.29	117 ± 1
13	ICP-MS	1	0.523	93 ± 28
13	A	2	0.51–0.523	84 ± 16
16	A	3	1.95	82 ± 6
25	A	3	1	85.6 ± 5.1
26	A	2	0.5	117 ± 14
Number of reported laboratory means				11
Robust mean				88.3
Expanded uncertainty (k=2)				7.1

TABLE 16. RESULTS FOR ^{230}Th IN IAEA-465
(Reference date: 26 August 2012, unit: Bq kg^{-1})

Lab code	Method code	No. of results	Mass (g)	^{230}Th
1	A	2	5.5	72.6 ± 7.4
5	A	5	0.3	69 ± 5
11	ICP-MS	10	0.27	78.3 ± 3.1
25	A	3	1	78.3 ± 4.5
26	A	1	1.01	33.2 ± 2.9
Number of reported laboratory means				5
Robust mean				71.4
Expanded uncertainty (k=2)				9.3

TABLE 17. RESULTS FOR ^{226}Ra IN IAEA-465
(Reference date: 26 August 2012, unit: Bq kg^{-1})

Lab code	Method code	No. of results	Mass (g)	^{226}Ra
1	G	2	23.69–48.55	58.0 ± 13.0
4	G	3	49	52.6 ± 4.1
5	A	5	0.2875–0.3482	46.7 ± 5.4
5	G	1	4.8735	77.0 ± 17.0
6	G	3	31.425	56.3 ± 5.7
8	G	1	3.94	47.5 ± 1.0
10	G	1	28.46	57.9 ± 4.6
12	G	3	47.89	56.8 ± 3.0
13	G	3	48.9	55.0 ± 6.0
18	G	1	13.17	45.5 ± 7.8
18	G	1	3.81	55.1 ± 10.8
19	G	4	46.2	39.4 ± 1.3
22	G	3	40	49.6 ± 0.4
24	G	2	50	57.9 ± 0.5
25	LSC	9	1.04–1.09	56.7 ± 7.6
Number of reported laboratory means				15
Robust mean				51.4
Expanded uncertainty (k=2)				6.3

TABLE 18. RESULTS FOR ^{214}Pb and ^{214}Bi IN IAEA-465
(Reference date: 26 August 2012, unit: Bq kg^{-1})

Lab code	Method code	No. of results	Mass (g)	^{214}Pb*	^{214}Bi*
3	G	3	32–34	54.8 ± 2.5	56.7 ± 2.8
8	G	1	3.94	–	45.9 ± 4.1
11	G	1	11.819	51.0 ± 3.0	47.0 ± 4.0
15	G	6	44	51.0 ± 4.4	48.0 ± 4.4
21	G	4	39	44 ± 8	44 ± 8
22	G	3	40	45.5 ± 1.2	36.4 ± 2.1
24	G	2	50		57.4 ± 2.3
Number of reported laboratory means				5	7
Robust mean				49.3	47.9
Expanded uncertainty (k=2)				5.0	8.3

*the ^{214}Pb and ^{214}Bi values will be combined with ^{226}Ra (Table 17) to assign a final certified value for ^{226}Ra (for a total of 27 data sets)

TABLE 19. RESULTS FOR ^{210}Pb (^{210}Po) IN IAEA-465
(Reference date: 26 August 2012, unit: Bq kg^{-1})

Lab code	Method code	No. of results	Mass (g)	^{210}Pb(^{210}Po)[9]
1	G	2	23.69–48.55	241 ± 47
3	G	3	32–34	151 ± 6
5	G	1	4.8735	192 ± 50
5 (Po)	A	6	0.5258	199 ± 13
5 (Pb)	A	6	0.5258	192 ± 7.0
6	G	3	31.425	197 ± 22
8	G	1	3.94	206 ± 9
10 (Pb)	G	1	28.46	179 ± 48
10 (Po)	A	5	3.75–5.0	160 ± 12
11 (Pb)	G	1	11.819	201 ± 16
11 (Po)	A	1	0.3251	206 ± 8
12	G	3	47.89	206 ± 20
13	G	3	48.9	184 ± 23
13 (Po)	A	1	0.256	180 ± 60
13 (Pb)	A	1	0.256	190 ± 70
15	G	6	44	202 ± 28
16	G	3	19.5–38.9	202 ± 27
17	G	4	49.89	184 ± 28
18	G	1	13.17	161 ± 22
18	G	1	3.81	185 ± 34
21	G	4	7–39	201 ± 33
21 (Po)	A	2	0.4–0.5	175 ± 25
25 (Po)	A	3	0.5	178 ± 13
26 (Po)	A	4	0.5–1.0	126 ± 4

Number of reported laboratory means	24
Robust mean	189.4
Expanded uncertainty (k=2)	15.3

[9] The supported activity of ^{210}Pb and ^{210}Po was considered to be in secular equilibrium with ^{226}Ra, and the unsupported ^{210}Pb and ^{210}Po values were corrected t reference date assuming the transient equilibrium at 26 August 2012.

TABLE 20. RESULTS FOR ^{235}U IN IAEA-465
(Reference date: 26 August 2012, unit: Bq kg^{-1})

Lab code	Method code	No. of results	Mass (g)	^{235}U
3	G	3	32–34	4.0 ± 0.2
4	A	3	4.9	3.5 ± 0.7
5	A	5	0.2875–0.3482	4.1 ± 0.6
6	ICP-MS	5	0.2–0.5	3.93 ± 0.40
10	G	1	28.46	4.6 ± 0.7
10	A	3	5.9	3.7 ± 0.5
11	ICP-MS	10	0.26–0.29	5.07 ± 0.03
13	ICP-MS	1	0.523	3.9 ± 0.5
18	G	1	13.17	3.8 ± 0.6
18	G	1	3.81	4.0 ± 0.8
19	G	4	46.2	3.9 ± 0.2
22	G	3	40	4.6 ± 1.2
25	A	3	1	3.7 ± 0.8
26	A	2	0.5	4.3 ± 0.9

Number of reported laboratory means	14
Robust mean	4.03
Expanded uncertainty (k=2)	0.30

TABLE 21. RESULTS FOR ^{232}Th IN IAEA-465
(Reference date: 26 August 2012, unit: Bq kg^{-1})

Lab code	Method code	No. of results	Mass (g)	^{232}Th
1	A	2	5.52–5.54	60.3 ± 6.9
5	A	5	0.2875–0.3482	57.1 ± 3.8
11	ICP-MS	10	0.26–0.29	64.7 ± 2.3
12	G	3	47.89	69.8 ± 3.8
13	ICP-MS	1	0.523	68.0 ± 9.0
17	G	4	49.89	51.5 ± 7.2
24	G	2	50	62.2 ± 1.4
25	ICP-MS	3	0.12–0.13	66.8 ± 3.2
25	A	3	1	65.9 ± 4.0
26	A	1	1.01	34.9 ± 3.0

Number of reported laboratory means	10
Robust mean	62.1
Expanded uncertainty (k=2)	6.8

TABLE 22. RESULTS FOR ^{228}Ra IN IAEA-465
(Reference date: 26 August 2012, unit: Bq kg^{-1})

Lab code	Method code	No. of results	Mass (g)	^{228}Ra
1	G	2	23.69–48.55	67 ± 18
3	G	3	32–34	74.6 ± 4.2
4	G	3	49	109 ± 10
5	G	1	4.8735	70 ± 27
6	G	3	31.425	64.6 ± 8.1
8	G	1	3.94	68.2 ± 2.2
10	G	1	28.46	67.4 ± 5.4
11	G	1	11.819	54.0 ± 2.0
13	G	3	48.9	64.0 ± 8.0
15	G	6	44	71.0 ± 6.1
18	G	1	13.17	56.1 ± 8.5
18	G	1	3.81	59 ± 9
19	G	4	46.2	59.7 ± 3.5
21	G	4	39	57 ± 12
22	G	3	40	69.7 ± 1.7
Number of reported laboratory means				15
Robust mean				65.3
Expanded uncertainty (k=2)				7.8

TABLE 23. RESULTS FOR ^{228}Ac and ^{208}Tl IN IAEA-465
(Reference date: 26 August 2012, unit: Bq kg^{-1})

Lab code	Method code	No. of results	Mass (g)	^{228}Ac*	^{208}Tl[10]
3	G	3	32–34	74.6 ± 4.2	75.5 ± 3.7
7	G	2	27	–	54.4 ± 7.2[10]
8	G	3	3.94	–	62.5 ± 6.0
11	G	1	11.8	54 ± 2	–
15	G	6	44	71 ± 6	64.0 ± 6.4[10]
21	G	4	39	57 ± 12	58.4 ± 11.1[10]
22	G	3	40	62.8 ± 0.9	75.3 ± 1.7
24	G	2	50		59.1 ± 1.2
Number of reported laboratory means				5	7
Robust mean				64	64.2
Expanded uncertainty (k=2)				10	9.4

*^{228}Ac values were combined with ^{228}Ra (Table 22) to assign the final value for ^{228}Ra (for a total of 20 data sets)

[10]Thallium-208 values were corrected (by RML) for branching factor of 35.93 %

TABLE 24. RESULTS FOR ^{228}Th IN IAEA-465
(Reference date: 26 August 2012, unit: Bq kg^{-1})

Lab code	Method code	No. of results	Mass (g)	^{228}Th
4	G	3	49	273 ± 29
8	G	1	3.94	71.8 ± 1.2
10	G	1	28.46	66.4 ± 5.3
13	G	3	48.9	64.0 ± 7.0
19	G	4	46.2	59.6 ± 2.6
22	G	3	40	75.3 ± 1.7
25	A	3	1	67.9 ± 4.1
26	A	1	1.01	33.2 ± 2.9
Number of reported laboratory means				8
Robust mean				67.5
Expanded uncertainty (k=2)				12.3

TABLE 25. RESULTS FOR ^{40}K IN IAEA-465
(Reference date: 26 August 2012, unit: Bq kg^{-1})

Lab code	Method code	No. of results	Mass (g)	^{40}K
1	G	2	23.69–48.55	1050 ± 170
3	G	3	32–34	1180 ± 50
4	G	3	49	1143 ± 169
5	G	1	4.8735	1035 ± 129
6	G	3	31.425	1070 ± 110
7	G	4	27	948 ± 78
8	G	1	3.94	1131 ± 22
9	G	3	33	950 ± 40
10	G	1	28.46	1077 ± 65
11	G	1	11.819	963 ± 52
12	G	3	47.89	1159 ± 100
13	G	3	48.9	1050 ± 150
14	G	5	4.41–17.82	1168 ± 75
15	G	6	44	1161 ± 91
16	G	3	19.5–38.9	1219 ± 168
17	G	4	49.89	1015 ± 152
18	G	1	13.17	889 ± 99
18	G	1	3.81	1070 ± 140
19	G	4	46.2	972 ± 73
21	G	4	39	982 ± 250
22	G	3	40	1192 ± 21
23	G	2	4.6	1051 ± 144
24	G	2	50	1152 ± 8
25	G	3	49.39	1100 ± 120
Number of reported laboratory means				24
Robust mean				1074
Expanded uncertainty (k=2)				96

TABLE 26. RESULTS FOR THE LESS FREQUENTLY MEASURED RADIONUCLIDES REPORTED IN IAEA-465

(Reference date: 26 August 2012, unit: Bq kg^{-1})

Isotope	Lab code	Method code	No. of results	Mass (g)	Activity (Bq kg^{-1})
^{90}Sr	1	LSC	2	5.52–5.54	16.7 ± 2.4
^{155}Eu	12	G	3	47.89	7.11 ± 1.38
	9	G	3	99.77	1.87 ± 0.13
^{212}Bi	15	G	6	44	80 ± 13
^{212}Pb	3	G	3	32–34	81.3 ± 3.2
	7	G	3	27	66.4 ± 6.3
	11	G	1	11.8	57 ± 2
	15	G	6	44	71.0 ± 6.5
^{224}Ra	15	G	6	44	53 ± 8.5
^{227}Ac	10	G	1	28.46	3.5 ± 0.6
^{234m}Pa	3	G	3	32–34	72.9 ± 24.5
^{236}U	2	AMS	9	0.3	(1.97 ± 0.13) × 10^{-4}
^{239}Pu	2	AMS	9	0.3	1.158 ± 0.0027
	21	ICP-MS	2	1	1.90 ± 0.09
^{240}Pu	2	AMS	9	0.3	0.843 ± 0019
	21	ICP-MS	2	1	0.88 ± 0.11

TABLE 27. SUMMARY OF CERTIFIED VALUES FOR IAEA-465
(Reference date: 1 January 2020, unit: Bq kg^{-1})

Radionuclide	Certified value [Bq kg^{-1}]	Expanded uncertainty* [Bq kg^{-1}]	Relative uncertainty [%]
^{40}K	1074	70	6.4
^{137}Cs	90.2	5.4	6.0
^{210}Pb‡,	160	11	6.7
^{210}Po†	162	11	6.7
^{226}Ra$^{¤}$	51.5	3.7	7.2
^{228}Ra$^{\#}$	64.5	6.0	9.3
^{228}Th^{+}	64.5	6.0	9.3
^{232}Th	64.5	6.0	9.3
^{234}U	88.3	6.5	7.4
^{235}U	4.03	0.28	6.9
^{238}U	87.3	6.2	7.1
$^{239+240}$Pu	2.19	0.12	5.7

*The uncertainty is expressed as an expanded uncertainty using a coverage factor k = 2 estimated in accordance with the JCGM 100:2008 'Evaluation of measurement data - Guide to the expression of uncertainty in measurement' [7] and ISO Guide 35 [4].

†Polonium-210 is in transient equilibrium with the unsupported activity of ^{210}Pb.

‡Lead-210 values should be corrected for ingrowth from ^{226}Ra.

$^{¤}$Radium-226 values should be corrected for ingrowth from ^{230}Th.

$^{\#}$Radium-228 is assumed to be in equilibrium with ^{232}Th.

$^{+}$Thorium-228 is assumed to be in equilibrium with ^{232}Th and ^{228}Ra.

TABLE 28. SUMMARY OF INFORMATION VALUES FOR IAEA-465 RADIONUCLIDE CONCENTRATIONS
(Reference date: 01 January 2020, unit: Bq kg^{-1})

Radionuclide	Information [Bq kg^{-1}]	Expanded uncertainty* [Bq kg^{-1}]	Relative uncertainty [%]
^{230}Th	71.4	10.2	14.3
^{239}Pu	1.53	0.75	49.0
^{238}Pu	0.07	0.01	17.8
^{240}Pu	0.850	0.040	4.7
^{241}Am*	1.07	0.20	18.4

*Americium-241 values should be corrected for ingrowth from ^{241}Pu if value available.

TABLE 29. SUMMARY OF INFORMATION VALUES FOR IAEA-465 ISOTOPE RATIOS
(Reference date: 01 January 2020)

Ratio	Value	Expanded uncertainty*	Relative uncertainty [%]
$m(^{234}U)/[m(^{234}U)+m(^{235}U)+m(^{238}U)]$ [m]	0.000055	0.000004	7.5
$m(^{235}U)/[(m(^{234}U)+m(^{235}U)+m(^{238}U)]$ [m]	0.00712	0.00043	6.0
$m(^{238}U)/[m(^{234}U)+m(^{235}U)+m(^{238}U)]$ [m]	0.993	0.064	6.4
$m(^{240}Pu)/m(^{239}Pu)$ [m]	2.05	0.99	48
$^{238}Pu/^{239+240}Pu$[a]	0.032	0.004	13
$^{240}Pu/^{239}Pu$[a]	0.56	0.27	70

[m]Mass ratio

[a]Activity ratio

APPENDIX II.

FIGURES OF REPORTED RESULTS

Figures 2–9, 11 and 13–17 contain the original reported data and standard uncertainty with a reporting date of 26-08-2012. Reported values are coloured green with a circular marker; vertical lines represent the standard uncertainties reported (k=2). The horizontal red line is the robust mean for each nuclide on the reporting date and the red dot lines are the standard uncertainty of the robust mean (k=2). Figures 10 and 12 show the ingrowth and decay of ^{226}Ra and ^{210}Pb over time and are for information only.

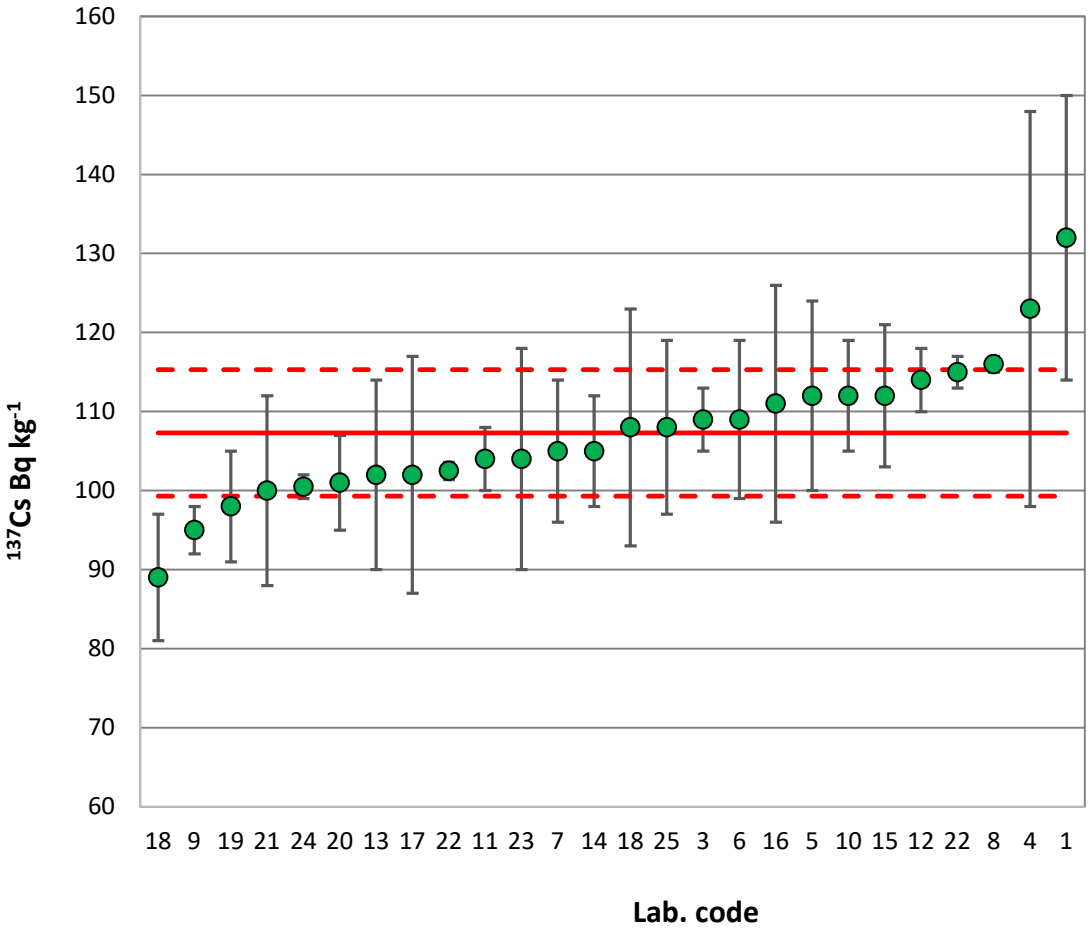

FIG.2. Laboratory results for ^{137}Cs

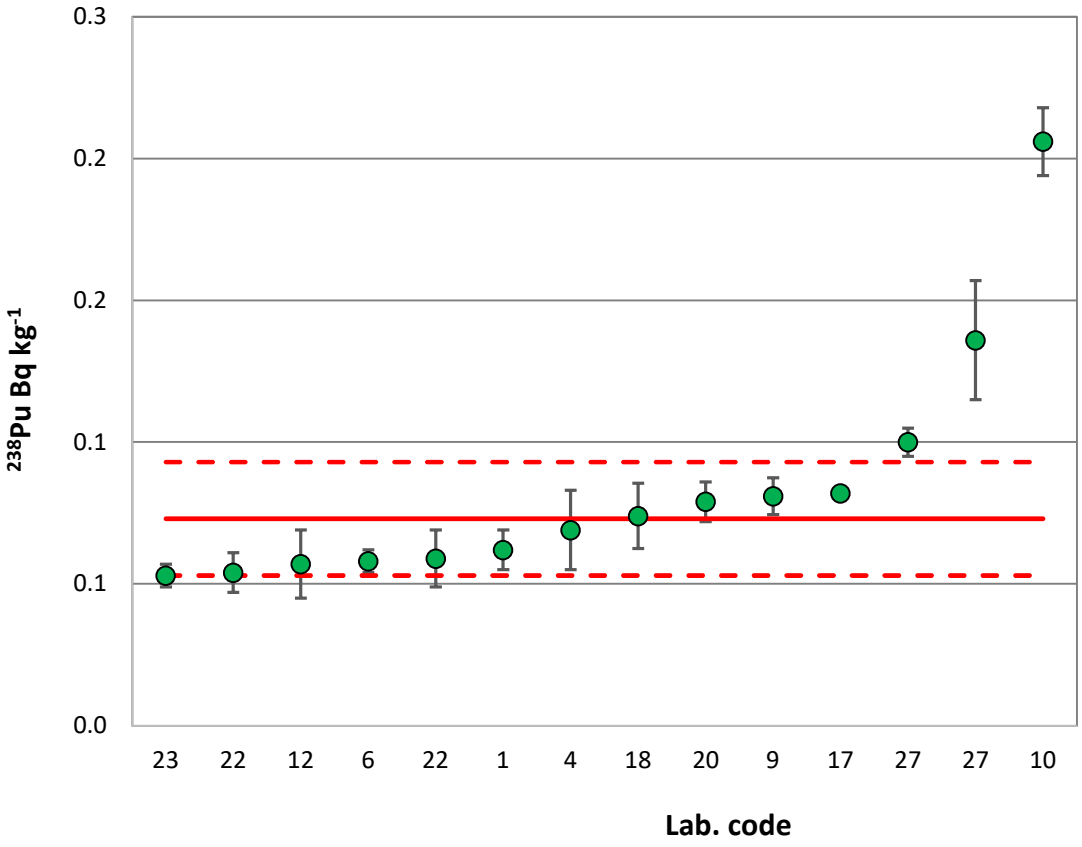

FIG.3. Laboratory results for ^{238}Pu

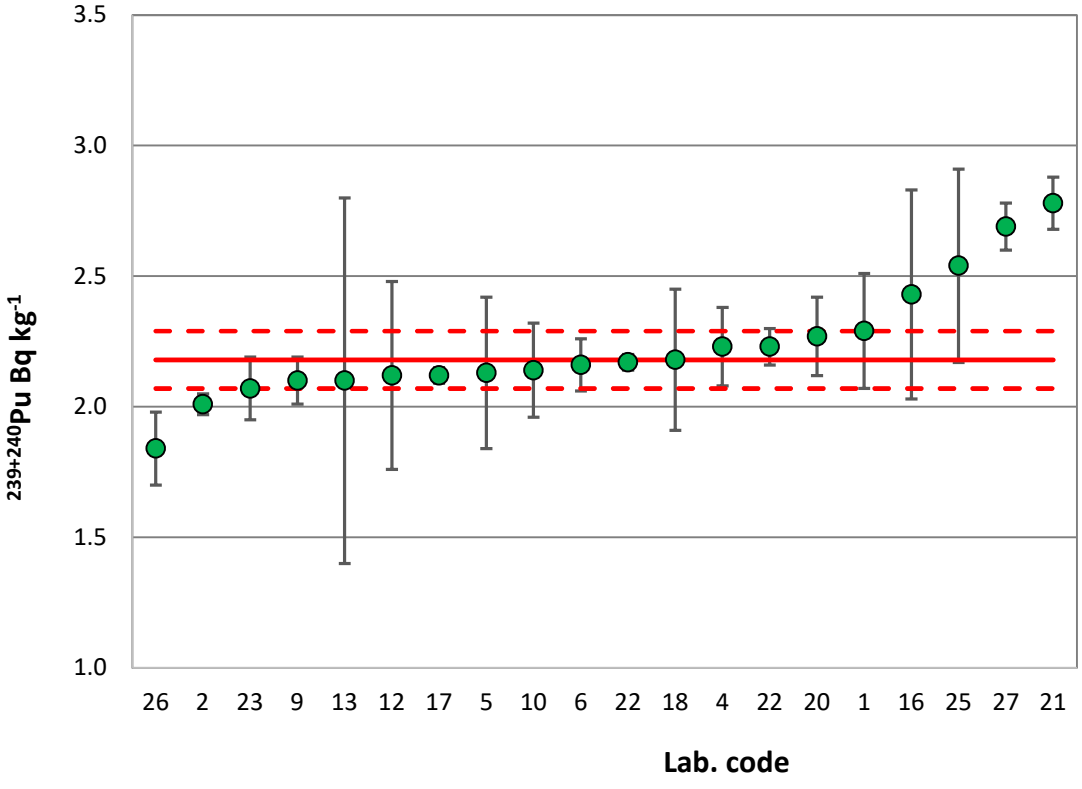

FIG.4. Laboratory results for $^{239+240}Pu$

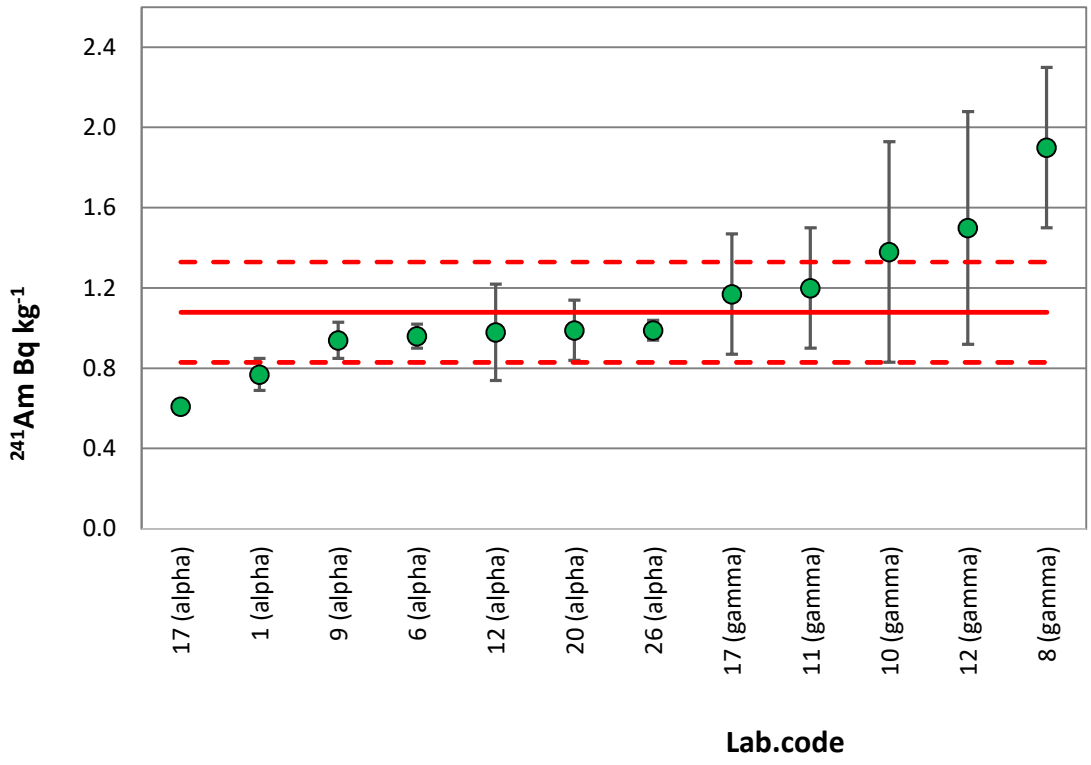

FIG.5. Laboratory results for ^{241}Am

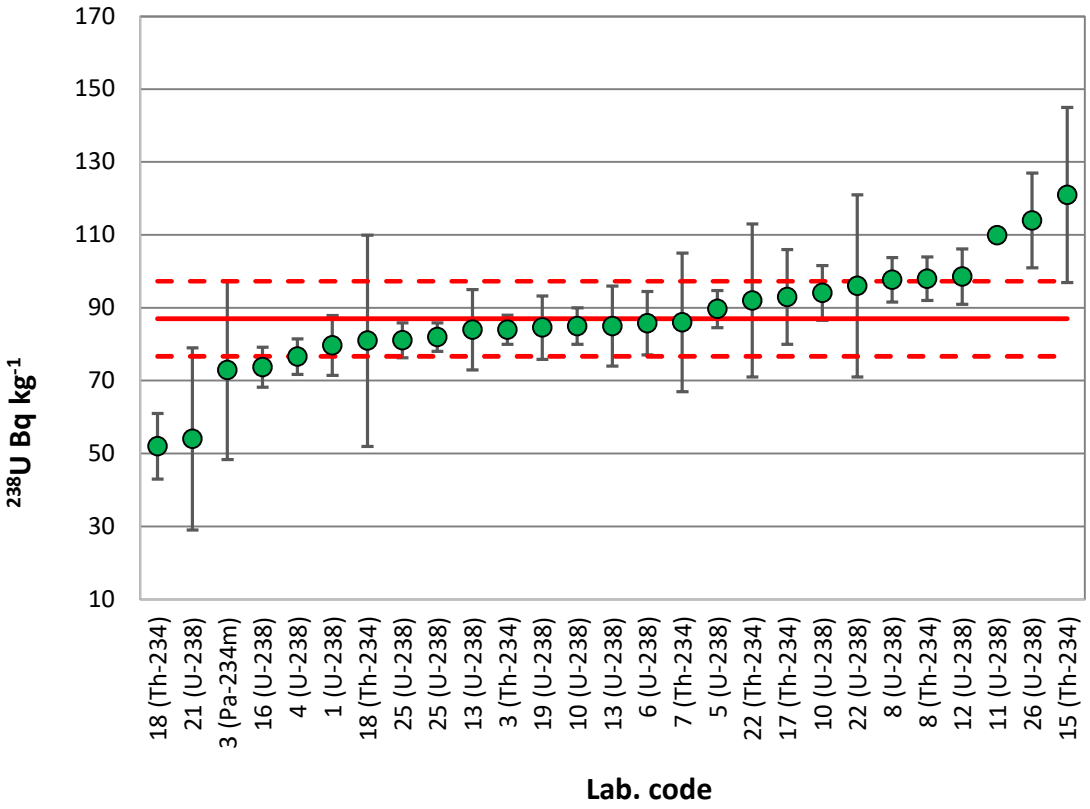

FIG.6. Laboratory results for ^{238}U

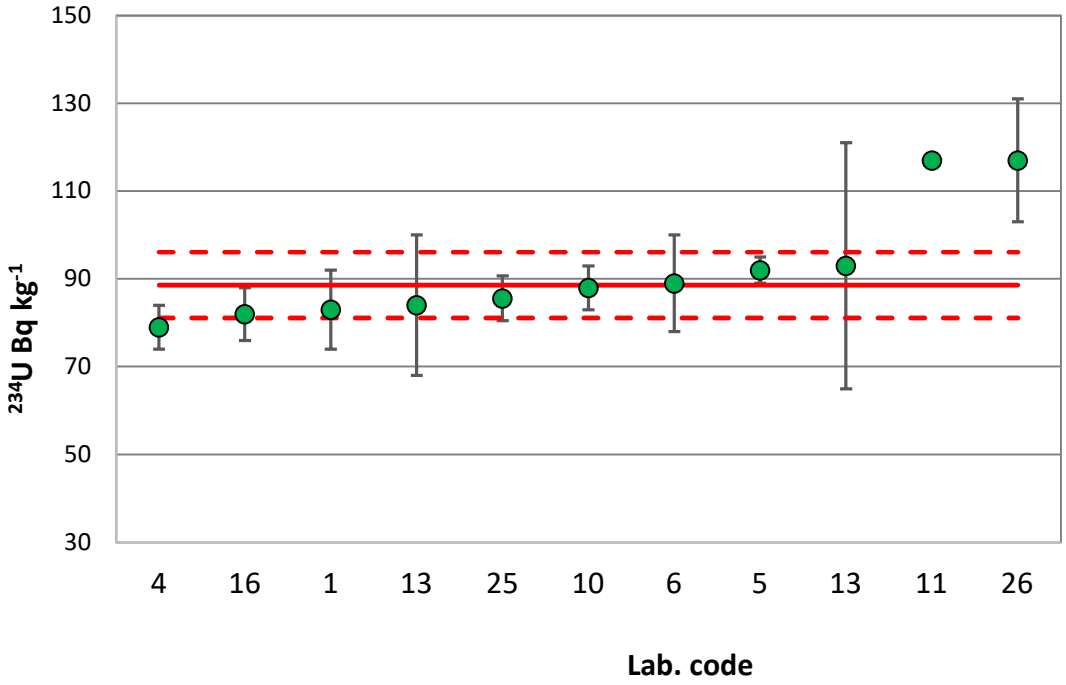

FIG.7. Laboratory results for ^{234}U

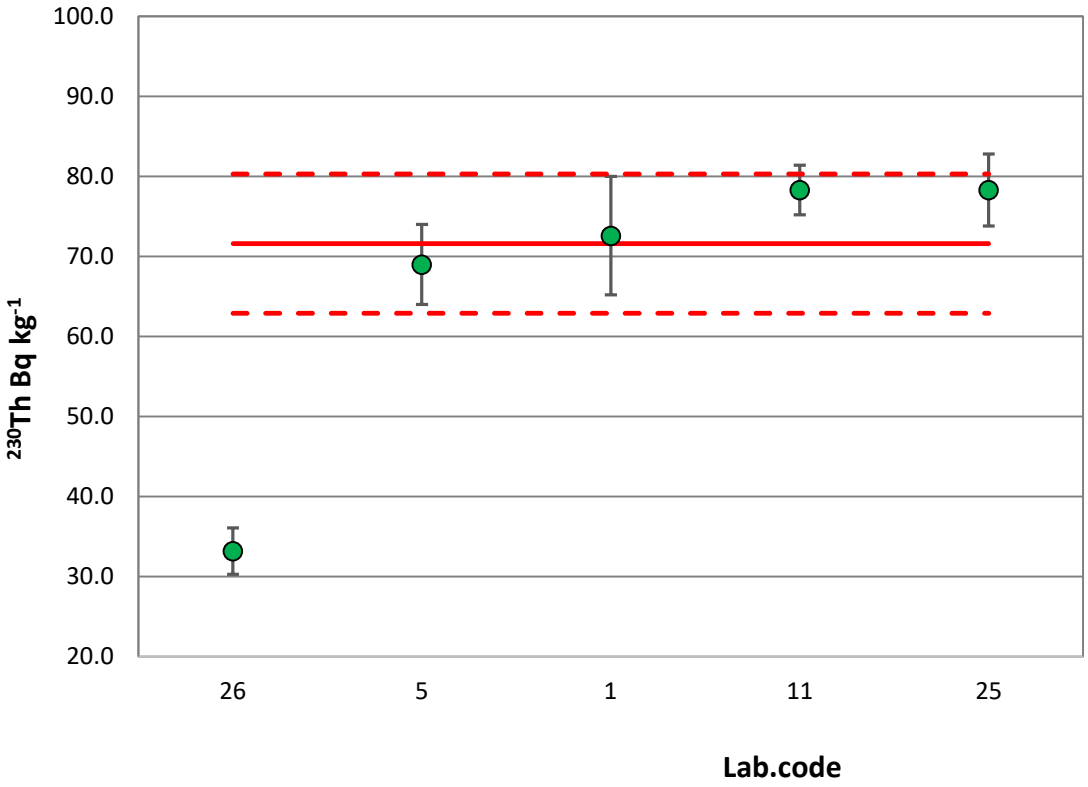

FIG.8. Laboratory results for ^{230}Th

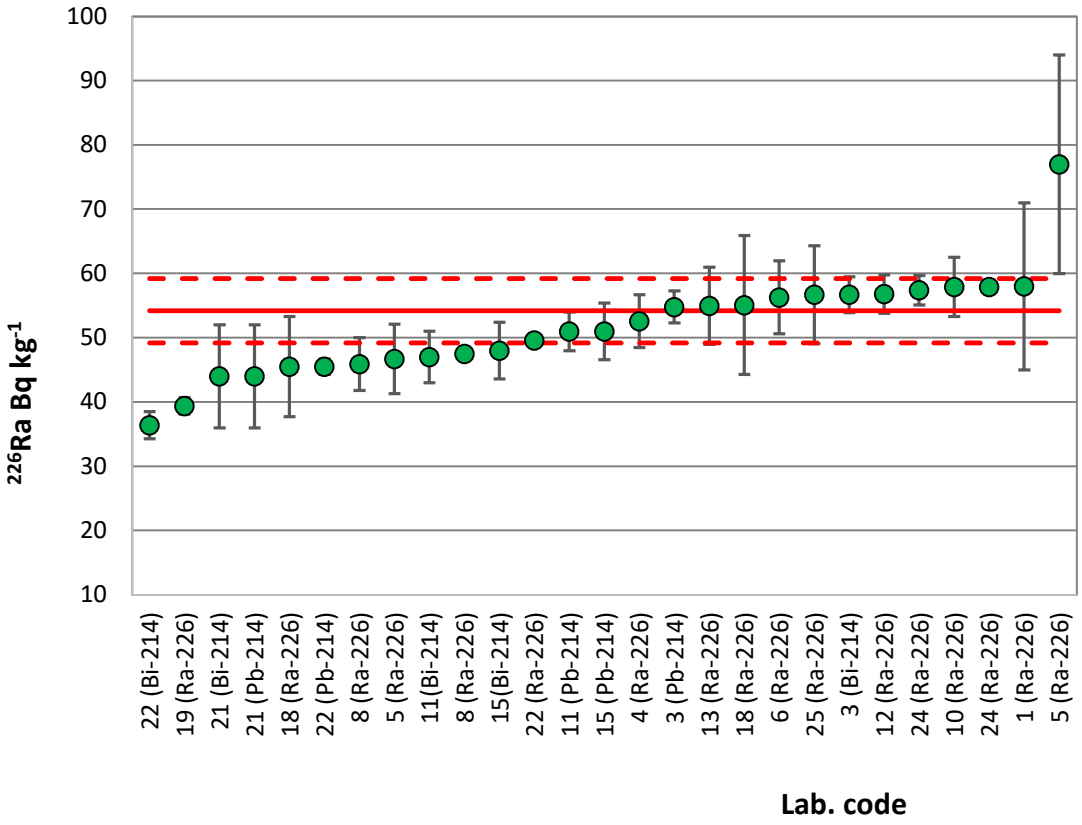

FIG.9. Laboratory results for ^{226}Ra

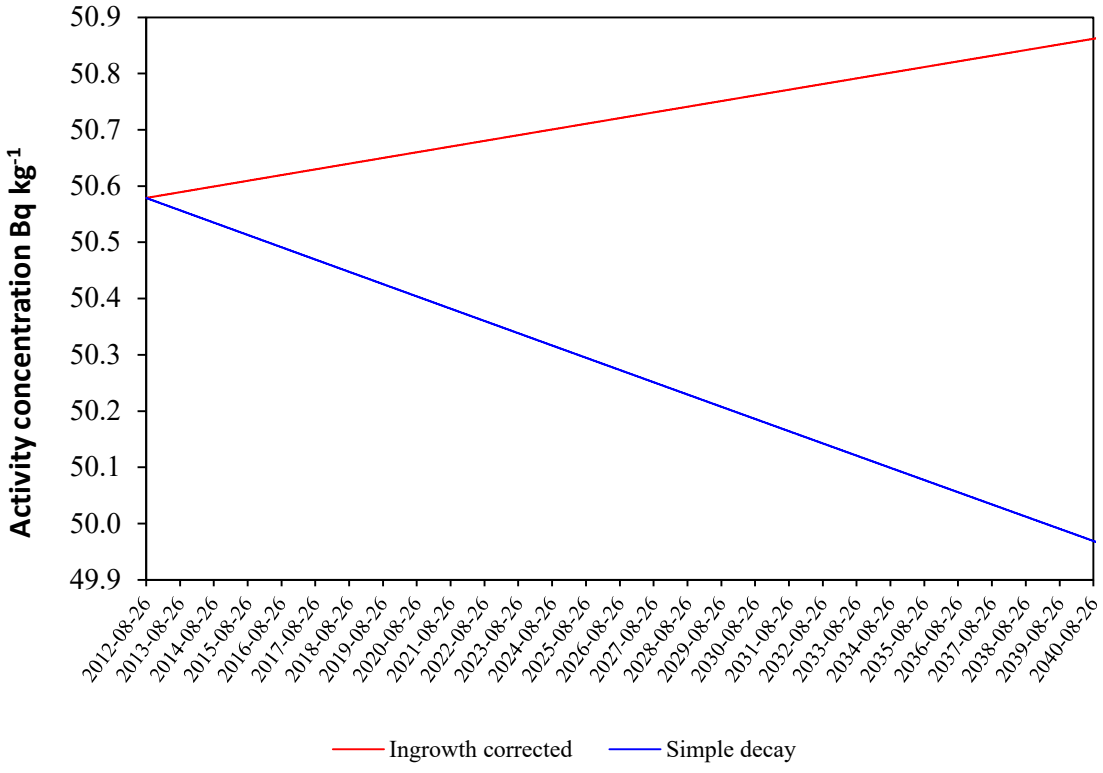

FIG.10. Decay and ingrowth of ^{226}Ra

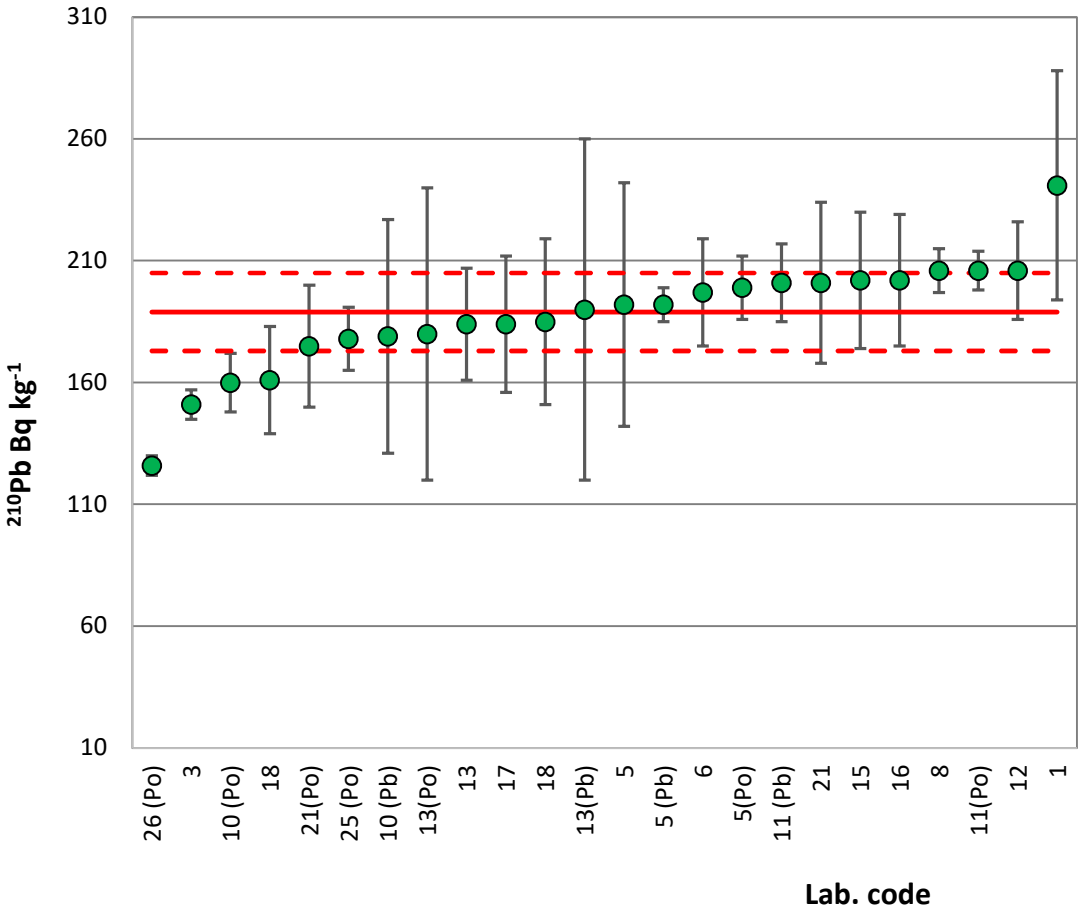

FIG.11. Laboratory results for ^{210}Pb

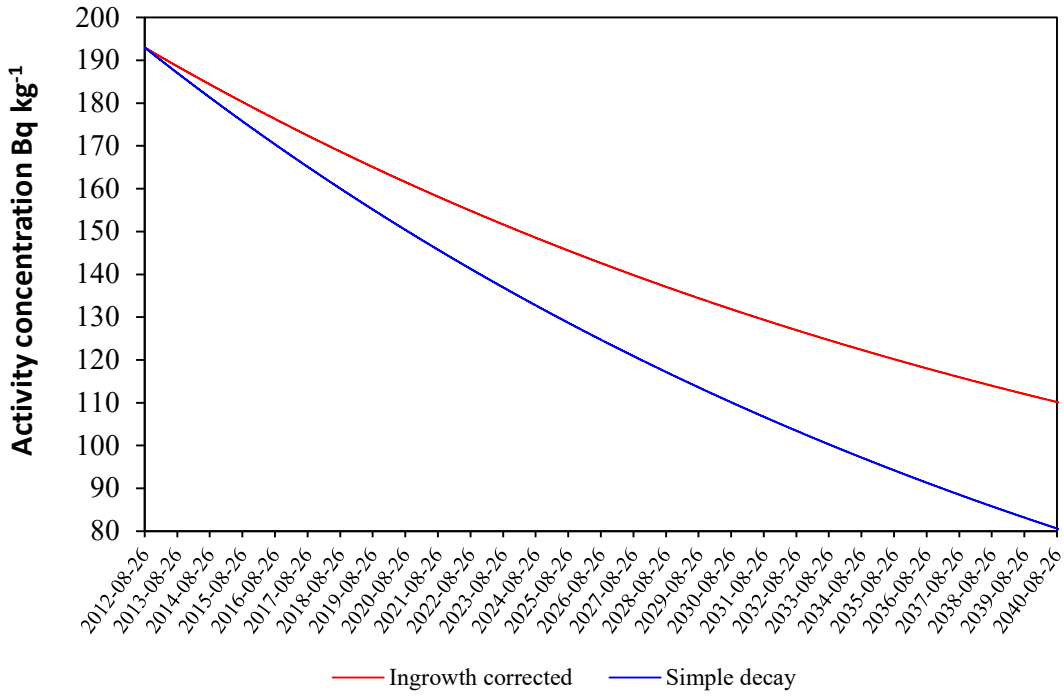

FIG.12. Decay and ingrowth of ^{210}Pb

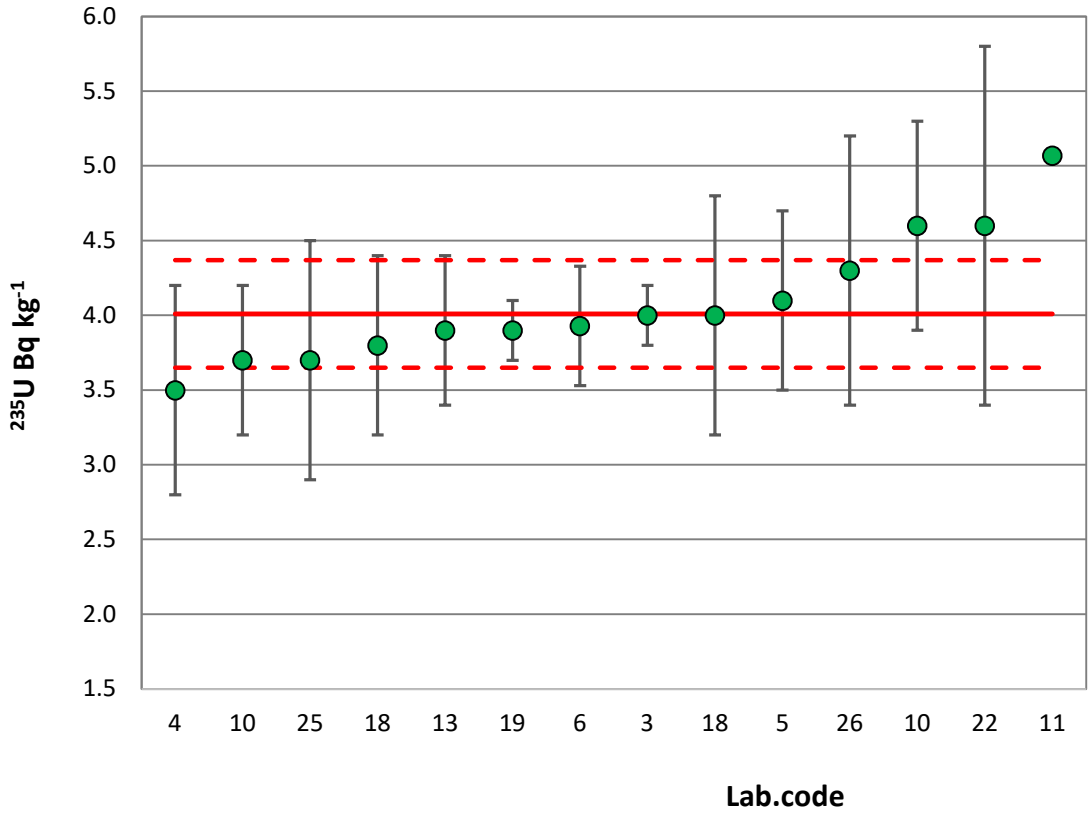

Fig.13. Data evaluation for ^{235}U

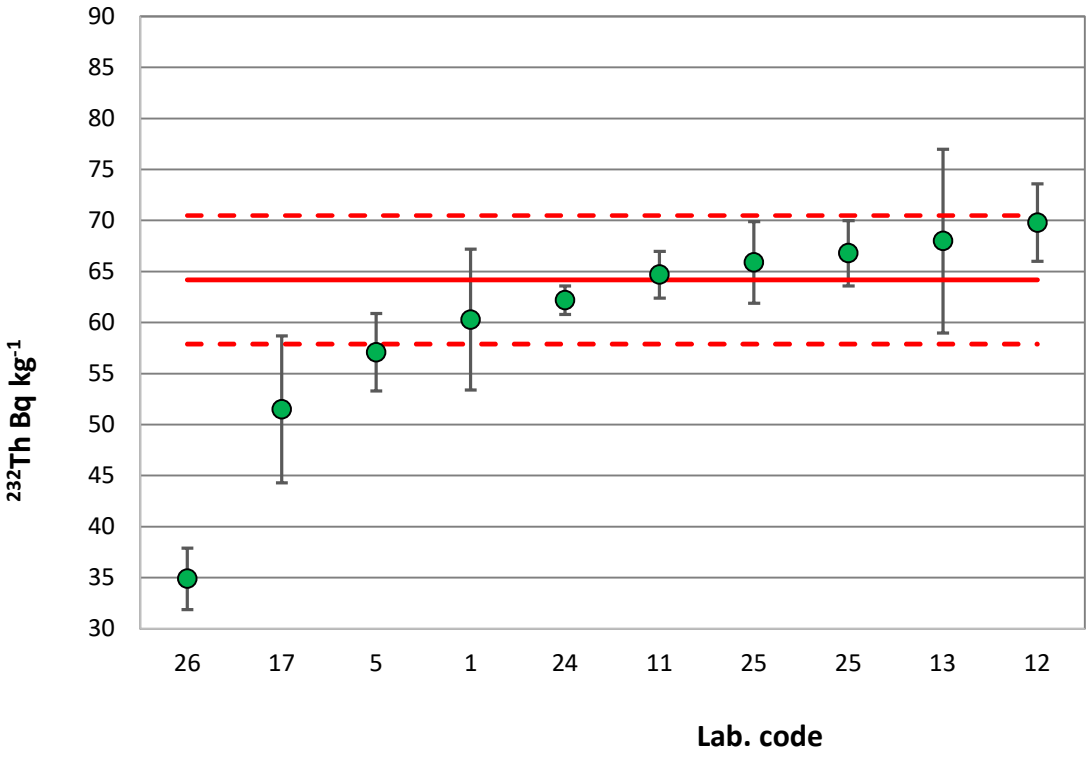

FIG.14. Laboratory results for ^{232}Th

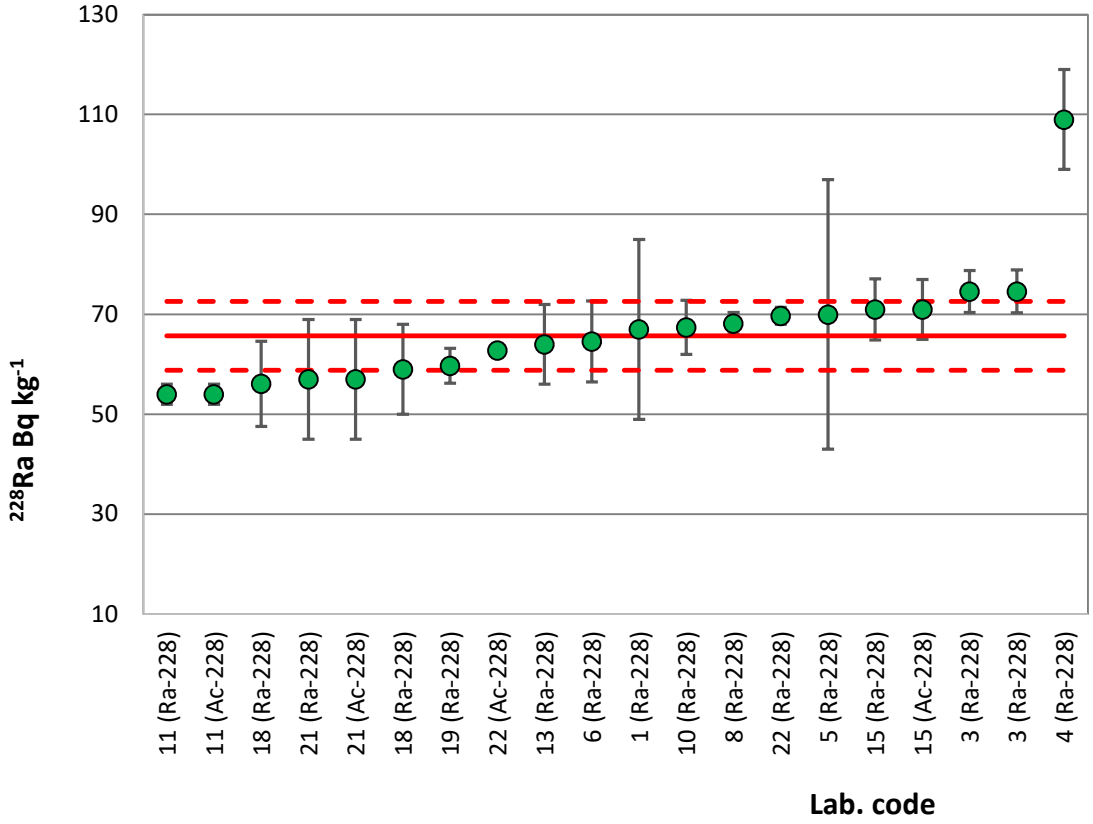

FIG.15. Laboratory results for ^{228}Ra

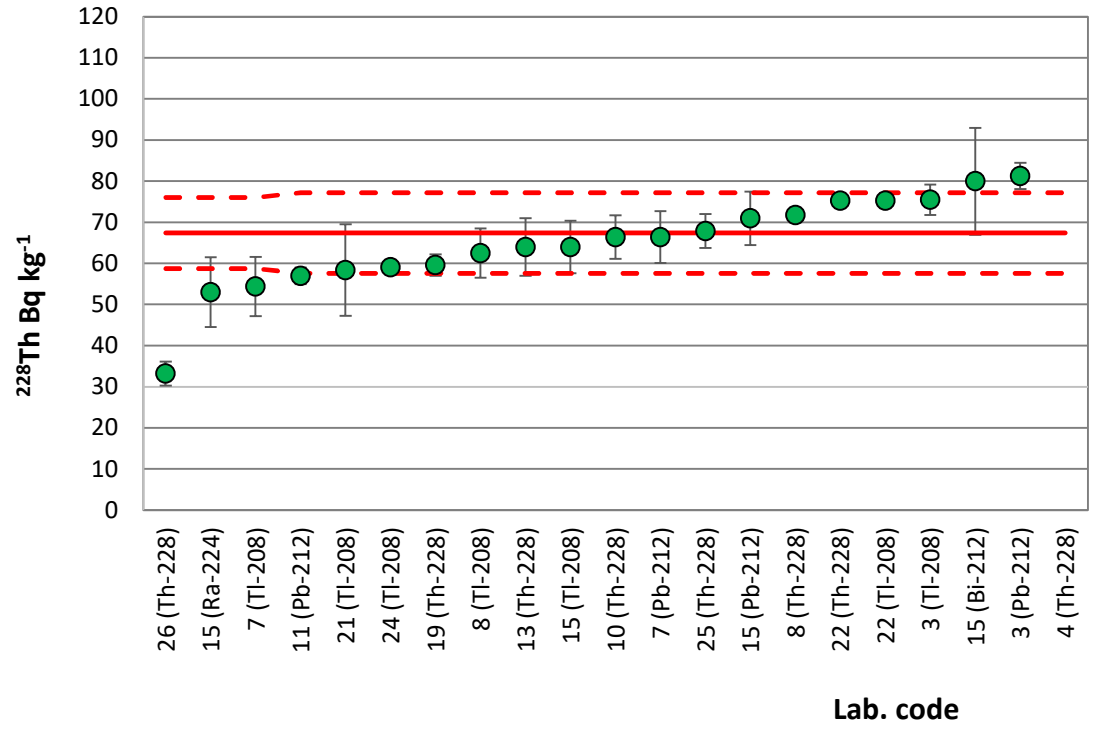

FIG.16. Laboratory results for ^{228}Th (the value of lab 4 is out of range)

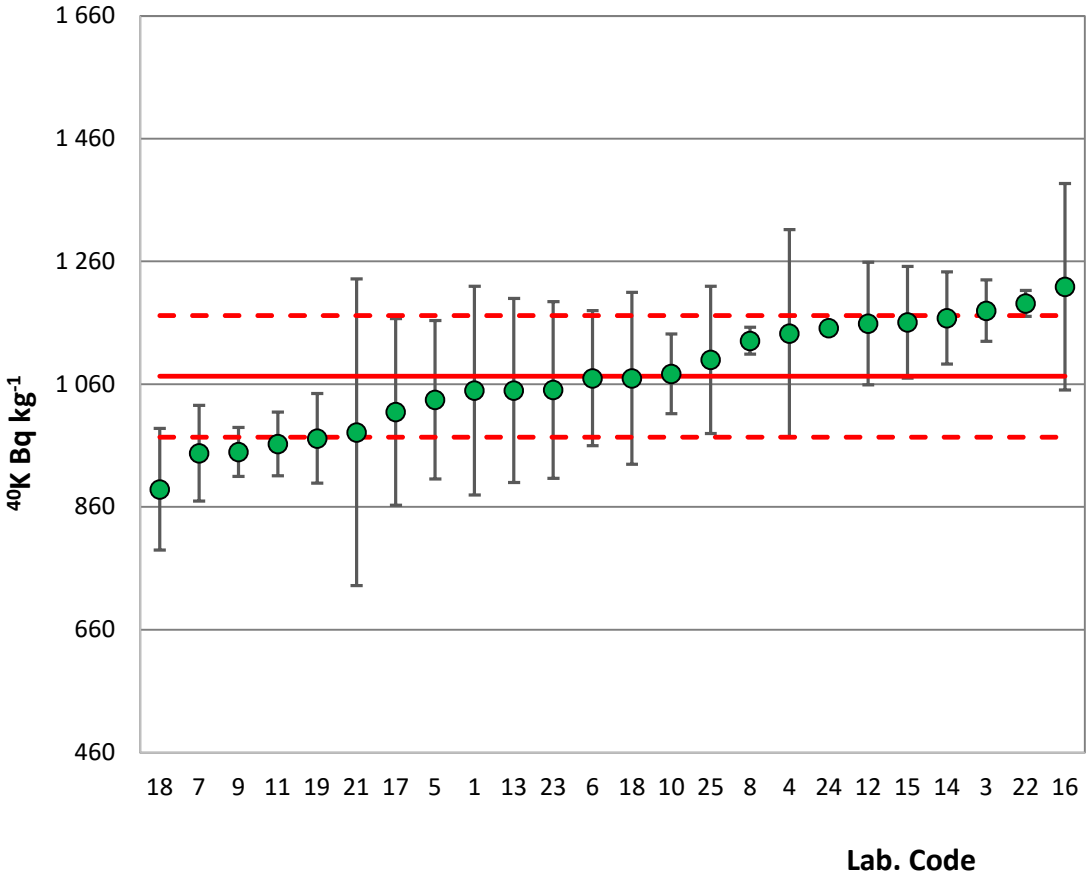

FIG.17. Laboratory results for ^{40}K

APPENDIX III.

DATA ANALYSIS

Deriving property values

Robust statistics as described in ISO 13528 [6] were used for the determination of the assigned values, where the robust mean and robust standard deviations were calculated as per Algorithm A as detailed described in Annex C.21 of ISO 13528 [6].

Individual results were ranked in increasing order:

$$(x_1, x_2, x_i, \ldots x_n)$$

Initial values of the robust average x^* and robust standard deviation s^* were calculated as:

$$x^* = \text{median of } x_i \quad (i=1,2,3\ldots.n) \qquad (Eq.\ 3)$$

Where n is the number of reported results

$$s^* = 1.483 \times \text{median } |x_i - x^*| \quad (i=1,2,3\ldots..n) \qquad (Eq.\ 4)$$

The initial values x^* and s^* were updated by calculating:

$$\delta = 1.5 \times s^* \qquad (Eq.\ 5)$$

For each x_i $(i = 1,2,3 \ldots . n)$ calculate

$$x_i^* = \begin{cases} x_i^* = x^* - \delta, & \text{if } x_i < x^* - \delta \\ x_i^* = x^* + \delta, & \text{if } x_i > x^* + \delta \\ x_i^* = x^*, & \text{otherwise} \end{cases} \qquad (Eq.\ 6)$$

New values for x^* and s^* were calculated as:

$$x^* = \frac{\sum_1^n x_i^*}{n} \qquad (Eq.\ 7)$$

$$s^* = 1.134 \sqrt{\frac{(x_i - x^*)^2}{(n-1)}} \qquad (Eq.\ 8)$$

The robust estimates of x^* and s^* were calculated by iteration by updating the values of x* and s* until they converged to the third significant figure.

REFERENCES

[1] POVINEC, P.P., PHAM, M.K., 2001. IAEA Reference Materials for Quality Assurance of Marine Radioactivity Measurements. Journal of Radioanalytical and Nuclear Chemistry, 248(1), 211–216. https://doi.org/10.1023/A:101063162

[2] SANCHEZ-CABEZA, J.-A., PHAM, M.K, POVINEC, P.P., 2008. IAEA Program on the Quality of Marine Radioactivity Data. Journal of Environmental Radioactivity, 99, 1680–1686. https://doi.org/10.1016/j.jenvrad.2008.04.007

[3] INTERNATIONAL ORGANISATION FOR STANDARDISATION, 2016. ISO 17034:2016, General Requirements for the Competence of Reference Material Producers. ISO, Geneva.

[4] INTERNATIONAL ORGANISATION FOR STANDARDISATION, 2017. ISO Guide 35, Reference materials – Guidance for Characterization and Assessment of Homogeneity and Stability. ISO, Geneva.

[5] INTERNATIONAL ORGANISATION FOR STANDARDISATION, 2015. ISO 18589-3:2015, Measurement of radioactivity in the environment – Soil – Part 3: Test Method of gamma-emitting Radionuclides Using gamma-ray Spectrometry. ISO, Geneva.

[6] INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, Statistical methods for use in proficiency testing by interlaboratory comparisons, ISO 13528:2015 (E), ISO, Geneva (2005).

[7] JOINT COMMITTEE FOR GUIDES IN METROLOGY, 2008. Evaluation of Measurement Data – Guide to the Expression of Uncertainty in Measurement. BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP and OIML Report, JCGM 100:2008

[8] BATEMAN, H., 1910. The Solution of a System of Differential Equations Occurring in the Theory of Radioactive Transformations. Proceedings of the Cambridge Philosophical Society, 15(V), 423-427

LIST OF PARTICIPATING LABORATORIES

AUSTRALIA

Cook, M.	Radiation and Nuclear Sciences Forensic and Scientific Services, Queensland Department of Health 39 Kessels Road Coopers Plains, QLD 4108

BELGIUM

Hult, M. / Jobbágy, V.	European Commission JRC - Geel Retieseweg 111 2440 Geel

DENMARK

Nielsen, S.P.	DTU Nutech Technical University of Denmark Frederiksborgvej 399, Risø Campus 4000 Roskilde

FINLAND

Vartti, V.-P.	STUK – Radiation and Nuclear Safety Authority P.O. Box 14 00881 Helsinki

FRANCE

Gurriaran, R.	IRNS/PRP-EVN/STEME/LMRE LMRE Bat 501 – Bois des Rames 91400 Orsay
Van Beek, P.	LEGOS/LAFARA Observatoire Midi Pyrénées 14 Avenue Edouard Belin 31400 Toulouse

GERMANY

Aust, M.- O. / Nogueira, P.	Johann Heinrich von Thünen-Institut Institut für Fischereiökologie Marckmannstraße 129b, Haus 4 20539 Hamburg
Degering, D.	VKTA – Strahlenschutz, Analytik & Entsorgung Rossendorf e. V. Postfach 510119 01314 Dresden
Herrmann, J.	Federal Maritime and Hydrographic Agency (FMHA) Radioactivity of the Sea Wuestland 2 22589 Hamburg
Ilchmann, C. / Pottiez, D.	Senatsverwaltung für Umwelt, Verkehr und Klimaschutz Abteilung II (Integrativer Umweltschutz) Strahlenmessstelle Berlin Rubensstraße 111-113 12157 Berlin
Rieth, U.	Landesmessstelle für Radioaktivität Behörde für Gesundheit und Verbraucherschutz Institut für Hygiene und Umwelt Marckmannstraße 129b, Haus 6 20539 Hamburg
Schikowski, J.	Georg-August-Universität Physikalische Chemie Tammannstr. 6 37077 Göttingen

ITALY

Laubenstein, M.	Laboratori Nazionali del Gran Sasso S.S. 17/bis km 18+910 67100 Assergi (AQ)

JAPAN

Nakano, M.	Japan Atomic Energy Agency 4-33, Muramatsu Tokai-mura, Naka-gun Ibaraki, 319-1194
Morimoto, T.	Japan Chemical Analysis Center

	295-3 Sanno-cho Inage-ku Chiba-shi, Chiba 263-0002
KOREA, Republic of	
Lee, S.-H.	Korea Research Institute of Standards and Science 1 Doryong-Dong, Yuseoung-Gu Daejeon 305-340
POLAND	
Mietelski, J. W. / Tomankiewicz, E.	Nuclear Physical Chemistry Department The Henryk Niewodniczanski Institute of Nuclear Physics, Polish Academy of Sciences PL-31-342 Krakow, Radzikowskiego 152
Suplinska, M.	Central Laboratory for Radiological Protection Konwaliowa 7 03-194 Warsaw
Zalewska, T.	Institute of Meteorology and Water Management, Maritime Branch Waszyngtona 42 81-342 Gdynia
PORTUGAL	
Carvalho, F.P.	Laboratório de Protecção e Segurança Radiológica Instituto Superior Técnico / Campus Tecnológico Nuclear Estrada Nacional 10, km 139,7 2695-066 Bobadela LRS
SLOVAKIA	
Povinec, P.P. / Sykora, I.	Faculty of Mathematics, Physics and Informatics Comenius University SK-84248 Bratislava
SPAIN	
Chamizo, E.	Centro Nacional de Aceleradores Isla de la Cartuja 41092 Sevilla

Spain

Gascó, C.

CIEMAT (RAyVR)
Edificio 70 Planta 2
Despacho 11 Avda de la Complutense 40
28040 Madrid

Mas, J.L. / Hurtado, S.

Servicio de Radioisotopos, CITIUS
Avda. Reina Mercedes 4B
41012 Sevilla

UNITED KINGDOM

Smedley, P.

Cefas Lowestoft Laboratory
Pakefield Road
Lowestoft, Suffolk NR33 0HT

USA

La Rosa, J. / Nour, S.

National Institute of Standards and Technology
100 Bureau Drive
Radiation Protection, Bldg. 245, room B131
Gaithersburg, MD 20899

INTERNATIONAL ATOMIC ENERGY AGENCY

Bartocci, J./ Blinova, O./ Fujak, M.
Levy, I./ Mc-Ginnity, P./ Pham, M.K.

IAEA – Environment Laboratories.
4a, Quai Antoine 1er
98000 Monaco

CONTRIBUTORS TO DRAFTING AND REVIEW

HARMS, A. V.	International Atomic Energy Agency
JEROME, S.M.	International Atomic Energy Agency
MAURING, A.	International Atomic Energy Agency
PATTERSON, S.	International Atomic Energy Agency
PHAM, M.K.	International Atomic Energy Agency
TARJAN, S.	International Atomic Energy Agency

IAEA
International Atomic Energy Agency

No. 26

ORDERING LOCALLY

IAEA priced publications may be purchased from the sources listed below or from major local booksellers.

Orders for unpriced publications should be made directly to the IAEA. The contact details are given at the end of this list.

NORTH AMERICA

Bernan / Rowman & Littlefield

15250 NBN Way, Blue Ridge Summit, PA 17214, USA
Telephone: +1 800 462 6420 • Fax: +1 800 338 4550

Email: orders@rowman.com • Web site: www.rowman.com/bernan

REST OF WORLD

Please contact your preferred local supplier, or our lead distributor:

Eurospan Group

Gray's Inn House
127 Clerkenwell Road
London EC1R 5DB
United Kingdom

Trade orders and enquiries:

Telephone: +44 (0)176 760 4972 • Fax: +44 (0)176 760 1640
Email: eurospan@turpin-distribution.com

Individual orders:

www.eurospanbookstore.com/iaea

For further information:

Telephone: +44 (0)207 240 0856 • Fax: +44 (0)207 379 0609
Email: info@eurospangroup.com • Web site: www.eurospangroup.com

Orders for both priced and unpriced publications may be addressed directly to:

Marketing and Sales Unit
International Atomic Energy Agency
Vienna International Centre, PO Box 100, 1400 Vienna, Austria
Telephone: +43 1 2600 22529 or 22530 • Fax: +43 1 26007 22529
Email: sales.publications@iaea.org • Web site: www.iaea.org/publications

21-02530E

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA