Environmental monitoring of plutonium at ultratrace level in natural water (Sea of Galilee—Israel) by ICP-SFMS and MC-ICP-MS†

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An analytical method for the determination of plutonium concentration and its isotope ratio at ultratrace level in natural water by inductively coupled plasma mass spectrometry (ICP-MS) is proposed. In order to preconcentrate Pu and to avoid matrix effects and clogging effects on the cones during the mass spectrometric measurements, an effective Pu separation procedure (on TEVA resin) from the matrix was applied. Studies of the separation procedure for 2.1 pg of ^{242}Pu spiked into 100 L of lake water from the Sea of Galilee result in a recovery of 62%. The detection limits of ^{239}Pu in 100 L lake water were determined as 1×10^{-19} g mL^{-1} and 3×10^{-20} g mL^{-1} using ICP-SFMS and MC-ICP-MS, respectively. ^{239}Pu was detected in the Sea of Galilee at a concentration level of about 3.6×10^{-19} g mL^{-1} with a ^{240}Pu/^{239}Pu isotope ratio of 0.17. This measured plutonium isotope ratio is the most probable evidence of plutonium contamination of the Sea of Galilee as a result of global nuclear fallout after the nuclear weapons tests in the sixties. This paper discusses applications of double-focusing sector field ICP-MS with single and multiple ion collection for the quantitative determination of plutonium and its isotope ratio at the 10^{-19} g mL^{-1} level in natural water.

1. Introduction

The Sea of Galilee is one of the three main potable water resources in Israel, supplying about 20% of national water consumption. Artificial pollution of the Sea of Galilee, also with long-lived radionuclides, has increased in the last few decades. Monitoring and identifying the origin of the long-lived radionuclides would therefore be a powerful tool for understanding possible sources of contamination.[1–5]

The most widely used analytical techniques for the determination of Pu isotopes are radioanalytical techniques, such as α-spectrometry or liquid scintillation radiometry.[4,6] However, a long counting period, which can take from days to several weeks, depending on the sensitivity and precision required,[2] significantly restricts usage of these techniques. In addition, radionuclide analysis of ^{239}Pu and ^{240}Pu by alpha spectrometry is very difficult, due to their similar alpha energies (5.24 and 5.25 MeV, respectively). Therefore, for accurate Pu isotope determination mass spectrometric techniques have to be established.

Accelerator mass spectrometry (AMS)[7,8] and thermal ionization mass spectrometry (TIMS)[9,10] have been used as ultrasensitive mass spectrometric techniques for Pu isotope analysis in different samples. However, AMS is very expensive and is not widely used. As an alternative to AMS, high-selective resonance ionization mass spectrometry (RIMS) was also applied for the determination of Pu at ultratrace level,[11–13] but at present RIMS instruments are not available on the analytical market. In addition, in all the mass spectroscopic techniques mentioned above, the sample preparation procedure is very complicated and, therefore, time- and labor-consuming.

Inductively coupled plasma mass spectrometry is one of the most suitable methods for the ultratrace isotope analysis of actinides,[14–16] in particular Pu, due to its high sensitivity, good accuracy and precision, and relatively simple sample preparation procedure.[17,18] A number of papers devoted to the determination of Pu by ICP-MS in different samples have been published in recent years,[3,19–23] which proves the capability of ICP-MS for the study of Pu at the ultratrace concentration level. However, uranium hydride formation (^{238}U^{1}H$^+$) and peak tailing from ^{238}U$^+$ are the limiting factors for the determination of ^{239}Pu at very low concentration levels in natural samples containing, relative to Pu, high concentrations of natural uranium. Moreover, depending on the matrix of the analyzed sample, other molecular ions, such as molecular ions from lead or rare earth elements, which can be expected in the actinide mass range (e.g., PbO$_2^+$, PbN$_2^+$, etc.),[24,25] will disturb the accurate determination of Pu.

To avoid these problems, several solutions have been proposed. To reduce hydride formation of uranium special sample introduction systems, such as micronebulizers with desolvator, were applied,[24] or heavy water for dilution of the samples was used.[26] In order to reduce the peak tailing effect, the medium mass resolution of sector field mass spectrometer instrument was successfully applied.[26]

For Pu determination in sea-water, urine, waste water samples, etc., mostly the chemical separation of ultratrace plutonium from U as well as matrix elements has been proposed. Ion-exchange and extraction chromatography on the resin have been widely used in different laboratories for this purpose.[2,4,25,27]

Recently, Kim et al.[27] studied ^{239}Pu and ^{240}Pu in sea-water using an on-line sequential injection technique with ICP-SFMS and an ultrasonic nebulizer USN 6000 for sample introduction. Limits of detection (LODs) for ^{239}Pu and ^{240}Pu of 0.64 fg mL^{-1} (1.4×10^{-6} Bq mL^{-1}) and 0.19 fg mL^{-1} (1.7×10^{-6} Bq mL^{-1}), respectively, were achieved. In the Sea of Galilee, where the concentration of Pu is very low, further enrichment of this transuranium element is required for accurate analysis. For this purpose, a combination of co-precipitation with extraction chromatography separation has been successfully established

in order to concentrate and separate Pu prior to analysis by α-spectrometry[28–30] or by ICP-MS.[22,25] A very promising aspect of the plutonium determination is the use of multiple ion collector ICP-MS (MC-ICP-MS), which allows a 10-fold improvement in sensitivity and precision of isotope ratio measurements[31–33] and becomes of extreme importance at the low concentration level of Pu in analysed samples.

The aim of this research is to develop and apply an analytical technique for ultrasensitive Pu determination and Pu isotope analysis at ultratrace level in lake water from the Sea of Galilee by double-focusing sector field ICP-MS (ICP-SFMS) and MC-ICP-MS after matrix separation and preconcentration.

Experimental

ICP-MS instrumentation

ICP-SFMS (ELEMENT, Thermo Electron GmbH, Bremen, Germany) was applied in the Central Division of Analytical Chemistry at the Research Center Juelich for Pu isotope ratio measurements in water samples from the Sea of Galilee. For sample introduction, the PFA-100 microconcentric nebulizer (CETAC Technologies, Inc., Omaha, NE, USA) was used. Aqueous solutions were introduced in the continuous flow mode using a peristaltic pump (Perimax 12, Spetec GmbH, Erding, Germany). The ICP torch was shielded with a grounded platinum electrode (GuardElectrode™, Thermo Electron GmbH, Bremen, Germany).

Comparative measurements of plutonium isotope ratio and concentration were performed using MC-ICP-MS with a Nier–Johnson geometry (Nu Instruments, UK, installed at the Geological Survey of Israel, Jerusalem). A microconcentric nebulizer with an Aridus desolvator (CETAC Technologies, Inc., Omaha, NE, USA) was used for solution introduction in MC-ICP-MS.

Standards and reagents

A laboratory standard solution of uranium NBS-3164 (0.5 ng mL^{-1}) with natural isotopic composition was used for optimization of the experimental parameters. For the determination of the precision and accuracy of ^{240}Pu/^{239}Pu isotope ratio measurements synthetically prepared aqueous laboratory isotope standard solution with known plutonium isotope composition (^{240}Pu/^{239}Pu = 0.2960 ± 0.0026, uncertainty 2s) was used. ^{242}Pu isotope standard (NIST SRM 4334F) was applied to control recovery of the developed procedure. Calibration standard solutions were prepared by dilution of 1 ng mL^{-1} aqueous ^{242}Pu to the following concentrations of ^{242}Pu: 1, 10, 50, 100, 200, 500 and 1000 fg mL^{-1}. 100 L of high-purity deionized water (18 MΩ cm^{-1}), obtained from Milli-Q-Plus water purifier (Millipore Billerica, MA, USA), was subjected to the same co-precipitation and separation procedures as the sample in order to obtain the procedural blank.

All chemicals used were of supragrade (Merck, Darmstadt, Germany). Nitric acid was further purified by sub-boiling distillation.

Sample preparation

100 L of water from the Sea of Galilee was collected in containers previously washed repeatedly with 2% v/v nitric acid in 18 MΩ cm water. The water sample was filtered (0.45 μm) in the field before acidification. The uranium concentration was 0.6 ng mL^{-1}. A schematic diagram of the sample preparation procedure is shown in Fig. 1.

Co-precipitation of Pu with MnO$_2$. The 100 L water sample was acidified with nitric acid to pH = 2. In order to determine the recovery of the method the sample was spiked with 2.1 pg of
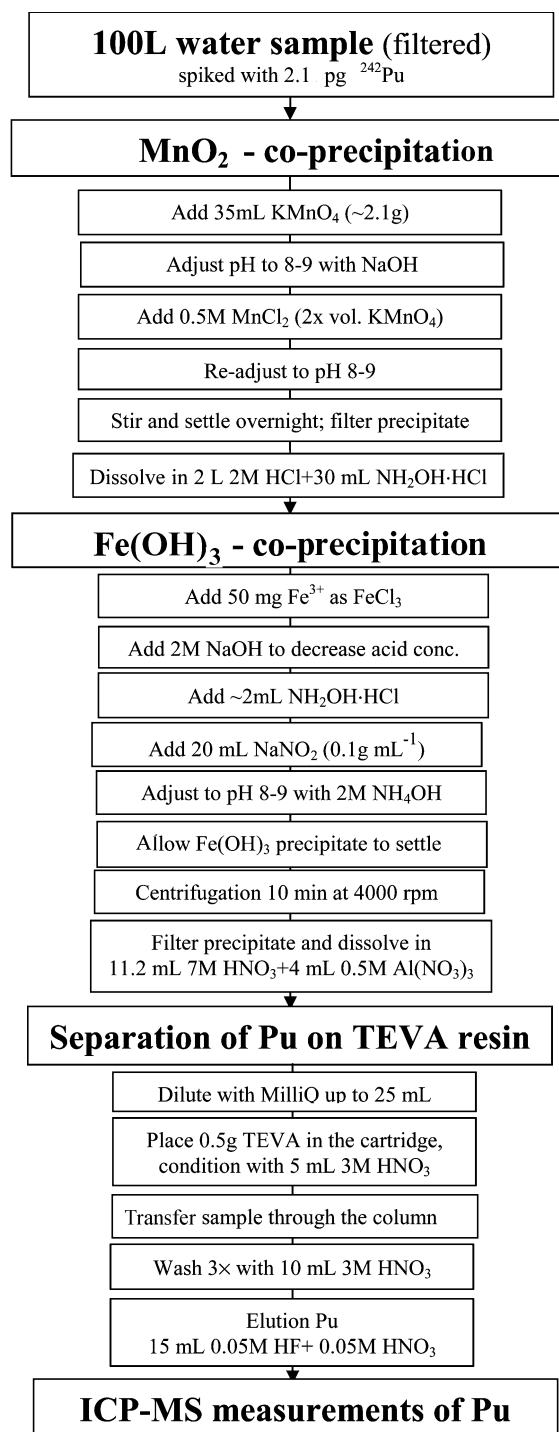
Fig. 1 Sample preparation procedure for Pu analysis in water samples from the Sea of Galilee.

^{242}Pu and thoroughly mixed. Then 35 mL of KMnO$_4$ (∼2.1 g) was added. All Pu present in this step was oxidized to the Pu^{6+} oxidation form. The solution was adjusted to pH = 8–9 with NaOH and 0.5 M MnCl$_2$ (2 × vol. of KMnO$_4$) was added in order to precipitate MnO$_2$. Ultratraces of Pu are co-precipitated together with MnO$_2$. After settling of the MnO$_2$ with co-precipitated Pu overnight it was filtered by gravity over the filter paper (cellulose nitrate filter, 0.45 μm, Sartorius, Goettingen, Germany) and dissolved in 2 L of 2 M HCl + 30 mL of NH$_2$OH·HCl (0.1 g mL^{-1}).

Co-precipitation of Pu with Fe(OH)$_3$. To the dissolved filtrate 50 mg of Fe^{3+} as FeCl$_3$ was added and the solution was neutralized with 2 M NaOH. In order to reduce Fe^{3+} to

Fe^{2+} and Pu^{6+} to Pu^{3+} ~2 mL of $NH_2OH \cdot HCl$ was added. After that, Pu^{3+} was oxidized with 20 mL of $NaNO_2$ (0.1g mL^{-1}) to Pu^{4+}, since tetravalent Pu is more favorable for separation on TEVA resin. The solution was adjusted to pH = 8–9 with 2 M NH_4OH and heated for ~2 hours (60–70 °C) to improve coagulation of the $Fe(OH)_3$ with co-precipitated Pu. After that, the precipitate was settled, transferred to a centrifuge tube and centrifuged for approximately 10 min at 4000 rpm. The supernatant was decanted and discarded to waste; the precipitate was dissolved with 11.2 mL 7 M HNO_3 + 4 mL 0.5 M $Al(NO_3)_3$ and diluted with MilliQ water up to a volume of ~25 mL so that a 3 M HNO_3 solution was obtained.

Chemical separation of plutonium. Plutonium was separated from the $Fe(OH)_3$ by extraction chromatography using Eichrom's TEVA resin (Eichrom Technologies, Inc. Darien, IL, USA; particle size 50–100 μm, active component aliphatic quaternary amine). 0.5 g of TEVA resin was placed into the appropriate cartridge tubes and preconditioned with 5 mL 3 M HNO_3. After that the sample solution was loaded on resin and rinsed 3 times with 10 mL of 3 M HNO_3. Then plutonium was eluted 3 times with 5 mL of 0.05 M HF + 0.05 M HNO_3 into a Teflon beaker. Because of the high concentration of U in the separated sample (U concentration was about 0.5 ng mL^{-1}), Pu was separated on the TEVA resin for a second time. After the first separation the Pu fraction was evaporated to dryness and the residue was dissolved with 11.2 mL of 7 M HNO_3. Then, 4 mL of 0.5 M $Al(NO_3)_3$ was added, the sample solution was made up to 25 mL with H_2O and then subjected to the same TEVA separation protocol as described above. The Pu concentration and the Pu isotope ratio were then measured by ICP-SFMS and MC-ICP-MS.

Optimization of experimental parameters in ICP-MS and measurement procedure

Optimization of the experimental parameters of the ICP-MS instrument was performed with respect to the maximum ion intensity of $^{238}U^+$ and minimum background at m/z 239 u using a laboratory standard solution of uranium with natural isotopic pattern. Instrument operation conditions are summarized in Table 1. The dead time correction for the ICP-SFMS in these measurements was considered to be neglible in this study because of the low concentration of Pu in analysed sample (even for the highest concentration level in the standard calibration curve (1000 fg mL^{-1}), the dead time correction is only 0.006%). The mass bias factor (assuming an exponential correction[34]) was found to be 0.0063 ± 0.0015 (n = 6) using a 0.5 ng mL^{-1} NIST U500 standard solution. Because after the second separation of the sample on TEVA resin the uranium

Table 1 Optimized experimental conditions of double focusing ICP-SFMS and MC-ICP-MS for determination of Pu in water sample from the Sea of Galilee

	ICP-SFMS Element	MC-ICP-MS Nu Instrument
Nebulizer type	PFA-100	Aridus
RF power/W	1199	1300
Cooling gas flow rate/L min^{-1}	18	13
Auxiliary gas flow rate^a/L min^{-1}	1.04	1.3
Nebulizer gas flow rate^a/L min^{-1}	0.91	0.6
Sweep gas flow rate^a/L min^{-1}	—	3.8
Solution uptake rate/mL min^{-1}	0.58	0.08
Spray chamber temperature/°C	—	70
Desolvator heating temperature/°C	—	160
Scanning mode	Peak hopping	—
Mass window (%)	10	—
Mass resolution, $m/\Delta m$	300	300

^{a} Optimized daily

concentration did not exceed 5 pg mL^{-1}, the influences of uranium hydride molecular ions, as well as the peak tailing effect from ^{238}U, on the background of m/z 239 u were considered negligible after their subtraction. Between each run the nebulizer was washed with mixture of pure 0.5 M HCl and 0.05 M HF.

For MC-ICP-MS two cycles were used in the simultaneous data collection mode. In the first cycle, two ion-counting collectors (IC0 and IC1) were used for $^{242}Pu^+$ and $^{240}Pu^+$ and IC2 alone for $^{238}U^+$ measurements. In the second cycle, IC0 and IC1 were used for $^{241}Pu^+$ and $^{239}Pu^+$ ion collection, which means that ^{239}Pu and ^{240}Pu isotopes were not measured simultaneously as might be expected from the name multi-collector-ICP-MS.

The zero measurements were made by deflecting the electrostatic analyzer potential. The mass bias of MC-ICP-MS is in the range for plutonium of about 0.8% per mass unit. Further details of the instrumentation and measurement procedure are given elsewhere.[14,33,35,36]

Results and discussion

Precision and accuracy of Pu measurement

The precision and accuracy of the $^{240}Pu/^{239}Pu$ isotope ratio of the developed method were studied using a laboratory Pu isotope standard solution (see Table 2). The results show sufficient agreement between the expected and measured values of the $^{240}Pu/^{239}Pu$ isotopic ratio with a precision (RSD, n = 10) and accuracy of 0.9% and 1.3%, respectively, which are comparable to our previous results.[14] For ten independent measurements of 100 fg mL^{-1} of ^{242}Pu solution a precision of ion intensity of 5% was determined.

Co-precipitation of plutonium

^{242}Pu spike was used to indicate the efficiency of the co-precipitation and separation of the plutonium in the developed method. A concentration of dissolved plutonium in 100 L of water sample from the Sea of Galilee was approximately 2.1×10^{-17} g mL^{-1} (5×10^{-9} Bq mL^{-1}). Therefore, for the determination of Pu at a low (such as ag mL^{-1}) concentration level further preconcentration steps are required. In addition, during these steps the matrix elements were removed (see Table 3), thus avoiding clogging effects of the solution introduction system and cones, matrix effects, etc. Using a co-precipitation procedure based on MnO_2 and $Fe(OH)_3$, concentration factors of more than 6600 were achieved.

Uranium interferences on Pu determination

Because of the presence of uranium in the analyzed sample (see Table 3) the accurate determination of ^{239}Pu by ICP-MS was difficult due to interferences from $^{238}U^1H^+$ ion formation and the peak tailing effect from $^{238}U^+$. These interferences led to an increase in the background signal of m/z 239 u (see Fig. 2), therefore necessitating separation of uranium from plutonium, especially if the uranium concentration is > 5 pg mL^{-1}. In ICP-SFMS and MC-ICP-MS, the hydride formation rate UH^+/U^+ was measured at 1×10^{-4} and 2×10^{-7}, respectively.

Table 2 $^{240}Pu/^{239}Pu$ isotopic ratio in synthetically prepared laboratory standard solution measured by ICP-SFMS (ELEMENT)

	$^{240}Pu/^{239}Pu$ isotopic ratio		Precision (%)	Accuracy (%)
Nebulizer	Measured	Expected		
PFA-100	0.3002 ± 0.0038	0.2960 ± 0.0026	0.9	1.3

Table 3 Concentration of major matrix elements and uranium in water samples from the Sea of Galilee before co-precipitation and after separation on TEVA resin measured by ICP-SFMS

	Concentration/μg mL^{-1}		
Element	Sea of Galilee	After Pu separation	Decontamination factor[a]
Na	131.2 ± 2.1	1.10 ± 0.02	120
Mg	35.0 ± 0.8	0.48 ± 0.2	75
Ca	50 ± 1	0.11 ± 0.01	455
U	$(0.64 \pm 0.01)\ 10^{-3}$	$(1.1 \pm 0.05)\ 10^{-6}$	582

[a] After being separated twice on TEVA resin
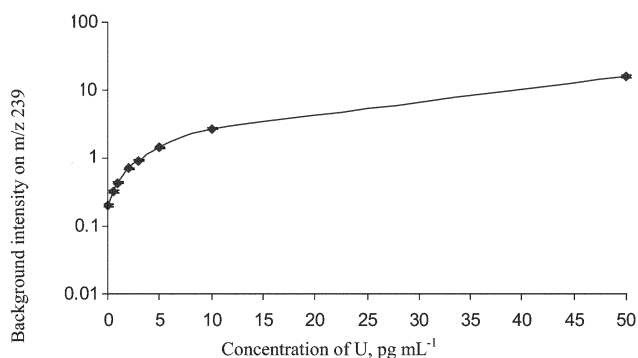
Fig. 2 Influence of U concentration on the background signal on m/z 239 u in ICP-SFMS.

Separation of plutonium on TEVA resin

From the $Fe(OH)_3$ precipitate plutonium was further separated from the uranium as well as matrix elements of the precipitate (mainly Fe and Na) by means of extraction chromatography using Eichrom's TEVA resin. Moreover, because after separation the concentration of uranium was about 0.5 ng mL^{-1}, the plutonium fraction was separated for the second time on TEVA resin. The total efficiency of the co-precipitation and two separation procedures in terms of the removal of matrix ions, as well as uranium, is shown in Table 3. The U concentration was determined as 1.1 pg mL^{-1}, and no increase in the background at m/z 239 u was observed. The procedural recovery of ^{242}Pu spike was found to be about 62%.

Pu concentration in the Sea of Galilee

After separation on TEVA resin, the water sample from the Sea of Galilee was measured by ICP-SFMS and MC-ICP-MS with respect to its plutonium content. The data, presented in Table 4, show a good agreement between the measurements on the two available instruments. The concentrations of ^{239}Pu in the Sea of Galilee were determined by short-term repeatability as $0.33 \pm 0.1 \times 10^{-18}$ g mL^{-1} (7.5×10^{-10} Bq mL^{-1}) and $0.39 \pm 0.01 \times 10^{-18}$ g mL^{-1} (8.9×10^{-10} Bq mL^{-1}), using ICP-SFMS and MC-ICP-MS, respectively. The LODs assuming the 3σ-criteria for ^{239}Pu and ^{240}Pu in 100 L water from the Sea of Galilee were determined as 1.2×10^{-19} g mL^{-1} and 1.3×10^{-19} g mL^{-1} for ICP-SFMS, respectively, and 1.3×10^{-20} g mL^{-1} for both isotopes with MC-ICP-MS. The

Table 4 Concentration of ^{239}Pu and ^{240}Pu/^{239}Pu isotopic ratio measurements in the water sample from the Sea of Galilee, measured by ICP-SFMS (ELEMENT) and MC-ICP-MS (Nu Instuments)

ICP-MS	Nebulizer	^{239}Pu concentration/ g mL^{-1}	^{240}Pu/^{239}Pu
ICP-SFMS	PFA-100	$(3.3 \pm 1.0)\ 10^{-19}$	<0.33
MC-ICP-MS	Aridus	$(3.9 \pm 0.1)\ 10^{-19}$	0.17 ± 0.05

intensity value of the procedural blank was applied for the evaluation of LODs and was always subtracted from the sample results.

^{240}Pu/^{239}Pu isotope ratio measurement in the Sea of Galilee water at ultratrace level

The optimized analytical method was applied to the measurement of the ^{240}Pu/^{239}Pu isotopic ratio in water from the Sea of Galilee after Pu matrix separation. Comparative measurements performed by ICP-SFMS and MC-ICP-MS are summarized in Table 4. The ^{240}Pu/^{239}Pu isotopic ratio measured by MC-ICP-MS was determined as 0.17 ± 0.05, which represents the value of contamination of the Sea of Galilee due to the global fallout after nuclear weapon tests in the sixties. Using ICP-SFMS, the ^{240}Pu/^{239}Pu isotopic ratio was found to be <0.33, whereby ^{240}Pu has been measured below the detection limit. Due to the very low concentration of ^{240}Pu in the sample and a higher detection limit of ICP-SFMS with a single ion collector, we are not able to measure the ^{240}Pu/^{239}Pu isotopic ratio at 10^{-19} g mL^{-1} level in comparison with MC-ICP-MS. Therefore, MC-ICP-MS has the advantage of analyzing the ^{240}Pu/^{239}Pu isotopic ratio with sufficient precision at the low ag mL^{-1} concentration level. In future, processing of the larger sample volume could be of interest in order to obtain more precise ^{240}Pu/^{239}Pu isotopic ratio.

Conclusions

This study demonstrates that double-focusing sector field ICP-MS with single and multiple ion collection, combined with preconcentration and matrix separation, represents a useful analytical technique suitable for the analysis of plutonium in water at the low 10^{-18} g mL^{-1} level. Disturbing interferences affecting the accurate determination of Pu that arise from the presence of U in the analyzed sample, as well as matrix elements, were successfully removed by co-precipitation and separation of the sample on Eichrom's TEVA resin. The limits of detection using ICP-SFMS and MC-ICP-MS achieved for ^{239}Pu in 100 L of lake water were 1.2×10^{-19} g mL^{-1} and 3×10^{-20} g mL^{-1}, respectively. The recovery obtained for 2.1 pg of ^{242}Pu dissolved in 100 L of water from the Sea of Galilee (concentration of ^{242}Pu: 21 ag mL^{-1}) was about 62%. Measured by ICP-SFMS and MC-ICP-MS, concentrations of ^{239}Pu in the Sea of Galilee were $3.3 \pm 0.5 \times 10^{-19}$ g mL^{-1} (7.5×10^{-10} Bq mL^{-1}) and $3.9 \pm 0.1 \times 10^{-19}$ g mL^{-1} (8.9×10^{-10} Bq mL^{-1}), respectively. Using the method presented in this study, the ^{240}Pu/^{239}Pu isotopic ratio in the Sea of Galilee was determined as 0.17 ± 0.05, which is the most probable evidence of plutonium contamination of the Sea of Galilee as a result of global nuclear fallout after nuclear weapons tests in the sixties.

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