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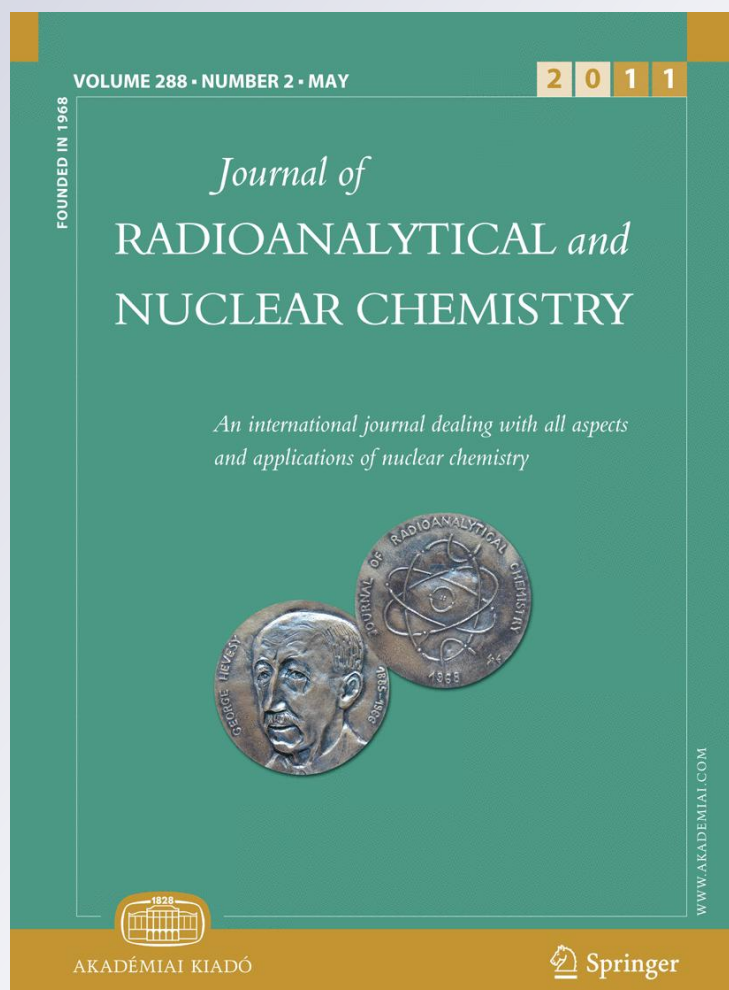
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A certified reference material for radionuclides in the water sample from Irish Sea (IAEA-443)

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Abstract A new certified reference material (CRM) for radionuclides in sea water from the Irish sea (IAEA-443) is described and the results of the certification process are presented. Ten radionuclides (^3H , ^{40}K , ^{90}Sr , ^{137}Cs , ^{234}U , ^{235}U , ^{238}U , ^{238}Pu , $^{239+240}\text{Pu}$ and ^{241}Am) have been certified, and information values on massic activities with 95% confidence intervals are given for four radionuclides

(^{230}Th , ^{232}Th , ^{239}Pu and ^{240}Pu). Results for less frequently reported radionuclides (^{99}Tc , ^{228}Th , ^{237}Np and ^{241}Pu) are also reported. The CRM can be used for quality assurance/quality control of the analysis of radionuclides in water samples, for the development and validation of analytical methods and for training purposes. The material is available in 5 L units from IAEA (<http://nucleus.iaea.org/rpst/index.htm>).

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Introduction

Anthropogenic radionuclides which have been released to the environment from nuclear industry sources such as nuclear reprocessing facilities and nuclear reactors [1], as well as global fallout from nuclear weapons tests carried out in the atmosphere [2] have been widely used as tracers to study exchange processes in the terrestrial and marine environments [3]. Such investigations require highly sensitive analytical techniques [4, 5] producing high quality radionuclide data sets which could be internationally comparable and stored in relational databases [6, 7] (<http://maris.iaea.org>).

To address the problem of data quality, the IAEA's Marine Environment Laboratories (IAEA-MEL) in Monaco have conducted interlaboratory comparison exercises on radionuclides in marine samples for the last forty years as part of their contribution to the IAEA's programme of analytical quality control service (AQCS), now renamed as "IAEA's Reference Products for Science and Trade" [8]. An important part of this activity was the production of reference materials (RMs), which were usually products of worldwide interlaboratory comparison exercises [9].

The IAEA's AQCS programme for radionuclides in the marine environment has recently focused on the production of certified reference materials (CRMs) with the aim to improve the accuracy and precision of analyses carried out by the laboratories and thus improve the quality of data,

and to provide traceability to SI standards [10–12]. CRMs are valuable for method development and validation: they can indicate the need to improve or change existing radioanalytical methods and/or the need of further training. In fact, reference methods should only be accepted on the basis of interlaboratory comparison tests performed on selected CRMs. RMs and CRMs should be available for all important marine matrices, such as sediment, biota, sea water and suspended matter.

Collection and preparation of large volume sea water samples (over 1000 kg) are necessary for the required long-term availability of RMs/CRMs (over 10 years) and for their long-term stability as well. The production of a new reference material is a long process, covering the identification of needs, sample collection, pre-treatment, physical homogenization, bottling, homogeneity tests, distribution to laboratories, evaluation of data, preliminary reporting, additional analyses by expert laboratories, certification of material (including the determination of proper values and their expanded uncertainties), and finally issuing the RM/CRM [13–15].

This work was performed on a sea water sample collected from the Irish sea, on which the elevated levels of anthropogenic radionuclides were expected due to the discharges from Sellafield reprocessing plant. Participating laboratories were requested to determine as many anthropogenic and natural radionuclides as possible by gamma-spectrometry, alpha-spectrometry, beta-counting and mass spectrometry. The certification process was completed and the material was issued as a CRM for radionuclides in sea water sample.

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Experimental

Description of the material

The Federal Maritime and Hydrographical Agency (BSH), Hamburg (Germany), in collaboration with IAEA-MEL, collected about 3600 litres of surface water from the Irish sea on September 7, 1993, onboard the research vessel *Valdivia*. Sampling was performed during a transect between two shallow (~20 m water depth) stations located at 54°24,89'N–3°33,62'W and 54°23,2'N–3°33,45'W. Water was sampled from 5 m water depth, stored in 600 L containers and acidified to pH < 1 immediately without any filtration.

A part of the sample was forwarded to IAEA-MEL and was used for the IAEA-381 interlaboratory comparison on anthropogenic and natural radionuclides. The results obtained from 28 laboratories were reported and the IAEA-381 certified reference material was issued [10, 16]. The original sample which was also collected in 1993 from the Irish sea together with IAEA-381, was kept by the Risø National Laboratory (Denmark) and provided in 2005 to IAEA-MEL (1100 L) with the aim to produce a new CRM as the IAEA-381 has already been sold out. As there could be changes in the radionuclide content of the sea water sample during the storage (e.g. adsorption of radionuclides on the walls), it was decided to carry out a new certification process. The sample was transferred into a container of 1500 L and mixed for 4 h using two pumps. The homogenised sample was then transferred into 5 L cubitainers and coded as IAEA-443.

Sample dispatch and data feedback

The sample aliquots were distributed to participating laboratories during 2007. It has been recommended by the Oslo-Paris Commission (OSPAR) that this sample could be used for an intercomparison exercise of OSPAR laboratories. Taking into account the limiting size of the sample, only 13 laboratories from ten OSPAR contracting parties received the sea water sample. Each participant received 5 L of the sample.

For each radionuclide analyzed, the following information was requested:

- (1) average weight of sample used for analysis;
- (2) number of analyses;
- (3) massic activity (Bq kg⁻¹) corrected for blank, background, etc.;
- (4) estimation of combined uncertainties;
- (5) description of chemical procedures and counting equipment;
- (6) standard solutions used for analysis;

- (7) chemical recoveries if any, counting time and decay corrections.

The preliminary results of this exercise have already been reported in IAEA analytical quality in nuclear applications series, report N°10 (IAEA/AQ/10) [17].

Sixteen more samples were sent to expert laboratories in 2009 with the aim to get high quality data for the certification process. The data from the interlaboratory comparison exercise and additional data from the expert laboratories were included in the certification process, results of which are reported in the present paper. The results of this exercise have allowed IAEA-MEL to produce a new CRM, replacing thus IAEA-381 which is not available anymore. Simultaneously, it has been possible to test the stability of the sea water sample after 15 years of conservation in high density polyethylene container [10].

Data treatment

The massic activities of anthropogenic and natural radionuclides in the sample were reported. Calculations are based on the assumption of non-parametric distribution of data to which distribution-free statistics are applicable. Laboratory means were calculated when necessary from individual results, and they are given either as arithmetic means with corresponding standard deviations when more than two results were reported, or as weighted means with weighted uncertainties in the case of only two results reported. The values below the detection limits are segregated from the results and the remaining values are checked for the presence of outliers using a Box-and-Whisker plot test. Median values are calculated from all results passing the test, rounded off to the most significant number of the uncertainty. These values are considered to be the most reliable estimates of the true values [18]. Confidence intervals were taken from a non-parametric sample population representing a two-sided interval at 95% confidence limits. Expanded uncertainty with a coverage factor of $k = 2$, corresponding to a level of confidence of about 95%, was also calculated according to the ISO [19] and NIST [20] guidelines.

Following the ISO [21] and IUPAC [22] recommendations for assessment of performance of laboratories, a Z-score methodology was used in the data evaluation. The Z-score was calculated using the formula

$$Z = (X_i - X_a) / S_b,$$

where X_i is the robust mean of massic activity values reported by the laboratory i , X_a is the assigned value (a mean value of accepted results), and S_b is the target standard deviation. The right target value depends on the objective of the exercise. For radionuclide analysis, laboratories were required to have a relative bias below

20% ($S_b < 10\%$). The uncertainty of the assigned value (S_{tu}) was included in the target value for bias [23]:

$$Z = (X_i - X_a) / \sqrt{S_b^2 + S_{tu}^2}$$

The performance of laboratories in term of accuracy was expressed by the Z-score for each radionuclide. It is considered to be acceptable if this relative difference between the robust mean of the laboratory and the assigned value is less than or equal to 2. A Z-score from 2 to 3 indicates that the results are of questionable quality, and the result of analysis is regarded as an outlier when $|Z| > 3$.

The Z-score distributions of IAEA-443 data were symmetric (after excluding outliers) and usually below 2, indicating that the performance of the laboratories was satisfactory. A typical example of the Z-score for ^{137}Cs is shown in Fig. 1. The Z-score evaluation represents a simple method which informs participating laboratories on their performance.

Criteria for certification

The certification process was carried out following the ISO Guide 35 [18] using the most precise and accurate data from interlaboratory comparison exercise and additional data from expert laboratories. For data sets comprising 5 or more accepted laboratory means, the median activities for the sets of individual data (after rejection of outliers) were chosen as the best estimations of the property values [10–15]. They are reported as certified values when

- (i) at least five laboratory means were available, calculated from at least three different laboratories;
- (ii) the relative uncertainty of the median did not exceed $\pm 5\%$ for activities higher than 100 Bq kg^{-1} , $\pm 10\%$ for activities from 1 to 100 Bq kg^{-1} and $\pm 20\%$ for activities lower than 1 Bq kg^{-1} .

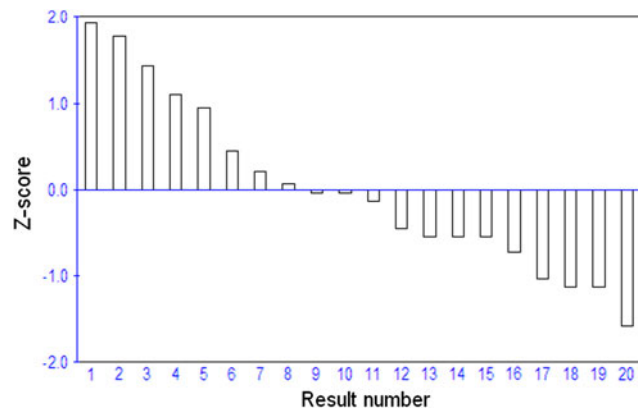


Fig. 1 Z-score values for ^{137}Cs in IAEA-443

An activity value was considered as an information value when at least five laboratory means calculated from the results of at least two different laboratories were available.

Expanded uncertainties with a coverage factor of $k = 2$, corresponding to a level of confidence of about 95%, were calculated according to the ISO and NIST guidelines [19, 20]. Evidence on metrological traceability to the SI units was provided by all laboratories in their reports.

Results and discussion

Homogeneity tests

Sample homogeneity was checked by measuring ^{137}Cs , ^{40}K , ^{90}Sr , ^{238}Pu and $^{239+240}\text{Pu}$ activities (using high-resolution low-background gamma-spectrometry, low-level beta proportional counter and alpha-spectrometry) in 2 L aliquots from five cubitainers chosen at random. Homogeneity was tested by using one-way analysis of variance. The coefficient of variation was below 10% for all radionuclides analysed. On the basis of the homogeneity tests, the sample could be of over 2 L.

An additional homogeneity test for major and trace elements (P, S, Cl, K, Ca, Fe, Ni, Cu, Zn, As, Br, Sr, I, Ba, Pb) for the sea water sample was done by XRF analysis of 4 g samples. The coefficient of variation was below 10% for XRF determined elements as well.

Radionuclides with certified values

Ten radionuclides (^3H , ^{40}K , ^{90}Sr , ^{137}Cs , ^{234}U , ^{235}U , ^{238}U , ^{238}Pu , $^{239+240}\text{Pu}$ and ^{241}Am) were certified in the certification process. The mean, median values with 95% confidence intervals, the number of accepted means which were used to calculate the certified activities and their expanded uncertainties are given in Table 1. The evaluation results in order of ascending massic activities, the distribution of medians and corresponding confidence intervals (95%) are shown in Figs. 2, 3, 4, 5.

^3H : liquid scintillation spectrometry was mostly used by participants to determine ^3H with prior distilled water sample. The data representing 13 laboratory means were used in the certification process. The Z-score values were below 2.0 showing good performance by the laboratories. The data show a good homogeneity, falling less than two standard deviations from the distribution mean (Fig. 2). The median given as the certified value is 37.2 Bq kg^{-1} , 95% confidence interval is $36.6\text{--}38.0 \text{ Bq kg}^{-1}$.

^{40}K : Gamma-spectrometry was mostly used by participants to determine ^{40}K . The data representing 19 laboratory means were used in the certification process. The Z-score values were below 2.0 showing good performance by the

Table 1 Certified massic activities in IAEA-443 water from the Irish sea (Reference date: 1st January 2007)

Radionuclide	Mean \pm SD (Bq kg ⁻¹)	Median (Bq kg ⁻¹)	Expanded uncertainty (Bq kg ⁻¹)	95% Confidence interval (Bq kg ⁻¹)	N ^a
³ H	37.2 \pm 1.1	37.2	0.5	36.6–38.0	12
⁴⁰ K	11.2 \pm 0.8	11.4	0.4	10.7–11.7	19
⁹⁰ Sr	0.107 \pm 0.012	0.110	0.005	0.095–0.115	13
¹³⁷ Cs	0.36 \pm 0.02	0.36	0.01	0.35–0.37	20
²³⁴ U	0.043 \pm 0.004	0.044	0.002	0.039–0.046	12
²³⁵ U	0.00186 \pm 0.00015	0.00185	0.00010	0.00152–0.00190	6
²³⁸ U	0.038 \pm 0.004	0.039	0.002	0.034–0.041	13
²³⁸ Pu	0.0031 \pm 0.0001	0.0031	0.0001	0.0029–0.0032	10
²³⁹⁺²⁴⁰ Pu	0.0146 \pm 0.0004	0.0147	0.0002	0.0143–0.0150	12
²⁴¹ Am ^b	0.0195 \pm 0.0014	0.0197	0.0010	0.0179–0.0204	10

^a Number of accepted laboratory means which were used to calculate the certified massic activities, the expanded uncertainty with a coverage factor of $k = 2$ and the corresponding confidence intervals

^b The values should be corrected for in-growth from ²⁴¹Pu

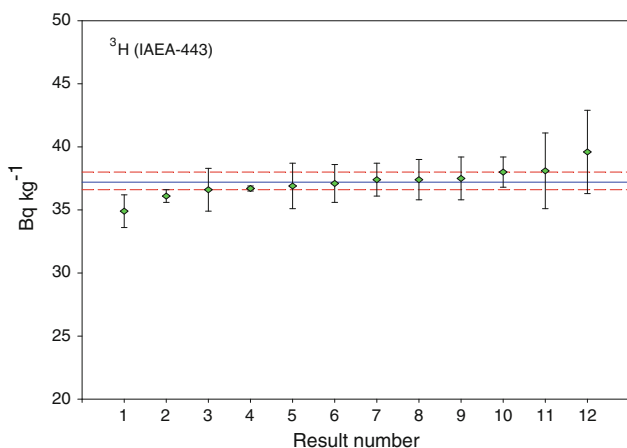


Fig. 2 Data evaluation for ³H in IAEA-443. The median (solid line) and corresponding 95% confidence intervals (dashed lines) are shown. The error bars correspond to the combined uncertainty reported by laboratories

laboratories. The data show a good homogeneity, falling less than two standard deviations from the distribution mean. The median given as the certified value is 11.4 Bq kg⁻¹, 95% confidence interval is 10.7–11.7 Bq kg⁻¹.

⁹⁰Sr: Thirteen laboratory means obtained by radiochemical treatment (mostly precipitation, ⁹⁰Y extraction) and gas or liquid scintillation counting were available for the evaluation. The data fell within less than 2 standard deviations from the distribution mean. The combined Z-score values were below 1.8. The median given as the certified value is 110 mBq kg⁻¹, 95% confidence interval is 95–115 mBq kg⁻¹.

¹³⁷Cs: The data set was evaluated using 20 laboratory means. The laboratories mainly used direct non-destructive gamma-spectrometry, some of them used AMP (Ammonium

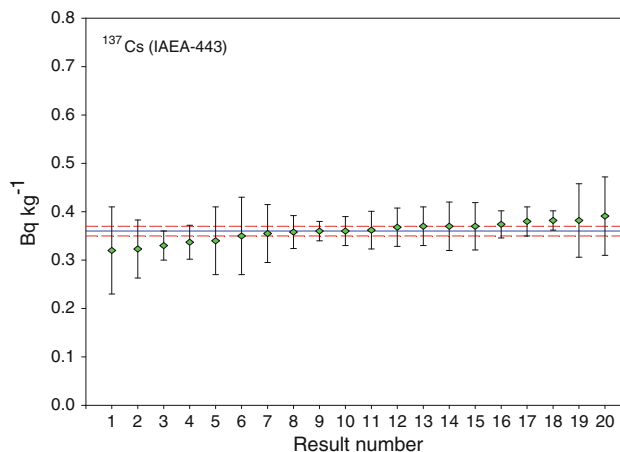


Fig. 3 Data evaluation for ¹³⁷Cs in IAEA-443. The median (solid line) and corresponding 95% confidence intervals (dashed lines) are shown. The error bars correspond to the combined uncertainty reported by laboratories

phospho-molybdate) for caesium enrichment/precipitation prior gamma-spectrometry measurements. The Z-score values were below 1.9 showing good performance of the laboratories (Fig. 1). The data were homogenous within two standard deviations of the distribution mean (Fig. 3). The median, given as the certified value is 0.36 Bq kg⁻¹, 95% confidence interval is 0.35–0.37 Bq kg⁻¹.

²³⁴U: Total dissolution followed by alpha-spectrometry, with the exception of one result obtained by ICP-MS, were used in the analysis. Twelve laboratory means were accepted for the certification process. The Z-score values were below 2.0 showing very good performance of the laboratories. The median, given as the certified value is 44 mBq kg⁻¹, 95% confidence interval is 39–46 mBq kg⁻¹.

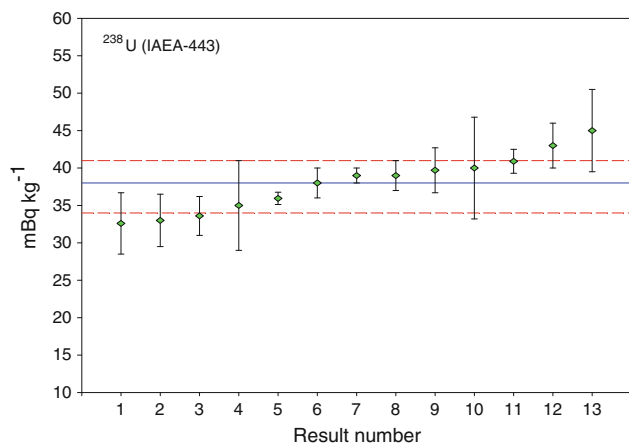


Fig. 4 Data evaluation for ^{238}U in IAEA-443. The median (solid line) and corresponding 95% confidence intervals (dashed lines) are shown. The error bars correspond to the combined uncertainty reported by laboratories

^{235}U : Total dissolution followed by alpha-spectrometry, with the exception of one result obtained by ICP-MS, were used in the analysis. One laboratory used both alpha-spectrometry and ICP-MS. Six laboratory means were accepted to be used in the certification process. The Z-score values were below 1.6 showing very good performance of the laboratories. The median, given as the certified value is 1.86 mBq kg^{-1} , 95% confidence interval is $1.52\text{--}1.90 \text{ mBq kg}^{-1}$.

^{238}U : Data representing 13 laboratory means were used in the certification process, of which 11 results were obtained by alpha-spectrometry and 2 by ICP-MS with prior radiochemical purification. One laboratory used both alpha-spectrometry and ICP-MS. The data fell within less than 2 standard deviations from the distribution mean (Fig. 4). The Z-score values were below 1.8 showing good performance by the laboratories. The median, given as the certified value is 39 mBq kg^{-1} , 95% confidence interval is $34\text{--}41 \text{ mBq kg}^{-1}$.

^{238}Pu , $^{239+240}\text{Pu}$: The majority of participants used conventional radiochemical methods based on sample treatment, ion-exchange separation followed by electro-deposition and alpha-spectrometry [24]. Some laboratories combined ion-exchange separation with liquid-liquid extraction, or used only liquid-liquid extraction. Resins (a single TRU columns or double UTEVA + TRU columns) for the separation and subsequent electro-deposition for alpha-spectrometry (^{238}Pu , $^{239+240}\text{Pu}$) and/or for direct ICP-MS analysis (^{239}Pu , ^{240}Pu) were also used. The samples for mass spectrometry analyses were either leached from stainless steel discs after alpha-spectrometry measurements, or in some case analyzed directly in mass spectrometers. A reasonable agreement was obtained between the alpha-spectrometry and mass spectrometry results.

Ten data sets of ^{238}Pu obtained by alpha-spectrometry and ICP-MS were included in the evaluation. The data

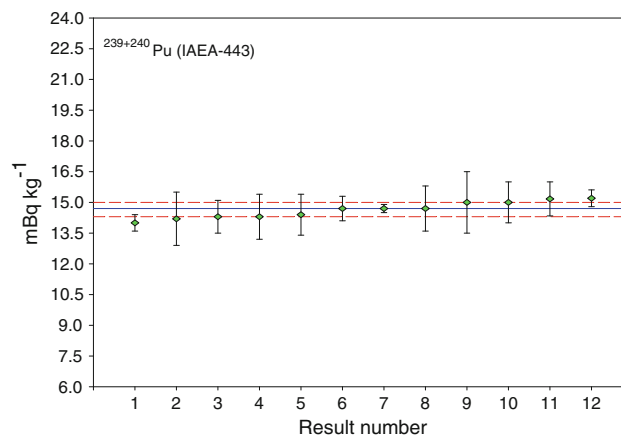


Fig. 5 Data evaluation for $^{239+240}\text{Pu}$ in IAEA-443. The median (solid line) and corresponding 95% confidence intervals (dashed lines) are shown. The error bars correspond to the combined uncertainty reported by laboratories

show a good homogeneity, within two standard deviations of the distribution mean. The Z-score values were below 1.6 showing a good performance of the laboratories. The median, given as the certified value is 3.1 mBq kg^{-1} , 95% confidence interval is $2.9\text{--}3.2 \text{ mBq kg}^{-1}$.

Twelve data sets of $^{239+240}\text{Pu}$ obtained by alpha-spectrometry and ICP-MS were included in the evaluation. The data shows a good homogeneity, within two standard deviations of the distribution mean (Fig. 5). The Z-score values were below 1.6 showing very good performance of the laboratories. The median, given as the certified value is 14.7 mBq kg^{-1} , 95% confidence interval is $14.3\text{--}15.0 \text{ mBq kg}^{-1}$.

^{241}Am : Ten results (nine obtained by alpha-spectrometry and one by gamma-spectrometry) were available for data statistical treatment. The data fell within less than two standard deviations from the distribution mean. The combined Z-score values were below 1.8. The median given as the certified value is 19.7 mBq kg^{-1} , 95% confidence interval is $17.9\text{--}20.4 \text{ mBq kg}^{-1}$.

Radionuclides with information values

Information values are given for five radionuclides: ^{230}Th , ^{232}Th , ^{239}Pu , ^{230}Pu and ^{241}Pu . The mean, median values with 95% confidence intervals, the number of accepted means which were used to calculate the activities and their expanded uncertainties are given in Table 2.

^{230}Th : Five laboratory means were obtained by both alpha-spectrometry and ICP-MS techniques. The median given as the information value is 0.5 mBq kg^{-1} , 95% confidence interval is $0.4\text{--}0.6 \text{ mBq kg}^{-1}$.

^{232}Th : Different techniques such as alpha-spectrometry and mass spectrometry were used in ^{232}Th analyses, one

Table 2 Information massic activities in IAEA-443 water from the Irish sea (Reference date: 1st January 2007)

Radionuclide	Mean ± SD (mBq kg ⁻¹)	Median (mBq kg ⁻¹)	Expanded uncertainty (mBq kg ⁻¹)	95% Confidence interval (mBq kg ⁻¹)	N ^a
²³⁰ Th	0.5 ± 0.1	0.5	0.1	0.4–0.6	5
²³² Th	0.19 ± 0.03	0.19	0.03	0.13–0.23	5
²³⁹ Pu	8.6 ± 1.0	8.2	0.8	7.7–10.0	6
²⁴⁰ Pu	7.3 ± 0.7	7.0	0.6	6.6–8.4	6
²⁴¹ Pu	166 ± 21	161	19	140–194	5

^a Number of accepted laboratory means which were used to calculate the information massic activities, the expanded uncertainty with a coverage factor of $k = 2$ and the corresponding confidence intervals

Table 3 Radionuclide activity ratios (Reference date: 1st January 2007)

¹³⁷ Cs/ ⁹⁰ Sr	¹³⁷ Cs/ ^{239,240} Pu	²³⁸ Pu/ ^{239,240} Pu	²⁴¹ Pu/ ^{239,240} Pu	²⁴¹ Am/ ^{239,240} Pu ^a	²⁴⁰ Pu/ ²³⁹ Pu ^b
3.45 ± 0.39	26.3 ± 2.9	0.23 ± 0.03	11.9 ± 0.8	1.43 ± 0.04	0.229 ± 0.006

^a The values should be corrected for in-growth from ²⁴¹Pu

^b Mass ratio

laboratory used both techniques. Five laboratory means, four obtained by mass spectrometry and one by alpha-spectrometry were considered. The Z-score values are below 1.5, showing good performance of laboratories. The median given as the information value is 0.19 mBq kg⁻¹, 95% confidence interval is 0.13–0.23 mBq kg⁻¹.

²³⁹Pu: Five laboratory means obtained by ICP-MS and one laboratory mean obtained by high resolution alpha-spectrometry [25] were available for the evaluation. The median given as the information value is 8.2 mBq kg⁻¹, 95% confidence interval is 7.7–10 mBq kg⁻¹.

²⁴⁰Pu: Five laboratory means obtained by ICP-MS and one laboratory mean obtained by high resolution alpha spectrometry [25] were available for the evaluation. The median given as the information value is 7.0 mBq kg⁻¹, 95% confidence interval is 6.6–8.4 mBq kg⁻¹. It is important to notice that the combined ²³⁹⁺²⁴⁰Pu value obtained by ICP-MS laboratories is in agreement with the ²³⁹⁺²⁴⁰Pu value obtained by alpha-spectrometry laboratories.

²⁴¹Pu: Five laboratory means obtained by alpha-spectrometry (calculated from the ²⁴¹Am in-growth), liquid scintillation spectrometry, and mass spectrometry (ID-SF-ICP-MS combined with two-stage anion-exchange chromatography) were available for the evaluation. The median given as information value is 161 mBq kg⁻¹, 95% confidence interval is 140–194 mBq kg⁻¹.

Less frequently reported radionuclides

⁹⁹Tc: Four laboratory means obtained by radiochemical treatment (mostly precipitation and extraction) and gas or liquid scintillation counting were available for the evaluation. The average massic activity is 199 ± 38 mBq kg⁻¹.

²³⁷Np: One laboratory mean obtained by gamma-spectrometry with prior radiochemical treatment was reported. The average massic activity is 7 ± 3 mBq kg⁻¹.

Radionuclide ratios

The activity ratios for ¹³⁷Cs/⁹⁰Sr, ¹³⁷Cs/^{239,240}Pu, ²³⁸Pu/^{239,240}Pu, ²⁴¹Pu/^{239,240}Pu, ²⁴¹Am/^{239,240}Pu and ²⁴⁰Pu/²³⁹Pu are given in Table 3. The ¹³⁷Cs/⁹⁰Sr activity ratio (3.45 ± 0.39) is much higher than the global fallout ratio (1.6), documenting that ¹³⁷Cs released from the Sellafield reprocessing plant has been dominating in the Irish Sea, as has been suggested in our previous paper [10]. The ²³⁸Pu/²³⁹⁺²⁴⁰Pu activity ratio (0.23 ± 0.03) confirms also that discharges from the Sellafield reprocessing plant are the main source of plutonium in the Irish sea (the expected ratio from global fallout is 0.03 ± 0.01). The ²⁴¹Pu/^{239,240}Pu activity ratio of 11.9 ± 0.8, as well as ²⁴¹Am/^{239,240}Pu ratio of 1.43 ± 0.04 also documents the impact of the Sellafield reprocessing facility.

The ²⁴⁰Pu/²³⁹Pu mass ratio determined in the IAEA-443 sample by ICP-MS [26] is higher than expected from global fallout (0.229 ± 0.006 vs. 0.186 ± 0.003), and also reflects the impact of the Sellafield reprocessing facility on the concentration of Pu isotopes in the Irish sea.

Stability of water sample during last 15 years

The values of ³H, ⁴⁰K, ⁹⁰Sr, ¹³⁷Cs, ²³⁸U, ²³⁸Pu, ²³⁹Pu, ²⁴⁰Pu and ²³⁹⁺²⁴⁰Pu obtained in this exercise have been compared with the ones reported for IAEA-381 [10]. The results are listed in Table 4. The differences between the medians are less than 11%, however, the results obtained

Table 4 Comparison of massic activities in IAEA-443 and in IAEA-381 (Reference date: 1st January 2007)

Radionuclide	IAEA-381 Median (95% confidence interval) ^a (Bq kg ⁻¹)	IAEA-443 Median (95% confidence interval) (Bq kg ⁻¹)	Difference between medians (%)
³ H	33.5 (28.2–39.4)	37.2 (36.6–38.0)	11.0
⁴⁰ K	11.5 (10.5–12.2)	11.4 (10.7–11.7)	0.9
⁹⁰ Sr	0.093 (0.090–0.096)	0.110 (0.095–0.115)	7.5
¹³⁷ Cs	0.35 (0.34–0.36)	0.36 (0.35–0.37)	2.9
²³⁸ U	0.041 (0.038–0.048)	0.039 (0.039–0.046)	4.9
²³⁸ Pu	0.0029 (0.0028–0.0032)	0.0031 (0.0029–0.0032)	6.9
²³⁹ Pu	0.0081 (0.077–0.0085)	0.0082 (0.0077–0.010)	1.2
²⁴⁰ Pu	0.0067 (0.0065–0.0070)	0.0070 (0.0066–0.0084)	4.5
²³⁹⁺²⁴⁰ Pu	0.0135 (0.0131–0.0145)	0.0147 (0.0143–0.0150)	8.9

^a Values were decay corrected to 1st January 2007

for all radionuclides in the IAEA-443 are within 95% confidence intervals reported for the IAEA-381. This would indicate that the content of radionuclides in the acidified sea water sample stored in high density polyethylene container did not change during the last 15 years (except for the radioactive decay).

Conclusion

A sea water sample from the Irish Sea collected in 1993 has been certified for radionuclides according to ISO certification criteria. The sample has been issued as the IAEA-443 certified reference material. Certified values have been obtained for 10 radionuclides (³H, ⁴⁰K, ⁹⁰Sr, ¹³⁷Cs, ²³⁴U, ²³⁵U, ²³⁸U, ²³⁸Pu, ²³⁹⁺²⁴⁰Pu and ²⁴¹Am). Information values are given for 5 radionuclides (²³⁰Th, ²³²Th, ²³⁹Pu, ²⁴⁰Pu and ²⁴¹Pu). It has also been found that the content of radionuclides in the acidified sea water sample, stored in high density polyethylene container, did not change during 15 years of storage.

The IAEA-443 CRM is intended to be used for quality assurance/quality control of radionuclide analyses of sea water samples using radiometric and mass spectrometry techniques, for the development and the validation of analytical methods, for the development of reference methods and for training purposes. The CRM is available from IAEA in 5 L units and can be ordered through IAEA website (<http://nucleus.iaea.org/rpst/>).

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