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■ 논 문 ■

Determination of ^{241}Pu in Environmental Samples Using Liquid Scintillation Counting System

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액체섬광계수기를 이용한 환경시료중 ^{241}Pu 분석

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Abstract - An optimized method for determining beta-emitting ^{241}Pu in the presence of alpha-emitting nuclides was developed using a liquid scintillation counting system. Pulse shape analysis (PSA) level was set using pulse-shape discrimination method and the ^{241}Pu counting channel was adjusted for maximum value of figure of merit using the ^{241}Pu standard source. The volume of scintillant was determined for the maximum value of counting efficiency. This optimized method has been applied to environmental samples to measure concentration of ^{241}Pu in soils and mosses. Also it has been identified the origin of Pu deposited in Korea from the activity ratio of $^{241}Pu/^{239,240}Pu$.

Key words : ^{241}Pu, liquid scintillation spectrometer, pulse shape analysis

요약 - 알파방출핵종 존재하에 베타방출핵종인 ^{241}Pu 최적 분석조건을 검토하였다. 펄스파고 분석 기법을 이용하여 PSA 준위를 설정하였다. ^{241}Pu 표준선원을 이용하여 figure of merit가 최대가 되도록 ^{241}Pu counting channel를 조정하였고 계측효율이 최대가 되도록 형광체 부피를 설정하였다. 최적화된 ^{241}Pu 분석법을 토양과 이끼등의 환경시료에 적용하여 ^{241}Pu 방사능농도를 측정하였고, $^{241}Pu/^{239,240}Pu$ 방사능 비율로 부터 우리나라의 일부 토양 및 이끼에 침적된 Pu의 근원을 규명하였다.

중심단어 : ^{241}Pu, 액체섬광계수기, 펄스파고분석

INTRODUCTION

A determination of plutonium in environmental samples has been mainly directed to the alpha emitting isotopes $^{239,240}Pu$ and ^{238}Pu which have high radiotoxicity. However, the largest contributor to the total plutonium radioactivity in environmental samples is the ^{241}Pu isotope, a beta emitter with a half-life of 14.4 years and maximum beta energy of 21 KeV. Though the radiotoxicity of ^{241}Pu itself is much lower than that of the alpha emitting plutonium isotopes, ^{241}Pu decays to ^{241}Am which is an highly radiotoxic alpha-emitting nuclide with a half-life of 433 years and a long residence time in animals and man. The radioactivity ratio of ^{241}Am to $^{239,240}Pu$ in the environment will increase in the long run due to the decay of ^{241}Pu.

A few procedures using modern instrumentration have been reported[1-4] although the simultaneous determination of $^{239,240}Pu$ and ^{241}Pu in the same sample using a single measurement was performed in the early 1970s[5]. This is mostly a result of the difference in the radiation characteristics of these nuclides. As ^{241}Pu is mainly a low β emitter, the techniques available for direct measurement are limited. Until now, liquid scintillation counting has often been used for detecting weak β radiation because it allows the problems of self-absorption of the radiation by the sample to be mostly avoided.

Recently, modern liquid scintillation spectrometers equipped with pulse height analysis (PHA) and pulse shape analysis (PSA) techniques have been developed[1]. The low-level liquid scintillation counter (Quantulus 1220) has an anticoincidence detector and a massive lead shield to minimize the background radiation. It is also equipped with a pulse shape analyzer, which allows discrimination between α and β pulses. The excitation produced in the scintillator depends on the type of radiation. α and β radiations produce mainly singlet states, which fluorescence in 1-2 ns, whereas α particles produce more triplet states, which can last 200-300 ns. The shape and duration of the resulting light pulses from the scintillator are different depending on nuclides, and the pulse shape analyser distinguishes the α and β pulses by comparing the fall time of a light pulse with its amplitude. The use of PSA enables the new liquid scintillation spectrometers to measure the spectra of both α and β-emitting nuclides simultaneously even at the low-levels present in environmental radioactivity. The purpose of this investigation is to optimize a procedure for the determination of ^{241}Pu using liquid scintillation spectrometry, then to apply this optimized procedure to environmental samples such as moss and soil samples, and to elucidate the origin of Pu deposited in Korea from the activity ratio of $^{241}Pu/^{239,240}Pu$.

METHODS

A low-level liquid scintillation specrometer, Quantulus 1220 (LKB, Wallac), was used for system optimization. A pure alpha and a pure beta standard sample as standards were used to set the pulse shape analyser. About 1000 dpm of ^{239}Pu was mixed with the water:cocktail having the ratio of 1 ml 0.1 M HCl to 19 ml Ultimagold AB (Packard Instrument Company) that is to be used in the actual analysis. A beta sample about 1000 dpm of ^{36}Cl was prepared in the similar way. All measurements were carried out with 20ml Teflon vials.

The determination of of ^{241}Pu was carried out an aliquots of 100g soil and 20g moss according to TOPO extraction method[6]. The samples were calcined at 600 ^{o}C for 24 h to eliminate organic matter. After adding ^{242}Pu as a yield tracer, a leaching procedure using HNO_3, HF, and $Al(NO_3)_3$ solution is performed. Then, plutonium is extracted from this dissolved sample material into TOPO (trioctyl phosphine oxide) in cyclo-

hexane. This very effective extraction step separates Pu from most of the matrix elements like Si, Fe, alkali and alkaline earth elements. TOPO phase is washed by 3M HCl, to wash out the residual HNO_3, which could disturb the re-extraction. Back extraction was done using ascorbic acid in HCl solution. The radiochemical purification of this Pu fraction is performed in two steps: coprecipitation with LaF_3 and anion exchange. The separation scheme is presented in Fig. 1.

A portion of the purified Pu fraction was taken for the determination of ^{241}Pu. The sample was evaporated to dryness. 5ml of conc. HCl was added and the solution was again evaporated to dryness. Using 5 ml of 1 M HCl, the residue was transferred to a standard 20 ml Teflon counting vial. The counting vial was evaporated dryness on the sand bath and 1 ml of 0.1 M HCl and 19 ml of Ultimagold-AB scintillation liquid was added. The cocktail was allowed to stabilized in a cool, dark place place for 24h before the measurement. The samples were counted using 1024 channel per spectrum for 600 minutes.

RESULTS AND DISCUSSION

System optimization

To determine ^{241}Pu activities with the highest sentivity, the optimum counting condition must first be configured. This configuration can be affected by a variety of parameters such as α and β counting efficiencies, the pulse shape analysis discrimination factor of the instrument, background in the region of interest and scintillant volume.

The discrimination of the α and β pulses is based on the well-known difference between the decayed components of their fluorescence. To determined the optimum PSA (pulse shape analysis) level, one pure alpha (^{239}Pu) and one pure beta (^{36}Cl) sample were measured in α and β window, respectively, varing the PSA level from 60 to 140. As shown in the Table 1, β percentages in α window for measurement of ^{239}Pu were increased with PSA level while α percentage in β window for ^{36}Cl were decreased. This spillover data were plotted in Fig. 2. which shows typical alpha/beta crossover plot for ^{239}Pu and ^{36}Cl standards in Ultimagold AB cocktail. The optimum PSA level is where there is minimum spill of

Table 1. Percentage betas in ^{239}Pu and alphas in ^{36}Cl standard samples observed in the alpha and beta window as a function of PSA level setting in a Quantulus 1220.

	^{239}Pu(α)			^{36}Cl(β)		
PSA Level	cpm in α Window	cpm in β Window	β percentage*	cpm in α Window	cpm in β Window	α percentage**
60	1274.4	4.6	0.36	742.1	267.3	73.52
70	1286.7	12.9	0.99	598.2	573.1	51.07
80	1254.4	14.3	1.13	396.7	1156.3	25.52
90	1264.8	25.0	1.94	134.5	1322.9	9.23
100	1281.7	36.8	2.79	43.2	1684.8	2.50
110	1265.8	47.4	3.61	10.4	3703.9	0.28
120	1228.3	100.9	7.59	3.1	1406.1	0.22
130	1201.7	241.3	16.72	0.7	499.3	0.14
140	1105.7	429.6	27.98	0.3	333.0	0.09

*: (cpm in β window/total cpm in α and β windows)x100, **:(cpm in α window/total cpm in α and β windows)x100

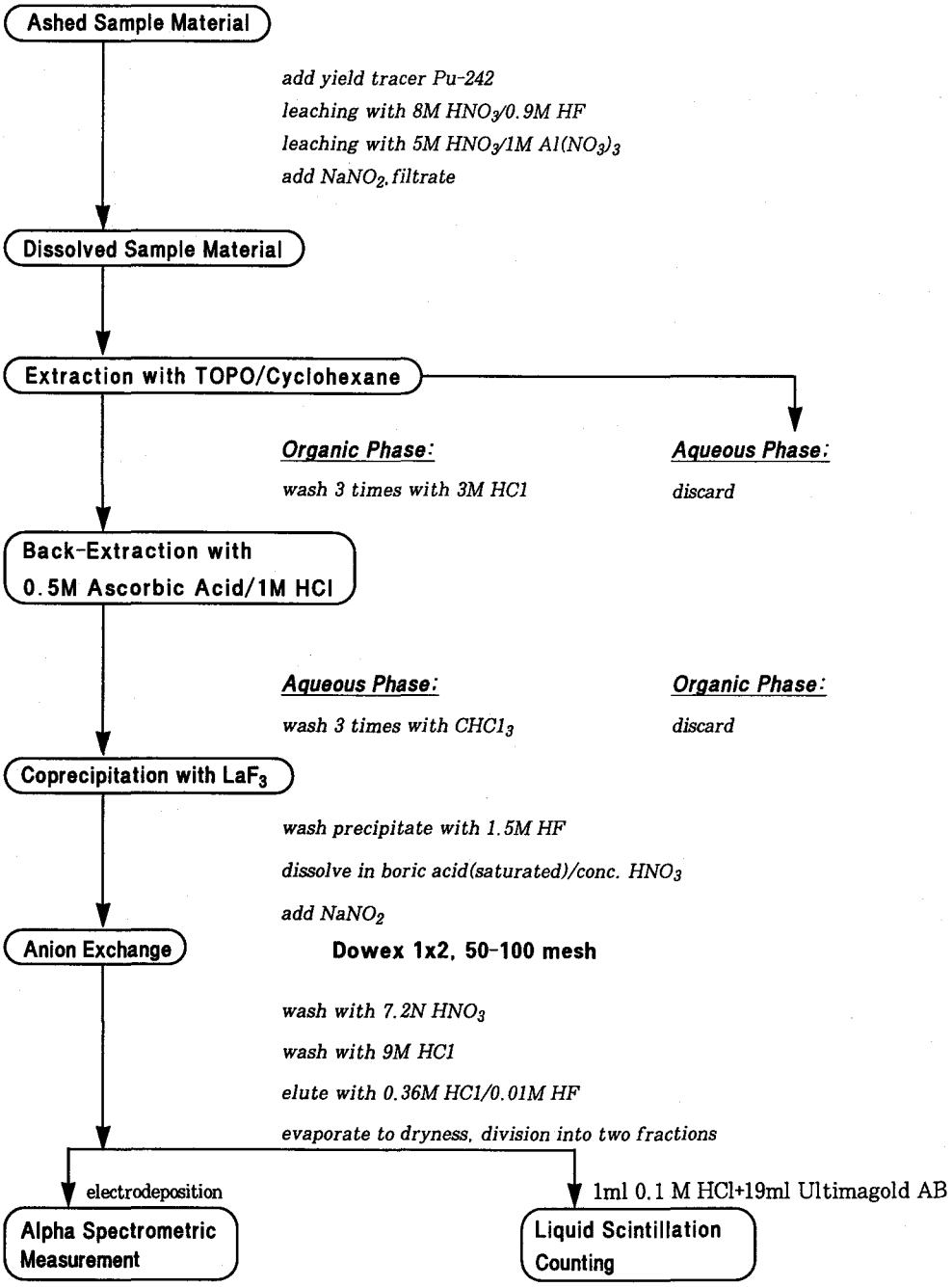

Fig. 1. Separation of ^{241}Pu from soil and moss samples.

both alpha counts into the beta MCA and beta counts into the alpha MCA.

Therefore, the PSA level for optimum counting was set at 100. Under optimum conditions, misclassification of alpha events into beta MCA and beta into alpha MCA is less than 3%. A typical alpha spectrum of ^{239}Pu and beta spectrum of ^{36}Cl obtained at the PSA level of 100 is presented in Fig. 3.

The the figure of merit (FM), defined as the square of counting efficiency divided by the background in the region of interest (E^2/B), was considered to be the best indicator of optium counting conditions. The ^{241}Pu counting channel was adjusted for maximum value of FM using ^{241}Pu standard source. As shown in Fig. 4. Left and Right channel were adjusted to 23 and 289, respectively, in which the value of FM was maximized.

To establish an optimum volume of scintillant, the optimum scintillant/water (0.1 M HCl) ratio was determined using the total available volume of 20 ml. For this, the FM was calculated for different proportions of scintillant volume and water at the PSA setting of 100. As shown in Fig. 5. the optimum scintillant volume was 19 ml, which gives the highest FM value.

Using a scintillant volume of 19 ml and PSA setting of 100, the counting efficiency for ^{241}Pu β particles (window 23-289) was 41 % and background count rate was between 1.5 and 2.0 cpm depending measuring time. The α particle efficiency was determined in a similar manner (window 500-800) and found to be 100% and the α background count rate was 0.06-0.1 cpm. At a counting time 600 min., detection limit was 0.0095 Bq/sample and 0.0030 Bq/sample for ^{241}Pu and alpha activity, respectively.

^{241}Pu activity determination

Paatero *et al.* calculated the ^{241}Pu activity from the following equation [7].

$$A_1 = \frac{A_2 R_1}{E R_2 \alpha M 60} \quad (1)$$

where A_1=the activity of ^{241}Pu in the sample(Bq/kg) at the time of measurement

A_2= activity of ^{242}Pu tracer (dpm)

R_1 = net count rate of ^{241}Pu (cpm)

E= counting efficiency of ^{241}Pu

R_2 = total α net count rate (cpm)

α = ratio ^{242}Pu α counts/total α counts measured by α-ray spectrometer

M= mass (kg)

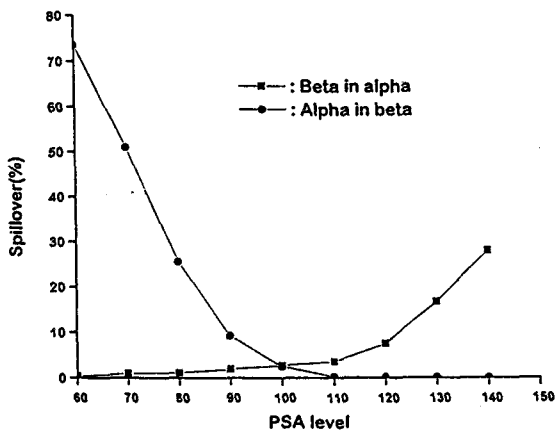

Fig. 2. Typical alpha/beta crossover plot for ^{239}Pu and ^{36}Cl standards in Ultimagold AB cocktail.

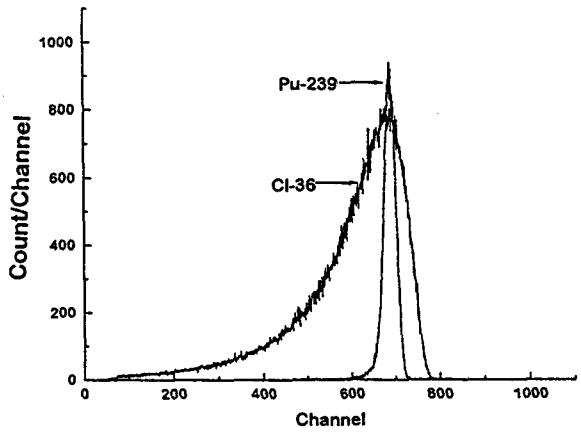

Fig. 3. Alpha spectrum of ^{239}Pu and beta spectrum of ^{36}Cl at PSA-level of 100.

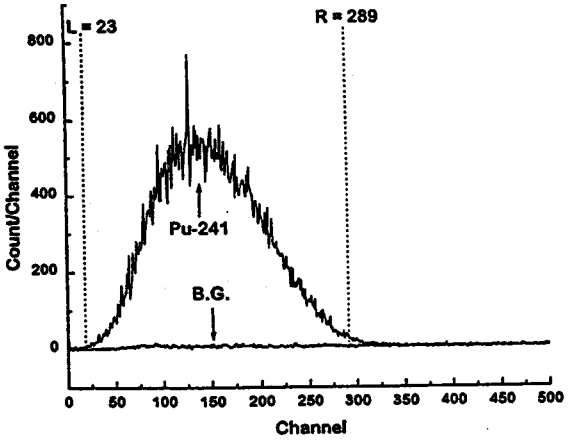

Fig. 4. Left and Right channel adjusted in the beta spectrum of ^{241}Pu standard source.

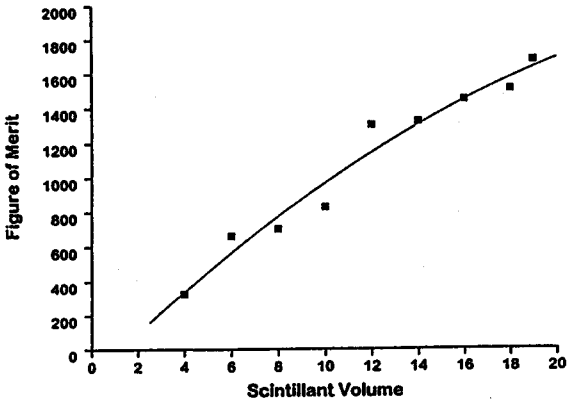

Fig. 5. Figure of merit vs. scintillant volume (PSA=100)

But, in case R_2 has a quite large value, it is necessary to correct of the spillover about alpha value in the beta window, because background in the beta window increase due to spillover with increasing R_2. For getting exact concentration of ^{241}Pu, the equation (1) can be transformed into the following equation (2) which was used for the calculation of ^{241}Pu activity in this study.

$$A_2=\frac{(R_1 * R_2 \times F)}{E\ Y\ M\ 60} \qquad (2)$$

where F = spillover correction value expressed as a β/α activity ratio at PSA level of 100 from Table 1 (~2.9 %)

Y = chemical yield of ^{241}Pu (R_2 α/A_2)

^{241}Pu measurement of environmental samples

The Pu contamination level in the terrestrial environment due to atmospheric fallout is highly variable with time and geographic location. Data for ^{241}Pu and ^{241}Pu/^{239,240}Pu in environmemtal samples contaminated by global fallout have been published by Hakanen *et al.*[1], Holm and Persson[8], Livingston *et al.*[9], Fukai *et al.*[10] and Krey *et al.*[11]. In the terrestrial environment, the soil and moss are the principal reservoir of artificial radionuclides and act as a media of migration systems, because the soil and moss accumulate the artificial radionuclides originating from the nuclear weapons and nuclear facilities[12,13].

The optimized procedure of ^{241}Pu has been applied to environmental samples such as moss and soil samples in this study. Table 2 shows data from the analysis of ^{241}Pu in 6 soil and 6 moss samples, collected from southern part of Korea in 1995. Data for ^{239,240}Pu in Table 2 were determined by alpha spectrometry. Typical liquid scintillation spectra of Pu in the soil are shown in Fig. 6. in which beta spectrum of ^{241}Pu was clearly separated from α spectrum of ^{239,240}Pu. The mean values with standard deviation in soils was 0.55 ±0.19 (range 0.32 to 0.79) Bq/kg-dry for ^{239,240}Pu, and 1.95 ± 0.74 (0.88 to 3.10) Bq/kg-dry for ^{241}Pu. In case of the moss samples, the mean values was 2.32 ± 2.10 (range 0.32 to 4.70) Bq/kg-dry for ^{239,240}Pu, and 8.00 ± 7.16 (1.28 to 17.5) Bq/kg-dry for ^{241}Pu. The highest value for plutonium was found in moss on rock. The average activity concentration of Pu isotopes in moss is greater than that in soil. The measured activity concentrations of Pu isotopes in moss samples are lower than those reported from Finland[7] and Sweden[8]. It may come

Table 2. Concentration of ^{239,240}Pu and ^{241}Pu and their activity ratios in soils and mosses.

Sample Name	Concentration(Bq/kg-dry)		$\frac{^{241}Pu}{^{239,240}Pu}$
	^{239,240}Pu	^{241}Pu	
KANGLUNG Soil	0.74±0.05	2.28±0.32	3.08±0.48
YEIJU Soil	0.38±0.04	1.60±0.41	4.21±1.17
SESAN Soil	0.32±0.03	0.88±0.19	2.75±0.65
KIMJE Soil	0.49±0.05	1.78±0.35	3.63±0.80
ULJIN Soil	0.55±0.04	2.05±0.36	3.78±0.71
HADONG Soil	0.79±0.06	3.10±0.61	3.92±0.83
Moss growing on rock(ULJIN)	4.70±0.71	15.2±1.85	3.23±0.63
Moss growing on soil(KONGJU)	0.39±0.04	1.84±0.35	4.72±1.02
Moss growing on stone(KIMJE)	0.69±0.12	2.62±0.62	3.80±1.12
Moss growing on stone(MUJU)	3.23±0.10	9.53±1.02	2.95±0.33
Moss growing on soil(HADONG)	0.32±0.03	1.28±0.20	4.00±0.73
Moss growing on rock(JEJU)	4.61±0.65	17.5±1.52	3.80±0.63

from deposition influenced by geographical location and characteristics of moss such as species and life span of moss colony.

The activity ratio of ^{241}Pu/^{239,240}Pu varies depending on the source and can be utilized to identify the different sources of release. The activity ratio of ^{241}Pu/^{239,240}Pu in the releases from the Chernobyl accident, nuclear fuel reprocessing facilities, fallout from the 26th Chinese A-bomb test and in weapon-grade plutonium is in the order of 85, 25, 5.5 and 3, respectively[14]. As shown in Table 2, the activity ratio of ^{241}Pu/^{239,240}Pu in soils and mosses was found to be in the range of 2.75 to 4.72 with a mean value of 3.66 ±0.57, which is in good agreement with recently reported activity ratio of ^{241}Pu/^{239,240}Pu[15,16] influenced by fallout from nuclear weapon testings. The contribution of the Chernobyl-derived plutonium to the soil and moss in Korea was negligible relative to their concentrations from weapon testings, considering the reporting value of 94.8 of ^{241}Pu/^{239,240}Pu in the Chernobyl fallout over Finland[7].

SUMMARY

In this study, ^{241}Pu analysis was optimized using low-level liquid scintillation specrometer. Using Ultimagold-AB scintillation liquid, PSA-level for separation of alpha and beta nuclide was set at 100. The counting efficiency for ^{241}Pu β particles(window 23-269) was 41% and background count rate was between 1.5 and 2.0 cpm depending on the measuring time.

Optimized procedure of ^{241}Pu has been applied to moss and soil samples. The results of mean activity concentration in soils were 0.55 Bq/kg-dry for ^{239,240}Pu, and

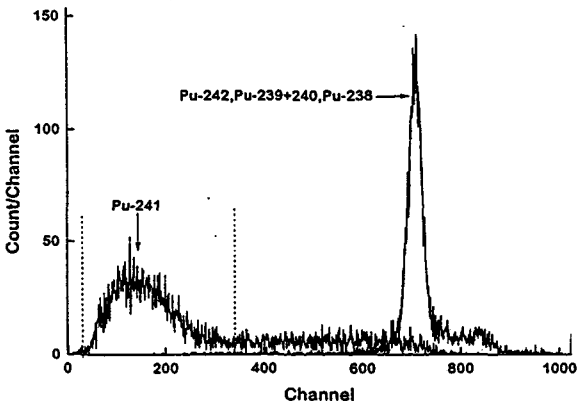

Fig. 6. Typical liquid scintillation spectra of Pu in the soil.

1.95 Bq/kg-dry for ^{241}Pu. In case of the moss samples, the mean values was 2.32 Bq/kg-dry for ^{239,240}Pu, and 8.00 Bq/kg-dry for ^{241}Pu. The ^{241}Pu/^{239,240}Pu activity ratios in soils and mosses were found to be in the range of 2.75 to 4.72 with a mean value of 3.66 ±0.57. These values are close to those observed in the cumulative deposit from the global fallout of nuclear weapon testing.

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