Interlaboratory comparison 2018 Determination of radionuclides in seawater, sediment and fish

Marine Monitoring: Confidence Building and Data Quality Assurance

IAEA Project Interim Report



SUMMARY REPORT

The IAEA Environment Laboratories in Monaco are assisting the Government of Japan in ensuring that its regularly updated Sea Area Monitoring Plan is comprehensive, credible and transparent through the project "Marine Monitoring: Confidence Building and Data Quality Assurance". During the period 2014 – 2017, seven interlaboratory comparisons (ILCs) and four proficiency tests (PTs) were organised within this project to test the sampling and analytical performance of Japanese laboratories monitoring radionuclides in seawater, sediment and fish as part of the Sea Area Monitoring Plan.

This report focuses on the ILC which was organised in 2018. As for previous ILCs in this project, a joint sampling campaign to collect seawater, sediment and fish samples was undertaken. In this case, sampling was conducted in October 2018 with observers from the IAEA and Japanese authorities involved in the Sea Area Monitoring Plan. Seawater and sediment samples were collected at offshore locations close to the Fukushima Daiichi Nuclear Power Station. Several species of fish were sampled from a market in Fukushima Prefecture. The samples were then homogenised, split and sent to each participating laboratory for analysis. The results of the analyses of each participating laboratory – nine from Japan (participating on behalf of the Japanese authorities); and the IAEA Environment Laboratories – were subsequently collected and evaluated by the IAEA.

Comparisons of the results received for each sample and radionuclide demonstrate that the overwhelming majority are not significantly different from each other. A statistical analysis of the results shows that over 99% of the statistical tests applied passed with a high level of confidence (99%).

It can therefore be concluded with confidence that participating laboratories reported reliable and comparable results for the tested radionuclides in seawater, sediment, and fish samples, prepared and analysed according to each laboratory's regularly used methods (although levels of ¹³⁴Cs and ²³⁸Pu are close to the limits of detection in all sample types and thus difficult to intercompare).

On the basis of the results of ILC 2018, the IAEA can report that Japan's sample collection procedures continue to adhere to the appropriate methodological standards required to obtain representative samples. The results, as for those from other ILCs and PTs in this project, demonstrate a high level of accuracy and competence on the part of the Japanese laboratories involved in the analyses of radionuclides in marine samples as part of the Sea Area Monitoring Plan.

1. INTRODUCTION

The IAEA Environment Laboratories are assisting the Government of Japan in ensuring that its regularly updated Sea Area Monitoring Plan is comprehensive, credible and transparent through the project "Marine Monitoring: Confidence Building and Data Quality Assurance". During the period 2014 – 2017, seven interlaboratory comparisons (ILCs) and four proficiency tests (PTs) have been organised within this project to test the sampling and analytical performance of Japanese laboratories monitoring radionuclides in seawater, sediment and fish as part of the Sea Area Monitoring Plan.

PTs and ILCs are standard methods for participating laboratories to assess the quality of their measurement results in comparison with those of other participating laboratories, and to identify any potentially needed improvements. PTs involve evaluation of performance against pre-established criteria whereas ILCs involve organization, performance and evaluation of measurements on the same or similar items by two or more laboratories in accordance with predetermined conditions [1]. The PT and ILC results from this project published so far can be accessed on the IAEA web pages¹.

This report focuses on the ILC which was organised in 2018. It describes the joint sampling campaign to collect seawater, sediment and fish samples, the measurement results and the statistical evaluation of the results.

In total, ten laboratories participated in the ILC: nine from Japan (participating on behalf of the Japanese authorities); and the IAEA Environment Laboratories in Monaco. The participating laboratories are presented in Table 1, and participation of each in specific analyses in Table 2.

TABLE 1. PARTICIPATING LABORATORIES IN ILC 2018

Identifier	Participant
FP	Fukushima Prefectural Centre for Environmental Creation, Fukushima, Japan
FRA	Japan Fisheries Research and Education Agency, Yokohama, Japan
GSL	Chikyu Kagaku Kenkyusho Inc. (Geo-Science Laboratory), Nagoya, Japan
IAEA	IAEA Environment Laboratories, Monaco
JCAC	Japan Chemical Analysis Center, Chiba, Japan
KANSO	The General Environmental Technos Co. Ltd. (KANSO Ltd.), Japan
KEEA	Kyushu Environmental Evaluation Association, Fukuoka, Japan
MERI	Marine Ecology Research Institute, Onjuku, Japan
TPT	Tokyo Power Technology Ltd., Fukushima, Japan
TRK	Tohoku Ryokka Kankyohozen Co. Ltd., Tagajo, Japan

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¹ Published ILC and PT reports are accessible at:

TABLE 2. PARTICIPATION OF EACH LABORATORY IN SPECIFIC ANALYSES IN ILC 2018

Sample type	Nuclide	IAEA	FP	FRA	GSL	JCAC	KANSO	KEEA	MERI	TPT	TRK
	^{3}H	✓	×	×	✓	✓	✓	×	✓	×	×
Seawater	⁹⁰ Sr	✓	✓	×	×	✓	✓	×	×	√a	×
Seawater	¹³⁴ Cs	✓	✓	×	×	✓	✓	×	×	✓a	×
	¹³⁷ Cs	✓	✓	×	×	✓	✓	*	×	✓a	×
	¹³⁴ Cs	✓	✓	×	×	✓	×	×	×	✓	×
Sediment	¹³⁷ Cs	✓	✓	×	×	✓	×	×	×	✓	×
Sediment	²³⁸ Pu	✓	✓	×	×	✓	×	✓	×	×	×
	^{239,240} Pu	✓	✓	×	×	✓	×	✓	×	×	*
Fish	¹³⁴ Cs	✓	×	✓	×	×	×	*	✓	×	✓
	¹³⁷ Cs	✓	×	✓	×	×	×	*	✓	×	✓

NOTE: The symbol ✓ indicates that the laboratory participated in the specific analysis (sample type and radionuclide), the symbol × indicates that it did not participate.

^a Sampling location T-D1 only.

2. SEAWATER, SEDIMENT AND FISH SAMPLING AND PREPARATION

2.1. SEAWATER AND SEDIMENT SAMPLING LOCATIONS

Surface seawater samples were collected at five sampling locations (M-101, M-102, M-103, M-104, and T-D1) and sediment samples at three locations (F-P04, T-S3, and T-S8) offshore at the Fukushima Daiichi Nuclear Power Station. The sampling locations are shown in Figure 1 and their coordinates are provided in Table 3.

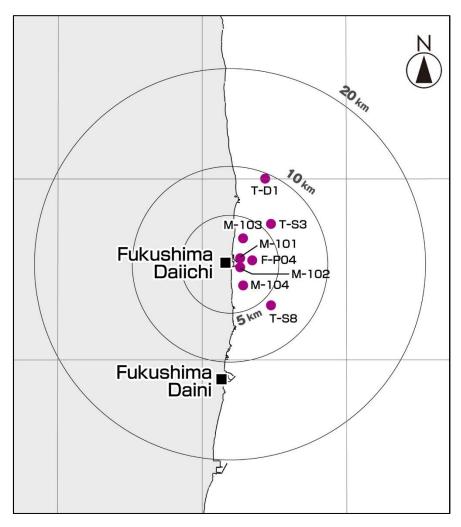


FIG. 1. Surface seawater and sediment sampling locations offshore the Fukushima Daiichi Nuclear Power Station.

TABLE 3. COORDINATES OF THE SURFACE SEAWATER AND SEDIMENT SAMPLING LOCATIONS

Sampling location	Latitude (N)	Longitude (E)
M-101 (seawater)	37°25′36″	141°02′36″
M-102 (seawater)	37°25′06″	141°02′36″
M-103 (seawater)	37°26′42″	141°02′48″
M-104 (seawater)	37°24′06″	141°02′48″
T-D1 (seawater)	37°30′00″	141°04′20″
F-P04 (sediment)	37°25′27″	141°03′26″
T-S3 (sediment)	37°27′30″	141°04′44″
T-S8 (sediment)	37°23′00″	141°04′44″

2.2. SEAWATER

During this mission, seawater samples were collected on 9-10 October 2018 from each sampling location for subsequent analysis for ⁹⁰Sr, ¹³⁴Cs and ¹³⁷Cs and, separately, for ³H.

2.2.1. Samples M-101, M-102, M-103 and M-104

Four laboratories planned to participate in the analyses for ⁹⁰Sr, ¹³⁴Cs and ¹³⁷Cs from sampling locations M-101, M-102, M-103 and M-104. The collection and distribution methods at each sampling location were:

- A 400 L plastic container with four valves was first filled with seawater.
- Separate 20 L cubitainers were filled simultaneously from each of the four valves. Four cubitainers were filled from each valve, resulting in a total of 16 20 L samples from each sampling location.
- Each sample was acidified to pH 1–2 with concentrated HCl.
- Three 20 L samples were provided to each laboratory.

The seawater sampling procedure and distribution matrix, meant to ensure the homogenisation of the samples, is shown in Table 4.

TABLE 4. SAMPLE DISTRIBUTION BETWEEN FOUR LABORATORIES (90Sr, 134Cs AND 137Cs)

Valve number	1	2	3	4
	1-1	2-1	3-1	4-1
Seawater sample codes	1-2	2-2	3-2	4-2
	1-3	2-3	3-3	4-3
Distribution nottons of the	A	В	С	D
Distribution pattern of the participating laboratories coded A,	1-1	2-1	3-1	4-1
B, C and D	2-2	3-2	4-2	1-2
b, C and D	3-3	4-3	1-3	2-3

For ³H, six laboratories planned to participate. The sample collection and distribution methods were:

- From the same 400 L plastic container from which the samples to be analysed for ⁹⁰Sr, ¹³⁴Cs and ¹³⁷Cs were taken, separate 2 L containers were filled, two at a time, from the first three of the four valves, resulting in a total of six 2 L samples from each sampling location.
- One 2 L sample was provided to each laboratory.

The seawater sampling procedure and the distribution matrix for ³H is shown in Table 5.

TABLE 5. SAMPLE DISTRIBUTION BETWEEN SIX LABORATORIES (3H)

Valve number	1		2		3		4	
Seawater sample codes	1-1		2-1		3-1		Not used	
Seawater sample codes	1-2		2-2		3-2			
Distribution pattern of the	A	В		С	D	E	Ξ	F
participating laboratories coded A, B, C, D, E and F	1-1	2-	1	3-1	1-2	2-	-2	3-2

2.2.2. Sample T-D1

Five laboratories planned to participate in the analyses for 90 Sr, 134 Cs and 137 Cs from sampling location T-D1. Two separate fills of the 400 L container were therefore required in order to facilitate provision

of the required sample volume to all participants. Otherwise the collection method was essentially the same as described above. The distribution method is shown in Table 6.

TABLE 6. SAMPLE DISTRIBUTION BETWEEN FIVE LABORATORIES (90Sr, 134Cs AND 137Cs)

Valve number	1	2	2		3	4	
	1-1	2-1	2-1		3-1	4-1	
Saggetar sample codes	1-2	2-2	2-2		3-2	4-2	
Seawater sample codes	1-3	2-3	2-3		3-3	4-3	
	1-4	2-4	2-4		3-4	Not used	
Distribution pattern of the	A	В	(C	D	Е	
Distribution pattern of the participating laboratories coded A,	1-1	2-1	3-	-1	4-1	1-2	
B, C, D and E	2-2	3-2	4-	-2	1-3	2-3	
D, C, D and E	3-3	4-3	1-	-4	2-4	3-4	

For ³H, the laboratories participating in the analysis of the sample collected at T-D1 were the same as for the other sampling locations. Therefore, the collection and distribution methods were identical to those described above.

2.3. SEDIMENT

Sediment samples were collected using a grab sampler on 9 October 2018 offshore from the Fukushima Daiichi Nuclear Power Station at locations F-P04, T-S3 and T-S8 (Fig. 1 and Table 3). The samples were subsequently oven-dried at 105 °C on large stainless-steel trays, crushed using stainless-steel spatulae, and sieved through a 2-mm mesh sieve at the KANSO laboratory. No grinding was required prior to sieving due to the sandy nature of the sediments. The fraction with grain size <2 mm was ground using a rotary ball mill, sieved to \leq 250 μ m, then placed in a plastic bag and mixed thoroughly to ensure homogeneity. An incremental division method was used for sample splitting. Each sample was split into two aliquots using a splitter; one aliquot was archived and the second one was further split until the required sample weight for each laboratory was attained. The sequence of splitting of each sample depended on the total weight of the sieved and sample. The samples were then bottled in 500 mL plastic bottles and shipped to the IAEA Environment Laboratories in Monaco where their ¹³⁷Cs homogeneity was checked using γ -ray spectrometry with high purity germanium (HPGe) detectors. Approximately 400 g of homogeneous dried sediment from each location was then shipped to each participating laboratory analysing for all radionuclides of interest (^{134,137}Cs, ²³⁸Pu, ^{239,240}Pu). For those analysing only for either Cs or Pu isotopes, approximately 200 g was provided.

2.4. FISH

In 2018, six batches of freshly landed fish samples, one each of crimson sea bream (*Evynnis tumifrons*), marbled sole (*Pseudopleuronectes yokohamæ*), ocellate spot skate (*Okamejei kenojei*), olive flounder (*Paralichthys olivaceus*), redwing sea robin (*Lepidotrigla microptera*) and shotted halibut (*Eopsetta grigorjewi*), were collected from the port of Hisanohama on 5 October 2018. The fish species were caught by bottom trawling on 5 October 2018 between 02:00 and 07:00 local time (17:00 to 22:00 UTC) in the vicinity of the Fukushima Daiichi Nuclear Power Station at the locations and depths shown in Table 8.

TABLE 8. COORDINATES AND DEPTHS OF THE CATCH LOCATIONS FOR ILC 2018

Sample: Species	Latitude (N)	Longitude (E)	Depth (m)
18FA0001: Ocellate spot skate	37°14′35″	141°07′36″	63
18FA0002: Redwing sea robin	37°14′35″	141°07′36″	63
18FA0003: Crimson sea bream	37°14′35″	141°07′36″	63
18FA0004: Marbled sole	37°11′04″	141°08′24″	61
18FA0005: Olive flounder	37°11′04″	141°08′24″	61
18FA0006: Shotted halibut	37°19′11″	141°12′14″	90

Each fish sample was prepared by homogenising the muscle tissue at MERI (Onjuku) on 17 October 2018. The six samples were first analysed for ¹³⁴Cs and ¹³⁷Cs at MERI on the same date. Subsequently, they were shipped to FRA (Yokohama) on 18 October 2018 and to TRK (Tagajo) on 19 October 2018 for the same analyses. The samples were then frozen and shipped to the IAEA Environment Laboratories in Monaco on 14 November 2018 where they were analysed later the same month.

All measurements were performed using γ -ray spectrometry with HPGe detectors (see next section for more details). The measurement times per sample were 1 hour for MERI, FRA and TRK and approximately 24 hours for the IAEA. All measurements conducted by Japanese laboratories comply with procedures set out in a testing manual for radioactive substances in food for emergencies published by the Ministry of Health, Labour and Welfare. As IAEA was the final recipient of the fish samples, it was possible to measure the fish samples for a longer time, thus resulting in smaller counting uncertainties.

3. METHODOLOGY OF RADIONUCLIDE DETERMINATION

3.1. SEAWATER

Radionuclides of interest in seawater were determined by six laboratories participating in ILC 2018: FP, GSL, JCAC, KANSO, and TPT, all participating on behalf of the Nuclear Regulation Authority, Japan, and IAEA (see Tables 1 and 2).

3.1.1. FP methodology for seawater

3.1.1.1. ⁹⁰*Sr analysis*

A cation exchange resin column was used for pre-concentration of strontium from each seawater sample, followed by precipitation of carbonates and an additional cation exchange resin column for separation of calcium. 90 Y was removed by scavenging and, once the sample reached secular equilibrium, was measured using a low background β counter.

3.1.1.2. ¹³⁴Cs and ¹³⁷Cs analysis

Chemical separation of caesium by ammonium molybdophosphate (AMP) and manganese dioxide (MnO_2) , followed by γ -ray spectrometry with a HPGe detector.

3.1.2. GSL methodology for seawater

3.1.2.1. ³*H analysis*

Low-background liquid scintillation counting after distillation and electrolytic enrichment.

3.1.3. IAEA methodology for seawater

3.1.3.1. ³*H* analysis

The samples were measured by liquid scintillation counting after double vacuum distillation (at 35°C) and electrolytic enrichment followed by a second distillation (under atmospheric pressure). An ultralow level liquid scintillation counter was used for the counting of an aliquot of the enriched and distilled sample mixed with a scintillation cocktail.

3.1.3.2. ⁹⁰Sr analysis

Liquid-liquid extraction with di-(2-ethylhexyl)phosphoric acid (HDEHP) was used for the separation of yttrium from seawater samples, while caesium was precipitated from the same sample by using ammonium molybdophosphate (AMP). The 90 Sr activity concentration was calculated based on the measurement of 90 Y (yttrium oxalate source) β activity using a proportional counter with an efficiency of up to 44%.

3.1.3.3. ¹³⁴Cs and ¹³⁷Cs analysis

Caesium was separated with AMP, followed by γ -ray spectrometry using a HPGe detector.

3.1.4. JCAC methodology for seawater

3.1.4.1. ³*H analysis*

The seawater samples were distilled, followed by electrolytic enrichment (500 mL reduced to 55 mL). 50 mL of the purified sample was mixed with 50 mL of liquid scintillation fluid and measured with a liquid scintillation counter.

3.1.4.2. ⁹⁰*Sr analysis*

A cation exchange resin column was used for pre-concentration of strontium from each seawater sample, followed by precipitation of carbonates and an additional cation exchange resin column for separation of calcium. 90 Y was removed by scavenging and, once the sample reached secular equilibrium, 90 Y was co-precipitated with iron hydroxide and then was measured using a low background β counter.

3.1.4.3. ¹³⁴Cs and ¹³⁷Cs analysis

Chemical separation of radiocaesium was undertaken using AMP and followed by γ -ray spectrometry using a HPGe detector.

3.1.5. KANSO methodology for seawater

3.1.5.1. ³*H analysis*

The samples were first purified by distillation in glass. Then, 1 L of the resultant material was electrolytically concentrated using a solid polymer electrolytic film. 50 mL of the purified sample was mixed with 50 mL of Ultima Gold LLT scintillant and then counted for 1000 minutes using a liquid scintillation counter.

3.1.5.2. ⁹⁰Sr analysis

An ion exchange resin was used for pre-concentration of strontium in each seawater sample, followed by precipitation of carbonates and barium chromate. After secular equilibrium was attained, ⁹⁰Y was separated using a ferric hydroxide co-precipitation technique and measured by a gas-flow counter.

3.1.5.3. ¹³⁴Cs and ¹³⁷Cs analysis

Chemical separation of radiocaesium was undertaken using AMP and followed by γ -ray spectrometry with a HPGe detector.

3.1.6. MERI methodology for seawater

3.1.6.1. ³*H* analysis

Each seawater sample was first purified by distillation. Then, ³H was concentrated by electrolysis (a sample volume of 500 mL was reduced to 50 mL). This enriched sample was further purified by distillation. 50 mL of the distillate was mixed with 50 mL of Ultima Gold uLLT scintillation cocktail to prepare a sample for measurement, then measured using a low background liquid scintillation counter.

3.1.7. TPT methodology for seawater

3.1.7.1. ⁹⁰Sr analysis

Strontium was first separated from seawater by alkaline precipitation with sodium carbonate (Na_2CO_3), further separated using cation exchange chromatography and then reprecipitated as strontium carbonate ($SrCO_3$). After attaining secular equilibrium between ^{90}Y and ^{90}Sr , ^{90}Y was separated using an iron hydroxide coprecipitation method and measured with a gas flow counter.

3.1.7.2. ¹³⁴Cs and ¹³⁷Cs analysis

Caesium was separated with AMP, followed by γ -ray spectrometry using a HPGe detector.

3.2. SEDIMENT

Radionuclides of interest in sediment samples were determined by five laboratories participating in ILC 2018: FP, JCAC, KEEA and TPT, participating on behalf of the Nuclear Regulation Authority, Japan, and IAEA (see Tables 1 and 2).

3.2.1. FP methodology for sediment

3.2.1.1. ¹³⁴Cs and ¹³⁷Cs analysis

γ-ray spectrometry using a HPGe detector.

3.2.1.2. ²³⁸Pu and ^{239,240}Pu analysis

 α -particle spectrometry with a Si detector after leaching, radiochemical separation and purification of plutonium by using an anion exchange resin column followed by electrodeposition from the purified solution.

3.2.2. IAEA methodology for sediment

3.2.2.1. ¹³⁴Cs and ¹³⁷Cs analysis

γ-ray spectrometry using a p-type coaxial HPGe detector.

3.2.2.2. ²³⁸Pu and ^{239,240}Pu analysis

Classical digestion followed by ion exchange, electrodeposition and counting by α -particle spectrometry. An aliquot of 5 g of sediment sample was ashed and spiked with a 242 Pu tracer. The sample was totally dissolved by using concentrated acids. After Fe(OH)₃ precipitation and plutonium oxidation state adjustment, double ion exchange (DOWEX 1×4) was used for Pu purification. Plutonium was electrodeposited from Na₂SO₄/H₂SO₄ electrolyte solution on stainless-steel discs and counted by α -particle spectrometry.

3.2.3. JCAC methodology for sediment

3.2.3.1. ¹³⁴Cs and ¹³⁷Cs analysis

Direct counting on a p-type coaxial HPGe detector with a relative efficiency 31%.

3.2.3.2. ²³⁸Pu and ^{239,240}Pu analysis

Plutonium isotopes were measured with a Si semiconductor detector after leaching, radiochemical separation and purification of plutonium by using an anion exchange resin column followed by electrodeposition from the purified solution.

3.2.4. KEEA methodology for sediment

3.2.4.1. ²³⁸Pu and ^{239,240}Pu analysis

Dried sediment samples were first heated to 450 °C. Then a 242 Pu isotope dilution tracer was added to each sample, and the plutonium recovered from the sediment with a 10 M HNO₃/0.1 M HF leach, followed by an 8M HNO₃ leach. This material had the plutonium oxidation stated adjusted with sodium nitrate(III) (NaNO₂). Plutonium was then separated and purified using Dowex 1×8 (100-200 mesh) anion exchange resin. Plutonium was electrodeposited onto stainless-steel plate and measured by silicon semiconductor detector.

3.2.5. TPT methodology for sediment

3.2.5.1. ¹³⁴Cs and ¹³⁷Cs analysis

γ-ray spectrometry using a p-type coaxial HPGe detector.

3.3. FISH

Radionuclides of interest in fish samples were determined by four laboratories participating in ILC 2018: FRA, MERI, and TRK, all participating on behalf of the Japan Fisheries Agency, and the IAEA (see Tables 1 and 2).

3.3.1. FRA methodology for fish

3.3.1.1. ¹³⁴Cs and ¹³⁷Cs analysis

Direct counting on p-type coaxial HPGe detectors with relative efficiencies between 29% and 33%. The samples were prepared in 2 L Marinelli beakers and measured for 1 hour.

3.3.2. IAEA methodology for fish

3.3.2.1. ¹³⁴Cs and ¹³⁷Cs analysis

Direct counting by a coaxial HPGe detector with relative efficiency of 48%. The mass of each sample was approximately 1 kg (wet mass) and the samples were measured for approximately 24 hours.

3.3.3. MERI methodology for fish

3.3.3.1. ¹³⁴Cs and ¹³⁷Cs analysis

Direct counting by p-type coaxial HPGe detectors with relative efficiencies between 28% and 46%. The samples were prepared in 2 L Marinelli beakers and measured for 1 hour.

3.3.4. TRK methodology for fish

3.3.4.1. ¹³⁴Cs and ¹³⁷Cs analysis

Direct counting by p-type coaxial HPGe detectors with relative efficiencies between 30% and 35%. The samples were prepared in 2 L Marinelli beakers and measured for 1 hour.

4. STATISTICAL EVALUATION OF THE RESULTS

The IAEA collected and evaluated the results reported by all ILC participants. The method used for the statistical evaluation depended on the number of results received for each sampling location, sample type and radionuclide.

If two or three measurement results above the detection limit were received, then one or three zeta tests [2] were performed. The zeta $\zeta_{i,j}$ test is defined as:

$$\zeta_{i,j} = \left| \frac{x_i - x_j}{\sqrt{u_i^2 + u_j^2}} \right| \tag{1}$$

where:

 x_i is the value of laboratory i [Bq unit⁻¹];

 x_j is the value of laboratory j [Bq $unit^{-1}$];

 u_i is the standard uncertainty for the value of laboratory i [Bq unit⁻¹];

 u_i is the standard uncertainty for the value of laboratory j [Bq unit⁻¹]; and

unit is the unit of volume of mass, L or kg, as appropriate for the particular sample type.

If two results were received, $\zeta_{1,2}$ was calculated, while for three received results $\zeta_{1,2}$, $\zeta_{1,3}$ and $\zeta_{2,3}$ were calculated.

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

If the data set contained four or more results, the statistical evaluation consisted of a method for calculating a comparison reference value as a power-moderated mean of the combined results [3]. After calculating a reference value, a relative degree of equivalence (DoE) was calculated for each submitted result and if this relative DoE was significantly different from zero, the corresponding result was evaluated as being discrepant. The relative DoE (%) was calculated according to:

DoE (%) =
$$\frac{x_{\text{lab}} - X_{\text{ref}}}{X_{\text{ref}}} 100$$
 (2)

where:

 x_{lab} is the individual laboratory result; and

 x_{ref} is the reference value calculated as the power-moderated mean of the combined results.

The standard uncertainty of the relative DoE, u_{DoE} , was calculated according to reference [2]. If the absolute value of the relative DoE exceeded 2.58 times u_{DoE} , the corresponding result was evaluated as being discrepant (at a 99% confidence level), as the relative DoE in this case would be significantly different from zero.

5. RESULTS

5.1. GENERAL

The results are presented in Tables 9 - 14 and Figures 2 - 11.

5.1.1. Uncertainties

In this report, the numerical result of an activity concentration measurement is stated in the format $x \pm y$, where the number following the symbol \pm is the numerical value of the combined standard uncertainty, i.e. with a coverage factor of k = 1.

Relative degrees of equivalence are also quoted in the format $x \pm y$. In this case, the number following the symbol \pm is the 99% confidence interval.

5.1.2. Reference time

All activity concentrations for seawater and sediment were reported at a reference time of 9 October 2018 12:00 UTC. All activity concentrations for fish were reported at a reference time of 5 October 2018 12:00 UTC.

5.2. SEAWATER

Table 9 contains the results reported by the participating laboratories (FP, GSL, JCAC, KANSO, MERI, TPT and the IAEA) for the activity concentrations of ³H, ⁹⁰Sr, ¹³⁴Cs and ¹³⁷Cs in the seawater samples. Figures 2 to 5 show the activity concentrations of these radionuclides in the seawater samples.

TABLE 9. ACTIVITY CONCENTRATIONS (mBq L^{-1}) IN SEAWATER

Nuclide	Commla	LATA	FP	GSL	JCAC	KANSO	MEDI	TPT	Reference
Nuclide	Sample	IAEA	Γľ	GSL	JCAC	KANSO	MERI	111	value
	M-101	124 ± 19	_	147 ± 15	123 ± 20	160 ± 14	170 ± 24	_	145 ± 9
	M-102	138 ± 20	_	133 ± 14	164 ± 22	160 ± 15	174 ± 23	_	151 ± 8
^{3}H	M-103	50 ± 13	_	94 ± 14	<55	94 ± 12	88 ± 22	-	81 ± 12
	M-104	65 ± 14	_	74 ± 13	<56	63 ± 12	128 ± 23	_	80 ± 15
	T-D1	44 ± 13	_	99 ± 13	59 ± 19	80 ± 12	101 ± 22	_	76 ± 12
	M-101	1.95 ± 0.11	2.3 ± 0.29	_	1.81 ± 0.17	2.2 ± 0.23	_	_	2.01 ± 0.11
⁹⁰ Sr	M-102	1.410 ± 0.080	1.7 ± 0.26	_	1.34 ± 0.15	1.6 ± 0.19	_	_	1.45 ± 0.08
	M-103	0.762 ± 0.047	1.3 ± 0.22	_	0.79 ± 0.12	1.0 ± 0.17	_	_	0.92 ± 0.12
	M-104	0.908 ± 0.055	1.0 ± 0.20	_	0.74 ± 0.12	0.91 ± 0.17	_	_	0.88 ± 0.06
	T-D1	0.730 ± 0.053	0.9 ± 0.20	_	0.92 ± 0.13	1.1 ± 0.17	_	<5	0.88 ± 0.08
	M-101	4.38 ± 0.18	4 ± 0.7	_	4.4 ± 0.4	4.2 ± 0.26	_	_	4.3 ± 0.2
	M-102	3.01 ± 0.14	3 ± 0.7	_	3.3 ± 0.3	2.6 ± 0.21	_	_	2.9 ± 0.2
¹³⁴ Cs	M-103	0.360 ± 0.047	<2.1	_	< 0.74	< 0.48	_	_	_
	M-104	0.742 ± 0.073	<2.1	_	1.4 ± 0.3	0.59 ± 0.15	_	_	_
	T-D1	0.34 ± 0.11	<2.1	_	< 0.68	< 0.48	_	< 0.9	_
	M-101	45.9 ± 2.0	48 ± 3.0	_	49.0 ± 3.0	44 ± 1.5	_	_	46.0 ± 1.2
	M-102	31.8 ± 1.5	34 ± 2.1	_	34.1 ± 1.8	30 ± 1.1	_	_	32.2 ± 1.1
¹³⁷ Cs	M-103	5.25 ± 0.34	6 ± 0.7	_	6.8 ± 0.4	5.2 ± 0.22	_	_	5.8 ± 0.4
	M-104	8.82 ± 0.79	8 ± 0.8	_	9.2 ± 0.6	7.9 ± 0.31	-	_	8.4 ± 0.4
	T-D1	4.54 ± 0.28	7 ± 0.7	_	5.3 ± 0.4	4.2 ± 0.20	_	4.7 ± 0.4	5.1 ± 0.5

Table 10 contains the degrees of relative equivalence for the activity concentrations of ³H, ⁹⁰Sr, ¹³⁴Cs and ¹³⁷Cs in the seawater samples.

TABLE 10. DEGREES OF EQUIVALENCE (%) IN SEAWATER SAMPLES

Nuclide	Sample	IAEA	FP	GSL	JCAC	KANSO	MERI	TPT
	M-101	-15 ± 31	_	1 ± 25	-15 ± 34	10 ± 24	17 ± 40	_
	M-102	-9 ± 31	_	-12 ± 21	8 ± 34	6 ± 22	15 ± 36	_
^{3}H	M-103	-38 ± 45	_	16 ± 48	DL	16 ± 45	9 ± 66	_
	M-104	-19 ± 55	_	-7 ± 55	DL	-21 ± 54	61 ± 74	_
	T-D1	-42 ± 49	-	31 ± 51	-22 ± 64	6 ± 49	33 ± 73	_
	M-101	-3 ± 15	15 ± 35	_	-10 ± 20	10 ± 26	_	_
	M-102	-4 ± 14	17 ± 43	_	-8 ± 24	10 ± 31	_	_
90 Sr	M-103	-18 ± 34	41 ± 59	_	-14 ± 40	8 ± 48	_	_
	M-104	3 ± 15	13 ± 55	_	-16 ± 30	3 ± 43	_	_
	T-D1	-17 ± 25	2 ± 54	_	4 ± 36	25 ± 44	_	DL
	M-101	1.8 ± 8.9	-7 ± 40	_	2 ± 22	-2 ± 13	_	_
	M-102	2 ± 14	2 ± 58	_	12 ± 24	-12 ± 18	_	_
¹³⁴ Cs	M-103	Note 1	DL	_	DL	DL	_	_
	M-104	Note 2	DL	_	Note 2	Note 2	_	-
	T-D1	Note 1	DL	_	DL	DL	_	DL
	M-101	-0.2 ± 9.6	4 ± 16	_	6 ± 16	-4.4 ± 7.3	_	_
	M-102	-1 ± 12	6 ± 16	_	6 ± 14	-6.7 ± 9.5	_	_
¹³⁷ Cs	M-103	-9 ± 21	4 ± 31	_	18 ± 22	-10 ± 19	_	_
	M-104	5 ± 22	-5 ± 23	_	10 ± 17	-6 ± 11	_	_
	T-D1	-10 ± 27	38 ± 38	_	5 ± 29	-17 ± 26	_	-7 ± 29

Note 1: No evaluation was possible as only one value above the detection limit was submitted.

Note 2: Values of -2.13, 0.92 and 2.4 for $\zeta_{1,4}$, $\zeta_{1,5}$ and $\zeta_{4,5}$, respectively.

DL: As a value less than the detection limit was submitted, no evaluation was performed.

 $\zeta_{i,j}$ indexes: number 1 refers to IAEA, number 2 refers to FP, number 3 refers to GSL, number 4 refers to JCAC, number 5 refers to KANSO, number 6 refers to MERI and number 7 refers to TPT.

5.3. SEDIMENT

Table 11 contains the results reported by the five participating laboratories (FP, JCAC, KEEA, TPT and the IAEA) for the activity concentrations of radionuclides in the sediment samples. Figures 6 to 9 show the activity concentrations of ¹³⁴Cs, ¹³⁷Cs, ²³⁸Pu and ^{239,240}Pu in the sediment samples.

TABLE 11. ACTIVITY CONCENTRATIONS (Bq kg^{-1} -dry) IN SEDIMENT

Nuclide	Sample	IAEA	FP	JCAC	KEEA	TPT	Reference value
	F-P04	2.74 ± 0.19	4.1 ± 0.4	3.2 ± 0.4	_	3.9 ± 0.3	3.5 ± 0.4
¹³⁴ Cs	T-S3	1.04 ± 0.12	0.95 ± 0.30	1.1 ± 0.3	_	1.10 ± 0.13	1.1 ± 0.1
	T-S8	2.42 ± 0.14	2.2 ± 0.3	2.6 ± 0.4	_	2.47 ± 0.23	2.4 ± 0.2
	F-P04	29.7 ± 1.4	41.2 ± 2.3	35.2 ± 1.8	_	32.2 ± 1.1	34.4 ± 2.5
¹³⁷ Cs	T-S3	10.7 ± 0.5	10.7 ± 0.7	10.8 ± 0.6	_	12.1 ± 0.4	11.1 ± 0.4
	T-S8	26.2 ± 1.2	26.6 ± 1.5	27.7 ± 1.5	_	27.2 ± 1.0	26.9 ± 0.7
	F-P04	0.0030 ± 0.0024	0.0047 ± 0.0011	< 0.012	< 0.012	_	_
²³⁸ Pu	T-S3	0.0038 ± 0.0013	0.0035 ± 0.0011	0.01 ± 0.003	< 0.012	_	_
	T-S8	0.0085 ± 0.0030	0.0070 ± 0.0016	< 0.013	< 0.011	_	_
	F-P04	0.398 ± 0.022	0.376 ± 0.018	0.374 ± 0.024	0.39 ± 0.03	_	0.38 ± 0.02
^{239,240} Pu	T-S3	0.382 ± 0.019	0.378 ± 0.020	0.384 ± 0.024	0.38 ± 0.03	_	0.38 ± 0.02
	T-S8	0.556 ± 0.026	0.564 ± 0.028	0.550 ± 0.030	0.52 ± 0.04	_	0.55 ± 0.02

Table 12 contains the degrees of relative equivalence for the activity concentrations of ¹³⁴Cs, ¹³⁷Cs, ²³⁸Pu and ^{239,240}Pu in the sediment samples.

TABLE 12. DEGREES OF EQUIVALENCE (%) IN SEDIMENT SAMPLES

Nuclide	Sample	IAEA	FP	JCAC	KEEA	TPT
	F-P04	-21 ± 26	19 ± 33	-7 ± 33	_	13 ± 29
¹³⁴ Cs	T-S3	-2 ± 25	-10 ± 67	4 ± 67	_	4 ± 27
	T-S8	0 ± 13	-9 ± 29	8 ± 39	_	2 ± 22
	F-P04	-14 ± 20	20 ± 23	2 ± 21	_	-6 ± 20
¹³⁷ Cs	T-S3	-4 ± 12	-4 ± 16	-3 ± 14	_	9 ± 11
	T-S8	-2.6 ± 10	-1 ± 13	3 ± 13	_	0.9 ± 7.5
	F-P04	Note 1	Note 1	DL	DL	_
²³⁸ Pu	T-S3	Note 2	Note 2	Note 2	DL	-
	T-S8	Note 3	Note 3	DL	DL	_
	F-P04	4 ± 13	-2 ± 11	-3 ± 15	2 ± 18	_
^{239,240} Pu	T-S3	0 ± 12	-1 ± 12	1 ± 15	0 ± 19	_
	T-S8	1 ± 11	2 ± 12	0 ± 13	-6 ± 17	_

Note 1: Value of -0.67 for $\zeta_{1,2}$.

Note 2: Values of 0.15, -1.92 and 2.03 for $\zeta_{1,2}$, $\zeta_{1,3}$ and $\zeta_{2,3}$, respectively.

Note 3: Value of 0.44 for $\zeta_{1,2}$.

DL: As a value less than the detection limit was submitted, no evaluation was performed.

 $\zeta_{i,j}$ indexes: number 1 refers to IAEA, number 2 refers to FP, number 3 refers to JCAC, number 4 refers to KEEA and number 5 refers to TPT.

5.4. FISH

Table 13 contains the results reported by the four participating laboratories (FRA, MERI, TRK and the IAEA) for the activity concentrations of radionuclides in the fish samples. Figures 10 and 11 show the activity concentrations of 134 Cs and 137 Cs in the fish samples.

TABLE 13. ACTIVITY CONCENTRATIONS (Bq kg⁻¹-wet) IN FISH

Nuclide	Sample number: Species	IAEA	FRA	MERI	TRK	Reference value
	18FA0001: Ocellate spot skate	0.241 ± 0.041	< 0.47	< 0.31	< 0.37	_
	18FA0002: Redwing sea robin	0.114 ± 0.036	< 0.39	< 0.28	< 0.40	_
¹³⁴ Cs	18FA0003: Crimson sea bream	< 0.076	< 0.46	< 0.55	< 0.40	_
Cs	18FA0004: Marbled sole	0.104 ± 0.034	< 0.47	< 0.34	< 0.37	_
	18FA0005: Olive flounder	0.049 ± 0.017	< 0.48	< 0.42	< 0.42	_
	18FA0006: Shotted halibut	0.116 ± 0.025	<0.38	< 0.49	< 0.45	_
	18FA0001: Ocellate spot skate	2.64 ± 0.16	2.88 ± 0.29	2.69 ± 0.21	2.66 ± 0.23	2.70 ± 0.11
	18FA0002: Redwing sea robin	1.31 ± 0.09	1.45 ± 0.20	1.39 ± 0.16	1.39 ± 0.19	1.37 ± 0.07
¹³⁷ Cs	18FA0003: Crimson sea bream	0.53 ± 0.11	0.63 ± 0.18	0.57 ± 0.16	< 0.47	_
Cs	18FA0004: Marbled sole	1.57 ± 0.10	1.43 ± 0.22	1.62 ± 0.17	1.66 ± 0.19	1.58 ± 0.09
	18FA0005: Olive flounder	0.514 ± 0.046	0.51 ± 0.17	< 0.48	0.47 ± 0.14	_
	18FA0006: Shotted halibut	1.16 ± 0.70	1.33 ± 0.18	1.54 ± 0.25	1.12 ± 0.19	1.23 ± 0.08

Table 14 contains the degrees of relative equivalence for the activity concentrations of ¹³⁴Cs and ¹³⁷Cs in the fish samples.

TABLE 14. DEGREES OF EQUIVALENCE (%) IN FISH SAMPLES

Nuclide	Sample: Species	IAEA	FRA	MERI	TRK
¹³⁴ Cs	18FA001: Ocellate spot skate	Note 1	DL	DL	DL
	18FA002: Redwing sea robin	Note 1	DL	DL	DL
	18FA003: Crimson sea bream	DL	DL	DL	DL
	18FA004: Marbled sole	Note 1	DL	DL	DL
	18FA005: Olive flounder	Note 1	DL	DL	DL
	18FA006: Shotted halibut	Note 1	DL	DL	DL
¹³⁷ Cs	18FA001: Ocellate spot skate	-2 ± 14	7 ± 24	0 ± 18	-1 ± 19
	18FA002: Redwing sea robin	-4 ± 15	6 ± 33	2 ± 26	2 ± 31
	18FA003: Crimson sea bream	Note 2	Note 2	Note 2	DL
	18FA004: Marbled sole	0 ± 16	-9 ± 33	3 ± 24	5 ± 28
	18FA005: Olive flounder	Note 3	Note 3	DL	Note 3
	18FA006: Shotted halibut	-6 ± 16	8 ± 34	25 ± 48	-9 ± 36

Note 1: No evaluation was possible as only one value above the detection limit was submitted.

Note 2: Values of -0.47, -0.17, and 0.26 for $\zeta_{1,2}$, $\zeta_{1,3}$ and $\zeta_{2,3}$, respectively.

Note 3: Values of 0.01, 0.29 and 0.18 for $\zeta_{1,2}$, $\zeta_{1,4}$ and $\zeta_{2,4}$, respectively.

DL: As a value less than the detection limit was submitted, no evaluation was performed.

 $\zeta_{i,j}$ indexes: number 1 refers to IAEA, number 2 refers to FRA, number 3 refers to MERI and number 4 refers to TRK.

6. CONCLUSION

A detailed data analysis was performed on the activity concentrations reported for ³H, ⁹⁰Sr, ¹³⁴Cs and ¹³⁷Cs in five seawater samples, the activity concentrations reported for ¹³⁴Cs, ¹³⁷Cs, ²³⁸Pu and ^{239,240}Pu in three sediment samples and the activity concentrations reported for ¹³⁴Cs and ¹³⁷Cs in six fish samples. All samples were collected offshore the Fukushima Daiichi Nuclear Power Station in October 2018. The samples were shared between ten laboratories: FP (Japan), FRA (Japan), GSL (Japan), IAEA (Monaco), JCAC (Japan), KANSO (Japan), KEEA (Japan), MERI (Japan), TPT (Japan) and TRK (Japan).

From this analysis it can be concluded that the overwhelming majority of results are not significantly different from each other. A global analysis of the whole data set demonstrated just one discrepant value from the 138 statistical tests applied to the data, i.e. over 99% were passed with a high level of confidence (99%). The only exception was one case where a relative DoE was significantly different from zero:

DoE (%) = 38 ± 38 for the ¹³⁷Cs activity concentration in the seawater sample from T-D1 submitted by FP.

Given the small number of cases where discrepant or significantly different results were reported (less than 1%), it can be said with confidence that the laboratories are reporting reliable and comparable results for the tested radionuclides in seawater, sediment and fish samples prepared and analysed according to each laboratory's regularly used methods.

Following this sampling mission, the IAEA can confidently report that Japan's sample collection procedures follow the appropriate methodological standards required to obtain representative samples. The results obtained in ILC 2018 demonstrate a continued high level of accuracy and competence on the part of the Japanese laboratories involved in the analyses of radionuclides in marine samples for the Sea Area Monitoring programme.

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- [2] INTERNATIONAL ORGANISATION FOR STANDARDISATION, Statistical methods for use in proficiency testing by interlaboratory comparisons. Geneva, ISO 13528:2015.
- [3] POMMÉ, S. and KEIGHTLEY, J.D. 2015. Determination of a reference value and its uncertainty through a power-moderated mean. Metrologia **52**, S200-S212.

APPENDIX: FIGURES

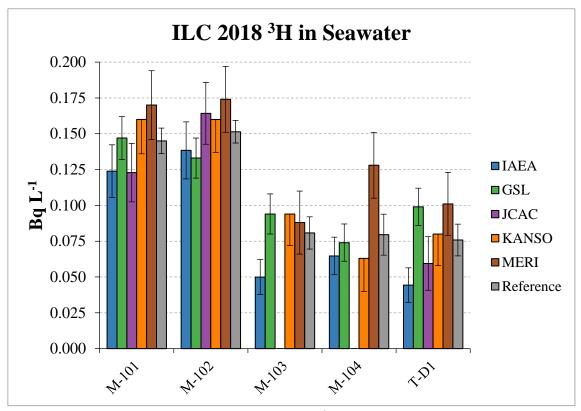


FIG. 2. Activity concentrations of ${}^{3}H$ in seawater samples.

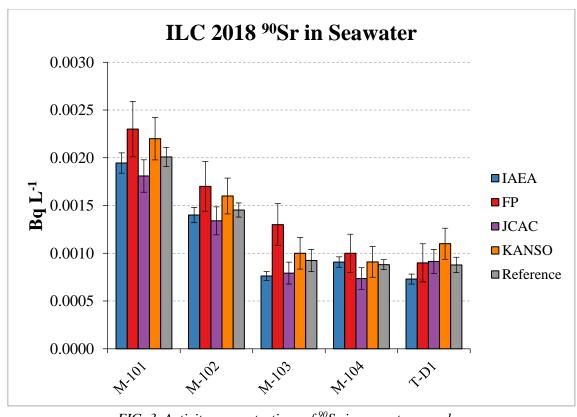


FIG. 3. Activity concentrations of ⁹⁰Sr in seawater samples.

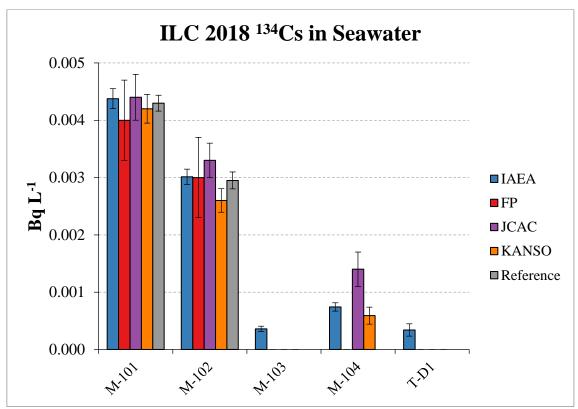


FIG. 4. Activity concentrations of ¹³⁴Cs in seawater samples.

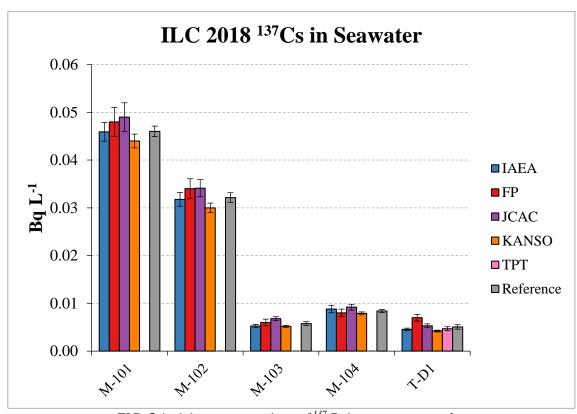


FIG. 5 Activity concentrations of ¹³⁷Cs in seawater samples.

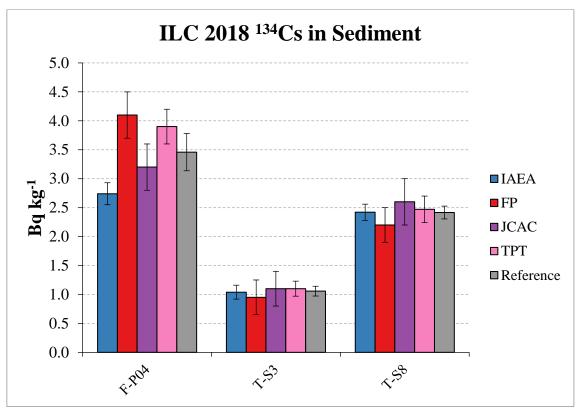


FIG. 6. Activity concentrations of ¹³⁴Cs in sediment samples.

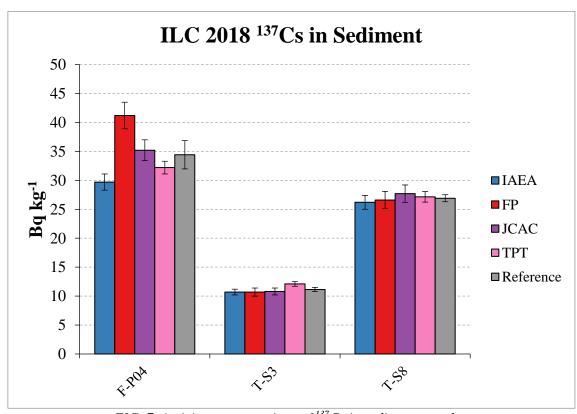


FIG. 7. Activity concentrations of ¹³⁷Cs in sediment samples.

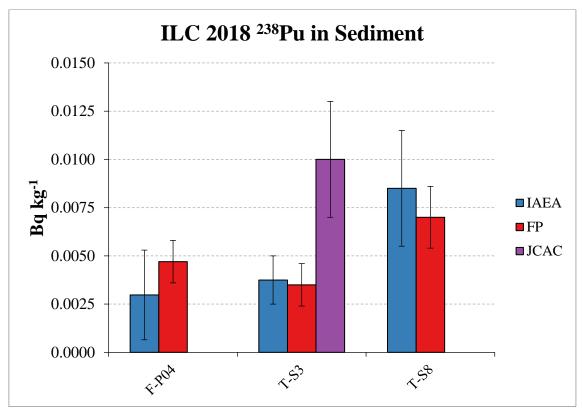
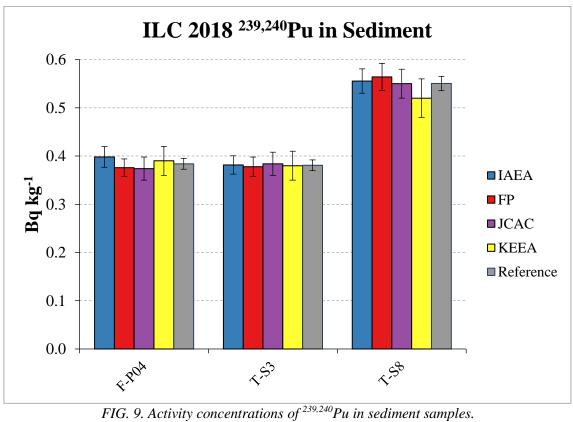


FIG. 8. Activity concentrations of ²³⁸Pu in sediment samples.



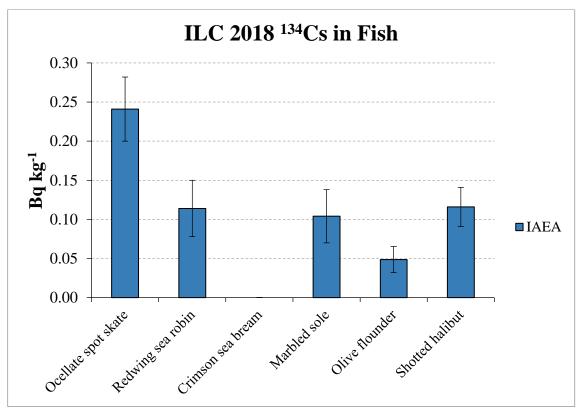


FIG. 10. Activity concentrations of ¹³⁴Cs in fish samples.

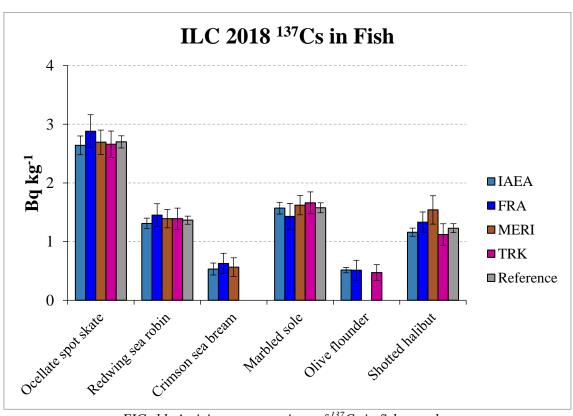


FIG. 11. Activity concentrations of ¹³⁷Cs in fish samples.