Development and application of radiochemical methods based on the use of ICP-MS instruments

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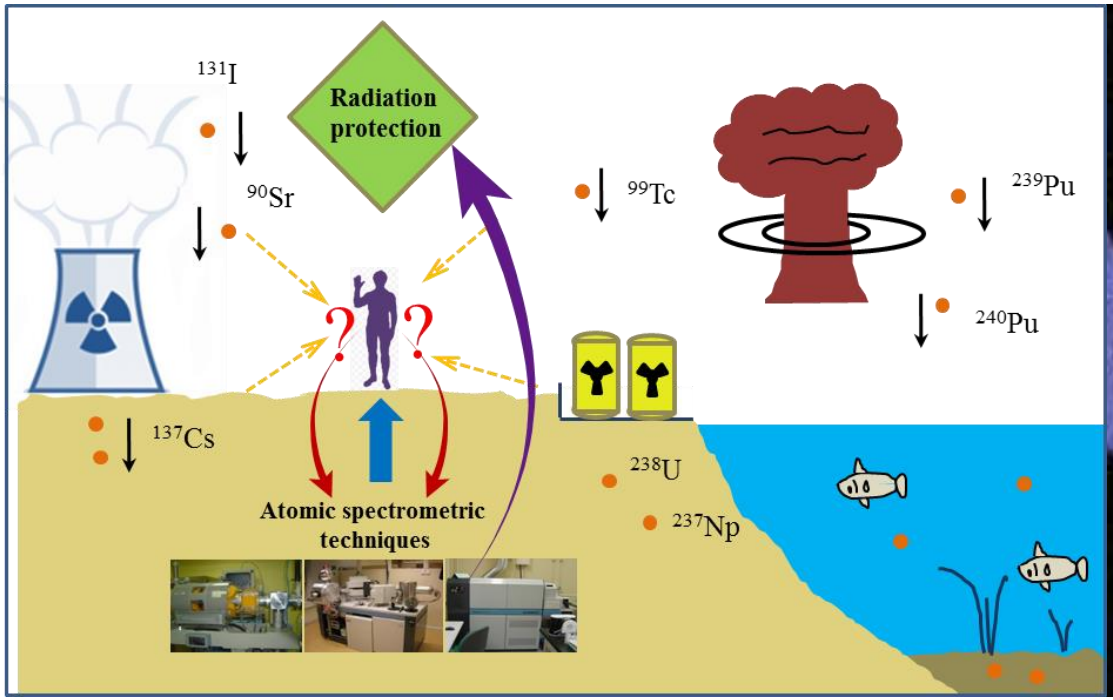

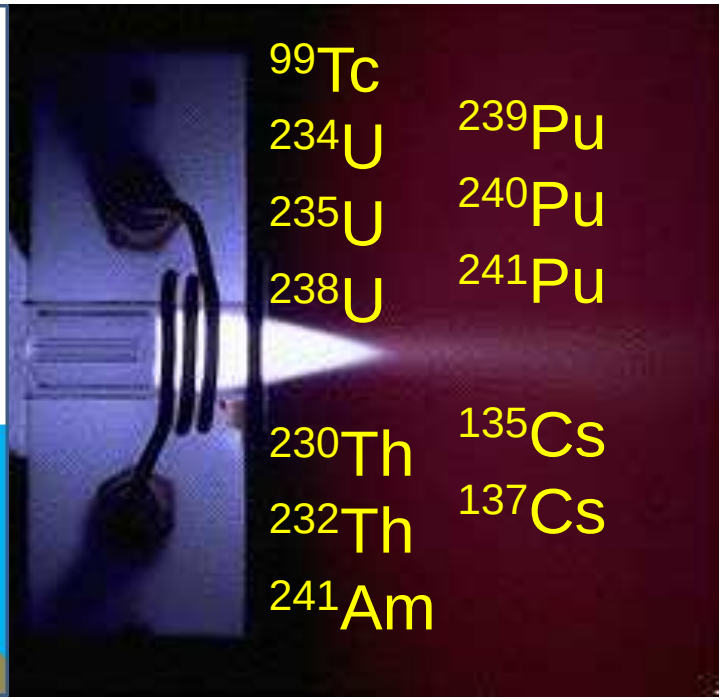

Hospital
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Dept. of Molecular Imaging and Theranostics
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Dept. of Radiopharmaceuticals Development
Dept. of Radiation Measurement and Dose Assessment
Dept. of Radiation Effects Research
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Human Resources Development Center
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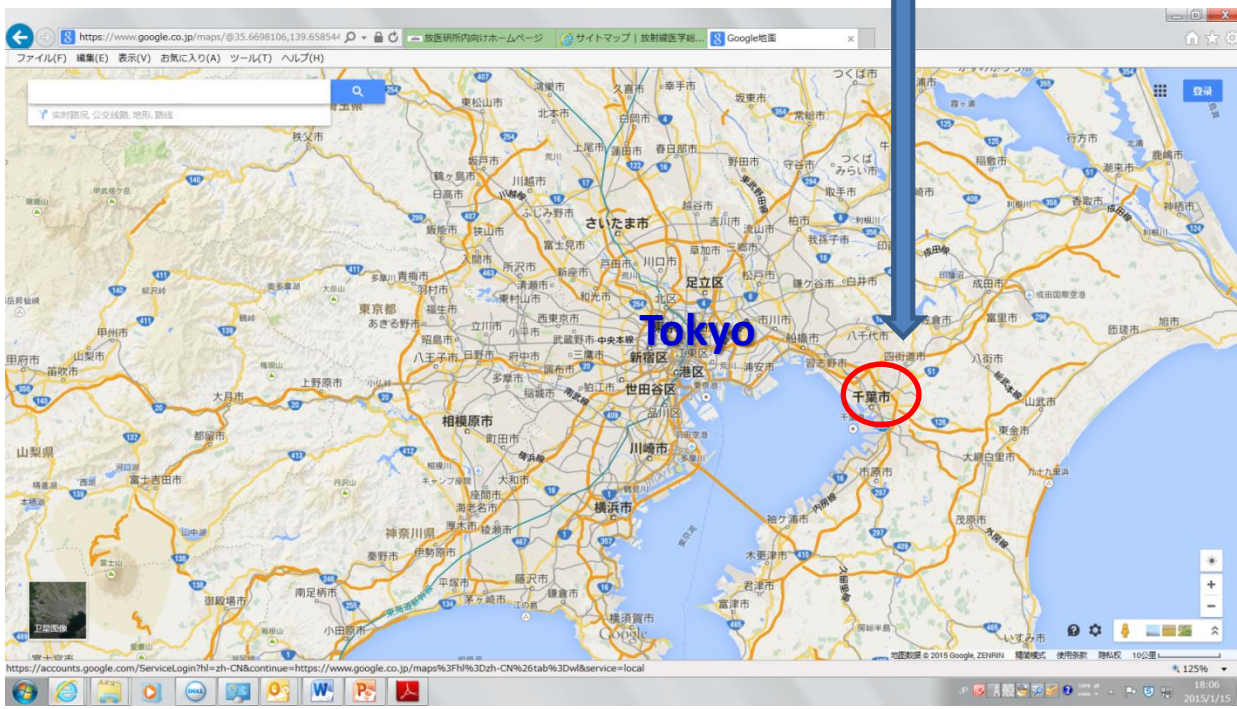
ICP-MS
Radionuclides analysis



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Contents

- **Development of advanced mass spectrometric techniques for radionuclide (actinides, Cs) analysis**
  - Sensitivity improvement
  - Chemical separation development
- **Pu isotopes as geochemical tracer: transport process in the ocean**
- **Tracing Fukushima nuclear accident released Pu and Cs isotopes in the environment**

Development of advanced mass spectrometric techniques for radionuclide analysis

RADIOISOTOPES, **40**, 42-52 (1991)

総　説

環境放射能分野への誘導結合プラズマ質量分析法の応用†

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Key Words : environmental radioactivity, inductively coupled plasma mass spectrometry, long-lived radionuclide, spectral interference, plugging phenomenon, matrix effect, detection limit, improvement of ion detection efficiency

1. はじめに

環境試料中の長半減期放射性核種の濃度レベルはきわめて低く，また壊変定数が小さいから，放射能濃度レベルも低い。したがって，放射能測定よりむしろ原子数を測定する方が手取り早い[1]。筆者らはここ数年

エネルギー(>15.75 eV) を持つ N, O, F, Ne, Cl 等の元素以外は，多くがほぼ 100% イオン化されることを利用している。したがって，ほとんどの元素を，しかも多元素を同時測定できる。また，溶液試料を装置に導入できる利点を有する。質量分析部の四重極分析計は，全質量を ms オーダーで高速掃引するので，通常

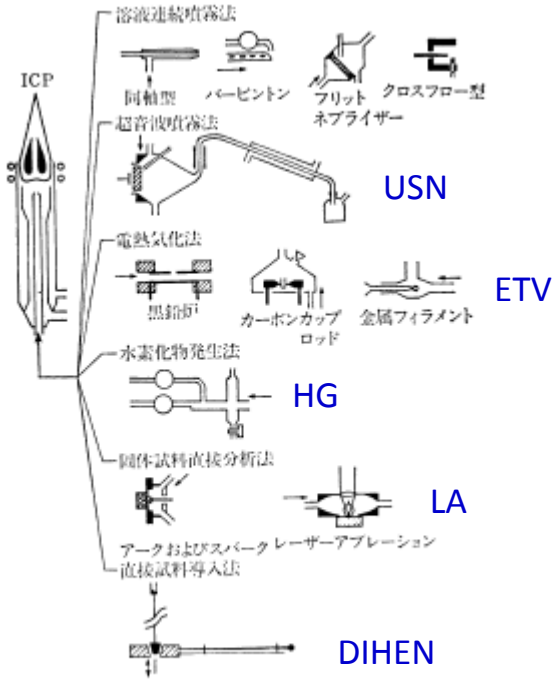
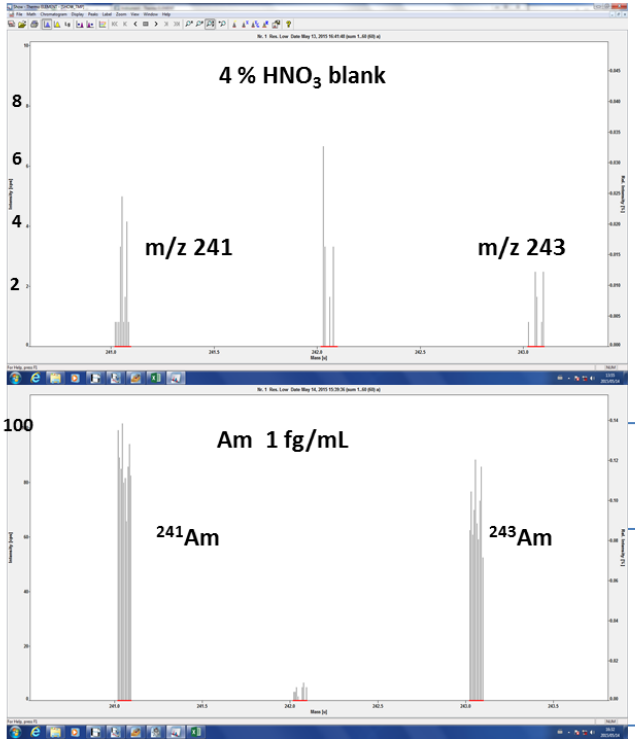


図 2　利用可能な試料導入法
Ref. 11 より許可を得て掲載

First review: sensitivity comparison between ICP-MS and radiometric techniques

Detection limit　0.16 – 0.38 pg/mL
For ^{99}Tc, ^{232}Th, ^{237}Np, ^{238}U, ^{239}Pu （long half-life)

Rapid development of ICP-MS analysis of radionuclides at NIRS: Pu, Am isotopes



2006

SF-ICP-MS desolvation

2015

SF-ICP-MS Jet-interface desolvation

10^{-13} g

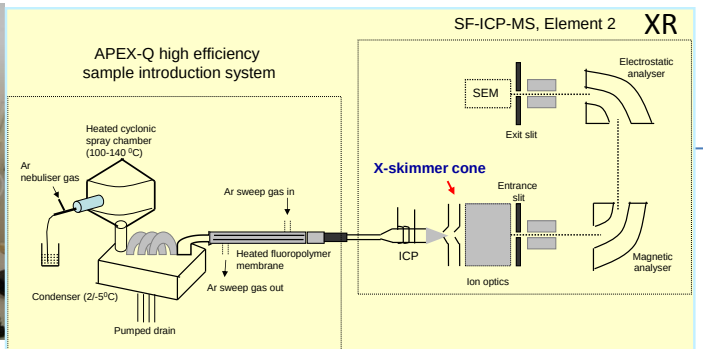
10^{-14} g

10^{-16} g

Attogram levels

10^{-18} g

High efficiency sample introduction: APEX or Aridus II



Zheng & Yamada, Talanta, 2006
Zheng & Yamada, J. Oceanogr. 2008
Zheng, JNRS, 2015

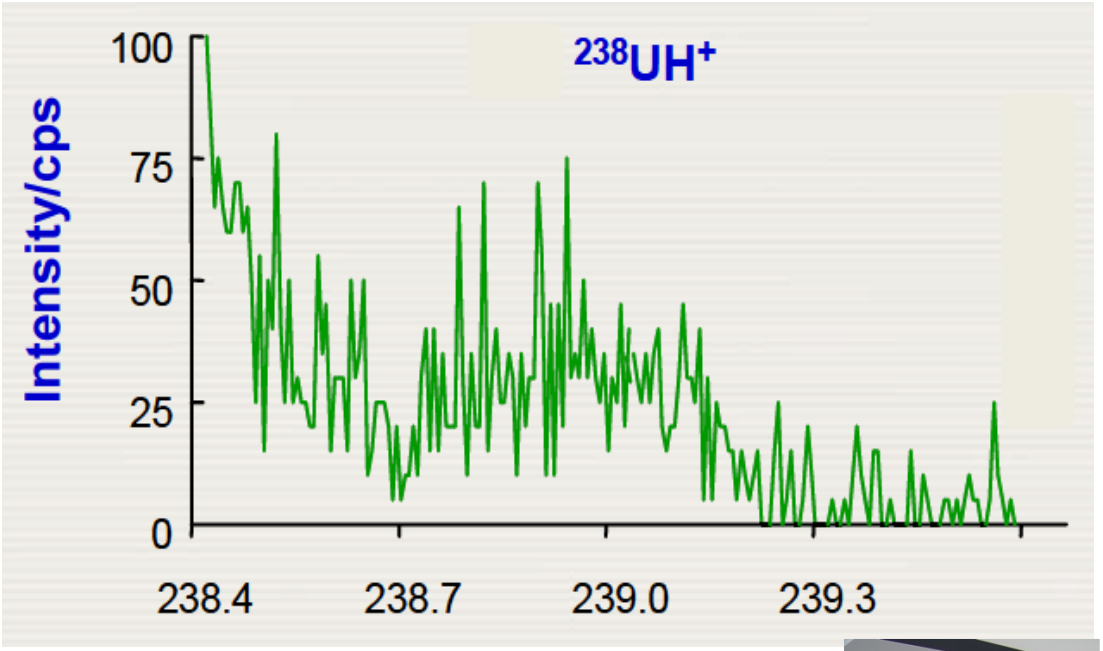
Major interferences for ultra-trace Pu-Am analysis using ICP-MS

Analyte	Interferences for ICP-MS analysis
^{239}Pu	$^{238}U^{1}H^{+}$, $^{207}Pb^{16}O_2^{+}$, $^{204}Pb^{35}Cl^{+}$, $^{199}Hg^{40}Ar^{+}$
^{240}Pu	$^{238}U^{1}H_2^{+}$, $^{208}Pb^{16}O_2^{+}$, $^{200}Hg^{40}Ar^{+}$,
^{241}Pu	$^{241}Am^{+}$, $^{206}Pb^{35}Cl^{+}$, $^{204}Pb^{37}Cl^{+}$, $^{209}Bi^{16}O_2^{+}$, $^{209}Bi^{32}S^{+}$,
^{241}Am	$^{241}Pu^{+}$, $^{206}Pb^{35}Cl^{+}$, $^{204}Pb^{37}Cl^{+}$, $^{209}Bi^{16}O_2^{+}$, $^{209}Bi^{32}S^{+}$, $^{201}Hg^{40}Ar^{+}$, $^{205}Tl^{36}Ar^{+}$
^{243}Am	$^{208}Pb^{35}Cl^{+}$, $^{207}Pb^{36}Ar^{+}$, $^{206}Pb^{37}Cl^{+}$, $^{209}Bi^{34}S^{+}$, $^{203}Tl^{40}Ar^{+}$

Using higher resolution (MR mode) can resolve most of the interferences, but result in decrease of sensitivity. Resolution between UH^{+} and ^{239}Pu can not be achieved with the highest resolution offered by SF-ICP-MS.

Chemical separation is essential for accurate determination.

Development of advanced mass spectrometric techniques for radionuclide analysis



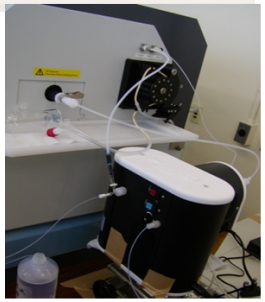
U concentration is 10^6-10^9 times higher than Pu in solid environmental samples such as soil, sediment

U in seawater: ca. 3 mg/m^3

Pu in seawater: ca. 0.2 pg/m^3

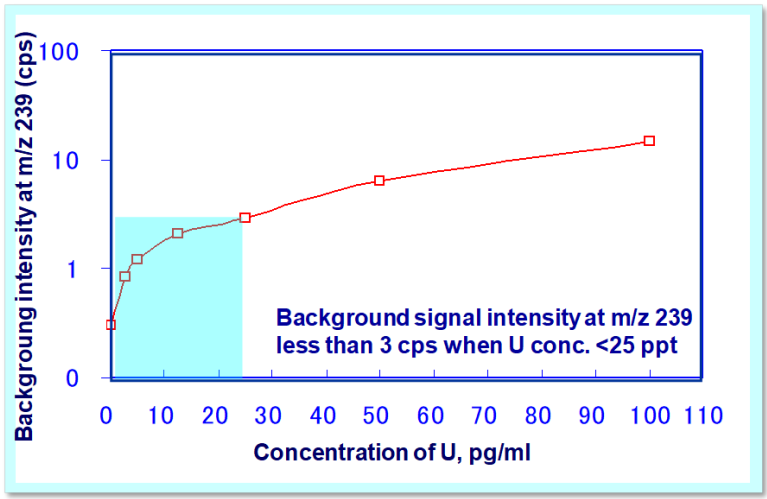
$$\frac{U}{Pu} = 10^{10}$$!!

Polyatomic interference from $^{238}UH^+$ and peak tailing of ^{238}U



UH^+/U^+
1.2-1.9x10^{-5}

APEX-Q-SF-ICP-MS analytical system



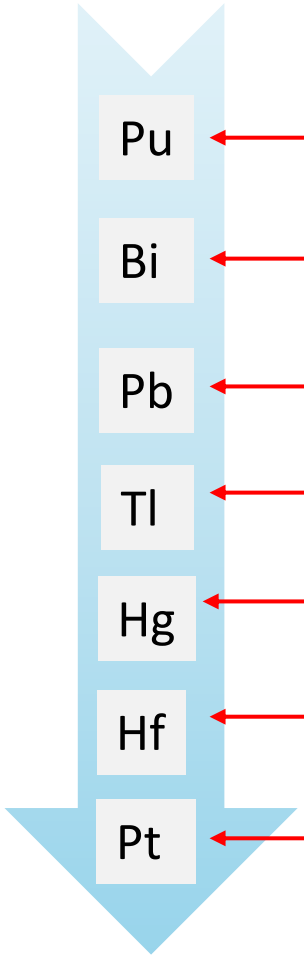
Elimination of UH^+ polyatomic interference

Zheng & Yamada, *Talanta*, 2006

Mathematical correction

$$^{239}Pu^+ \text{ signal} = \text{detected signal at m/z } 239 - \frac{^{238}UH^+}{^{238}U^+} \cdot (^{238}U^+ \text{ signal})$$

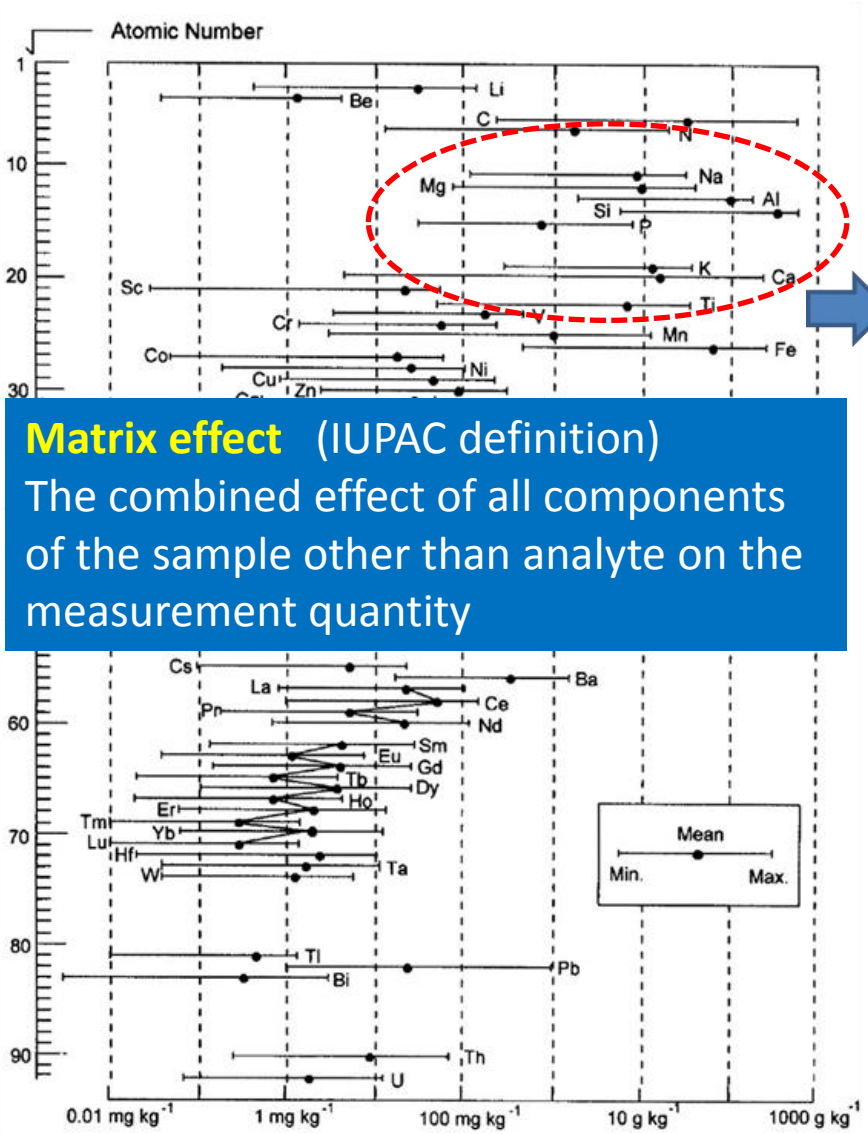
Isobaric/polyatomic interferences in ICP-MS analysis of ^{241}Am



Isobaric/Polyatomic interferences of ^{241}Am	Total mass	Resolution required (m/Δm)
^{241}Pu	241.05685	11,400,000
$^{240}Pu^{1}H$	241.06163	50122
$^{209}Bi^{32}S$	240.95246	2310
$^{209}Bi^{16}O_2$	240.97022	2784
$^{206}Pb^{35}Cl$	240.94331	2124
$^{204}Pb^{37}Cl$	240.93894	2045
$^{205}Tl^{36}Ar$	240.94197	2099
$^{207}Pb^{34}S$	240.94376	2132
$^{201}Hg^{40}Ar$	240.93268	1942
$^{179}Hf^{14}N^{16}O_3$	240.93363	1957
$^{178}Hf^{14}N^{16}O_3{}^{1}H$	240.93934	2052
$^{195}Pt^{14}N^{16}O_2$	240.95769	2432
$^{194}Pt^{14}N^{16}O_2{}^{1}H$	240.96340	2580
$^{204}Hg^{37}Cl$	240.93939	2053
$^{208}Pb^{16}O_2{}^{1}H$	240.97430	2921

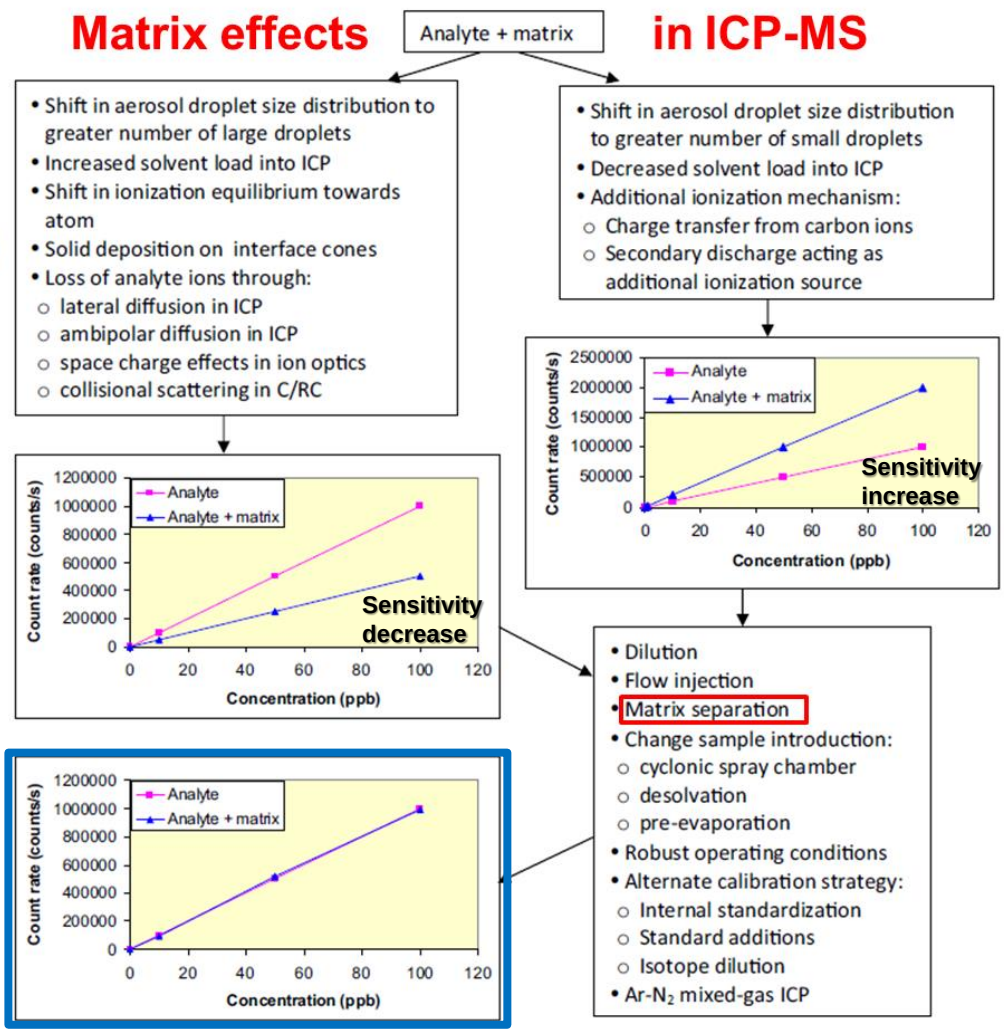
If medium resolution mode (m/Δm=4000) is used, most of interferences can be solved. →Decrease of sensitivity (^{241}Am, 432 y, lower sensitivity compared to Pu) →**large sample size for ultra-trace analysis**

Matrix effect in ICP-MS measurement



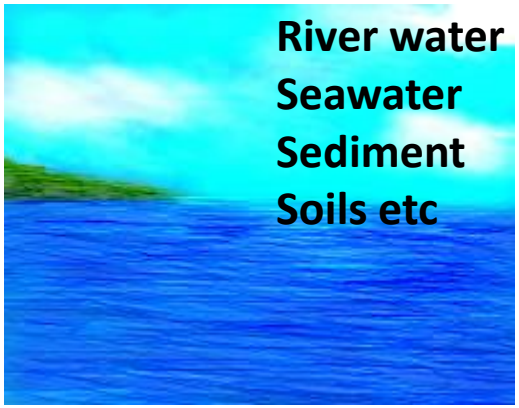
Matrix effect (IUPAC definition)
The combined effect of all components of the sample other than analyte on the measurement quantity

Concentration ranges of trace and ultra-trace elements in soils of Japan. Data from Yamasaki et al. 2001



Agatemor and Beauchemin, ACA, 2011

Determination of radionuclides in environmental samples by ICP-MS



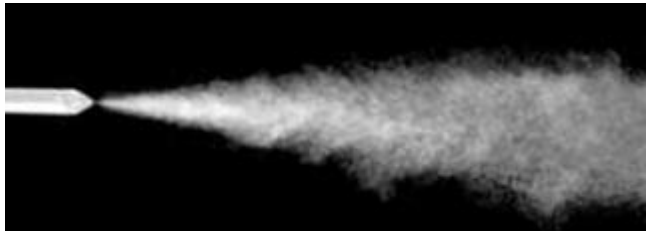
Liquid Samples → Concentration/separation → Sample Solution

Solid Sample → Ash → Digestion (Heat block digestion, Microwave digestion) → Sample Solution

Sample Solution → Extraction → Co-precipitation (Matrix removal) / Chromatographic separation

Sample Solution / Chromatographic separation → Liquid introduction ICP-MS

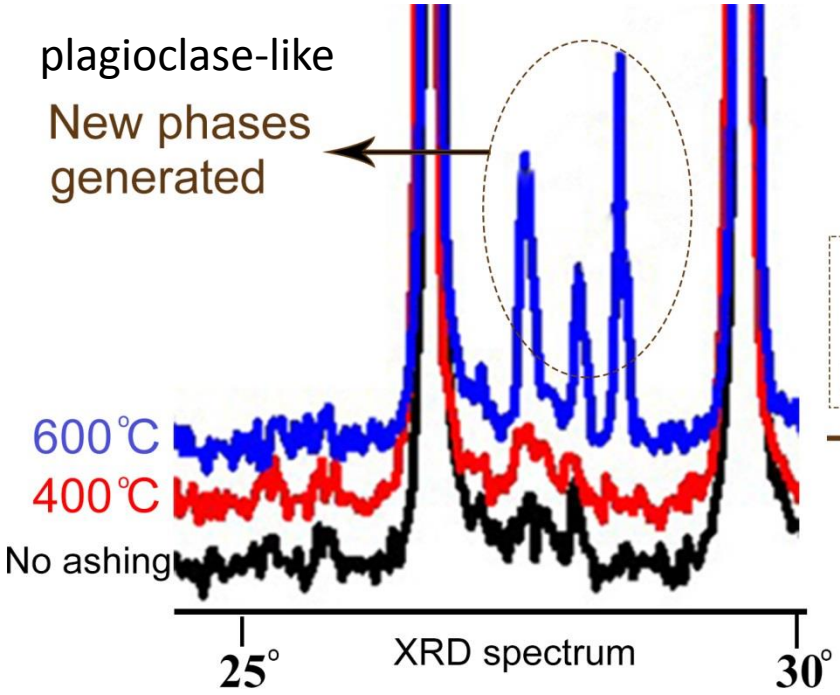
High Matrix Liquid Sample → Solid phase extraction / Co-precipitation → Pretreated Liquid Sample → Liquid introduction ICP-MS



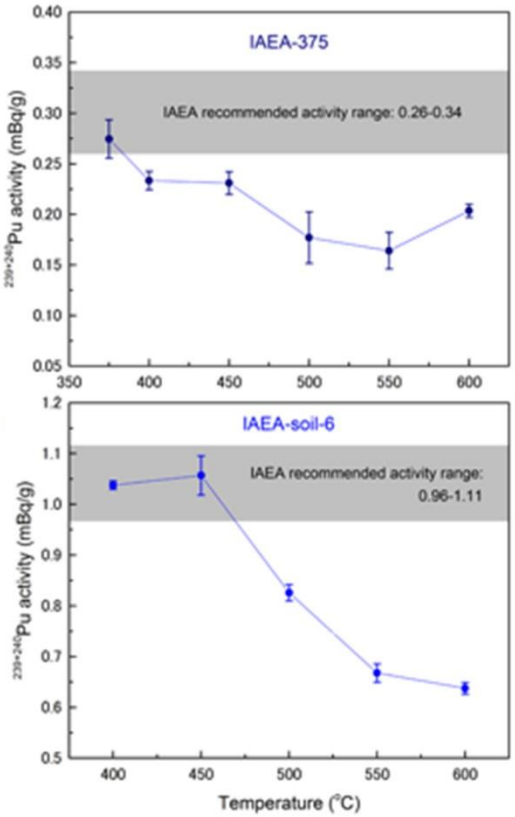
High efficiency sample introduction

NIRS

Ashing temperature effect on Pu analysis in soil samples



HNO_3 leaching
Pu separation
ICP-MS measurement



High temperature ashing for soil samples

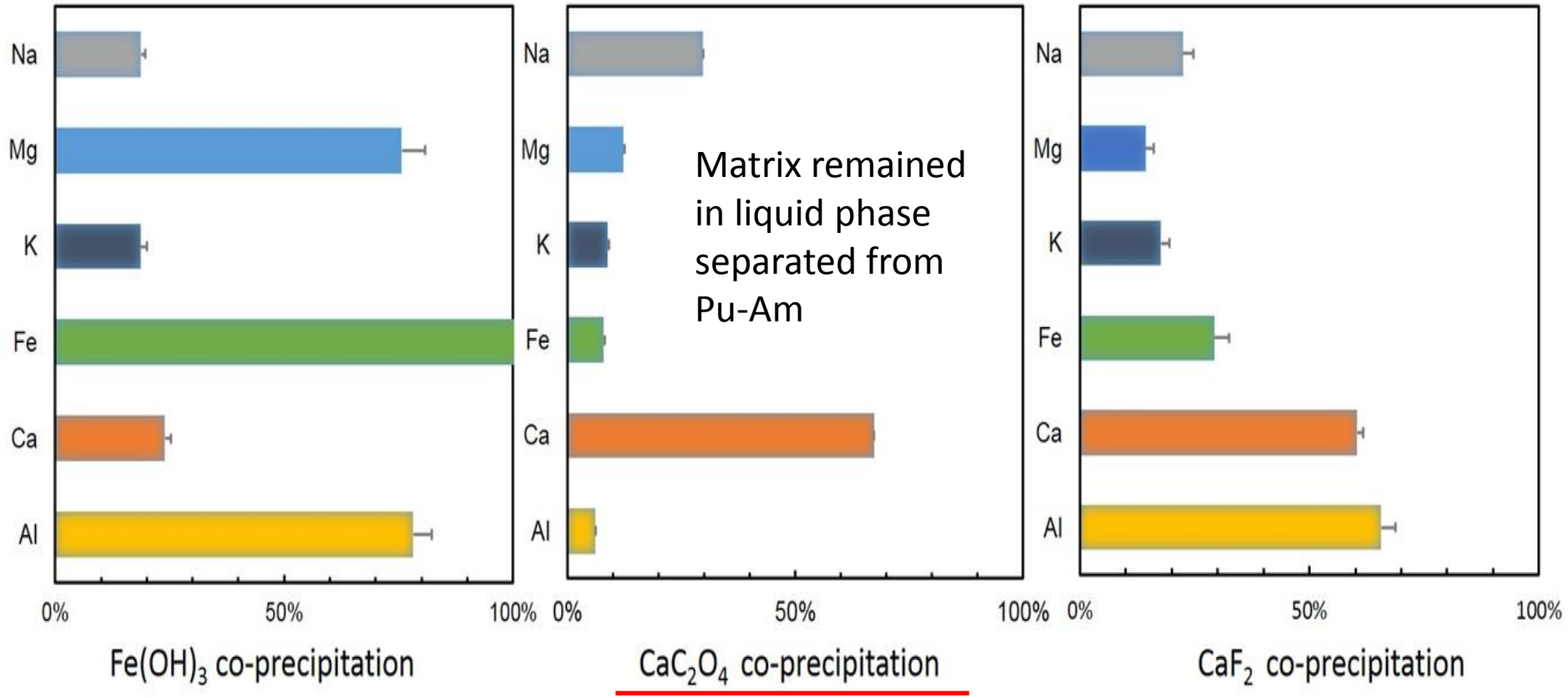
Refractory fractions formed during ashing → Insoluble in HNO_3 → Pu loss

High temperature ashing resulted in Pu loss

Wang, Yang, Zhneg et al. Anal Chem 2015*

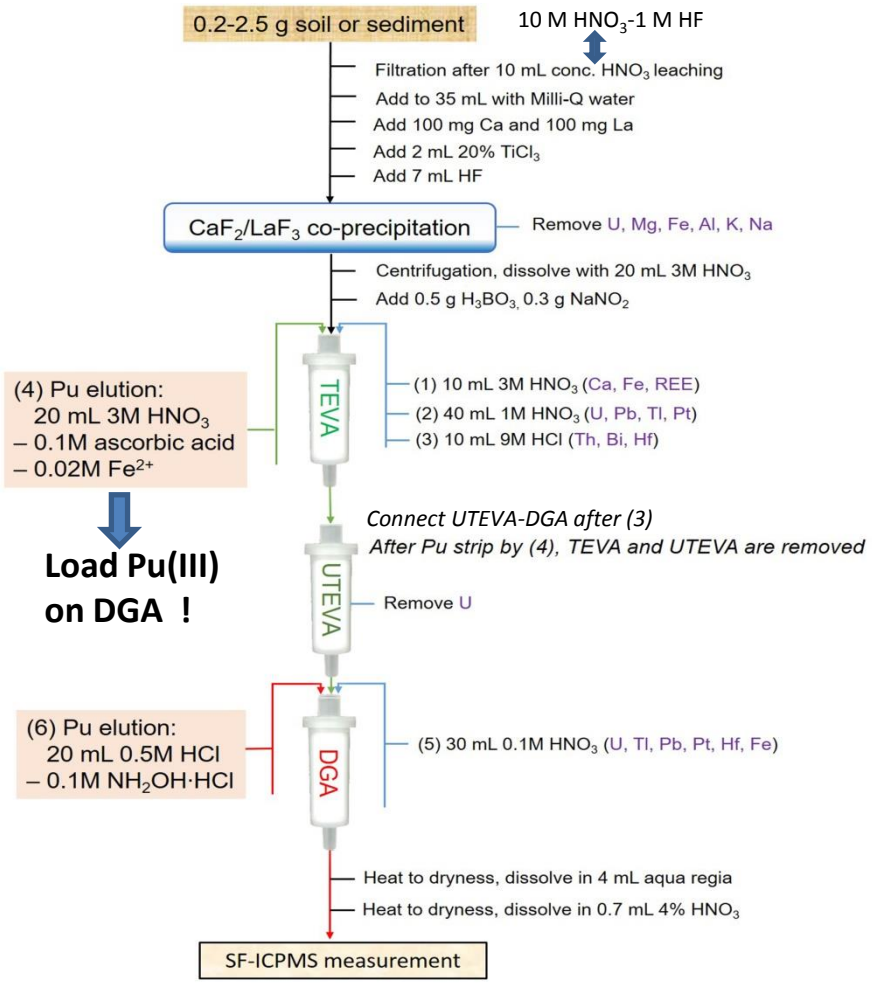
Matrix effect in ICP-MS measurement

Co-precipitation: matrix removal



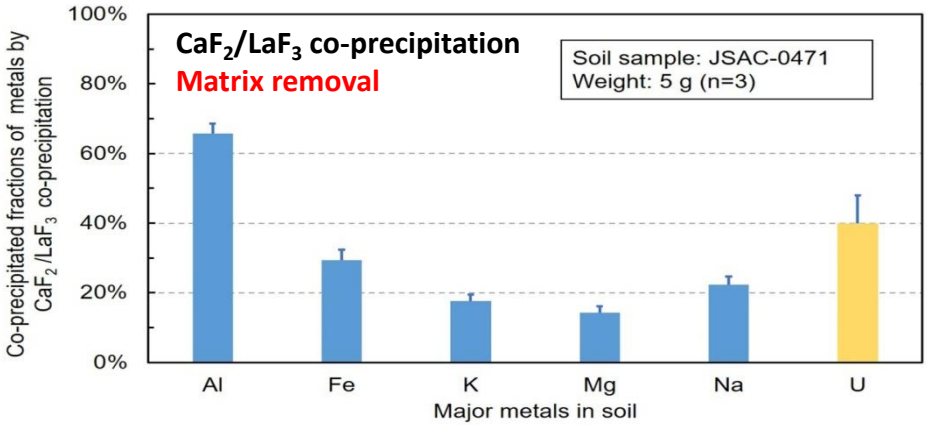
Co-precipitated percentage of soil matrix by $Fe(OH)_3$, CaC_2O_4 and CaF_2 co-precipitations (n=3)

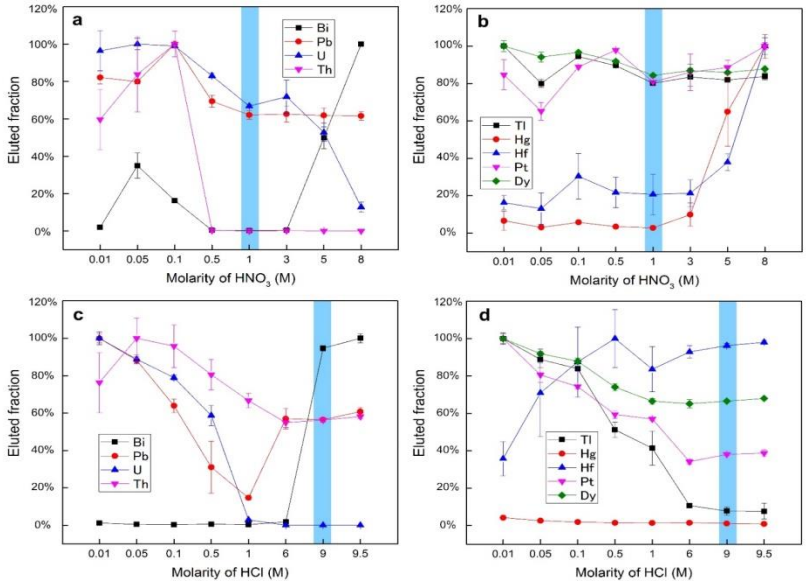
Pu separation based on extraction chromatography TEVA-UTEVA-DGA



Analytical procedure for soil, sediments

Wang, Zheng et al., Anal Chem. 2017*





Separation of interfering elements

Pu separation based on extraction chromatography

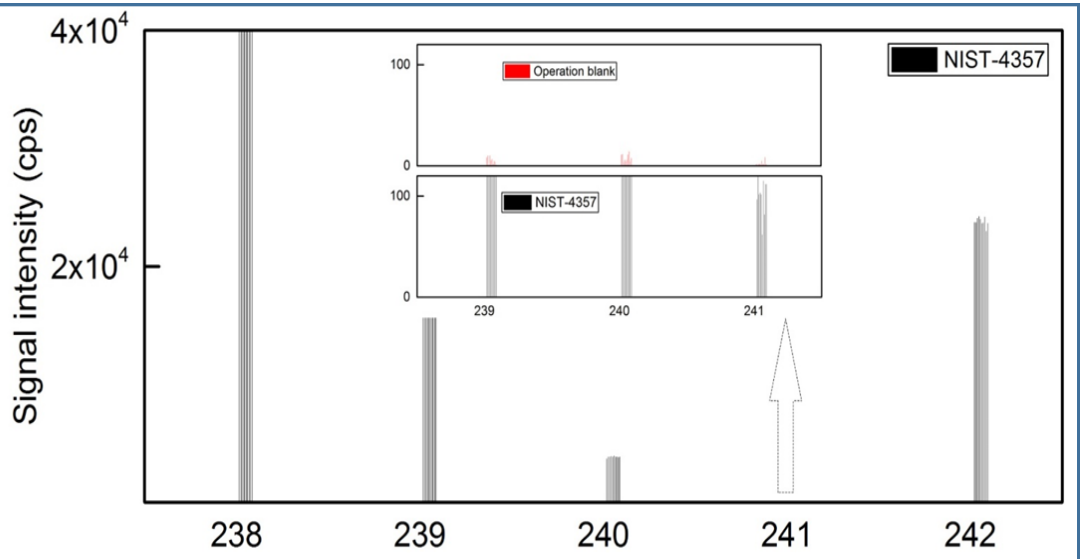
Soil/Sediment samples

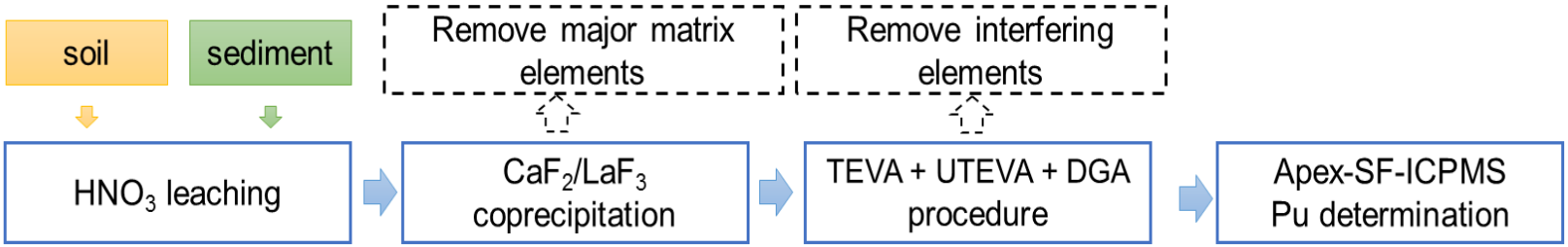
High Pu recovery
> 90 %

High U decontamination factor
1.6 x10^7

Low limit of detection
(1 g sample) 0.09-0.24 fg g^{-1}

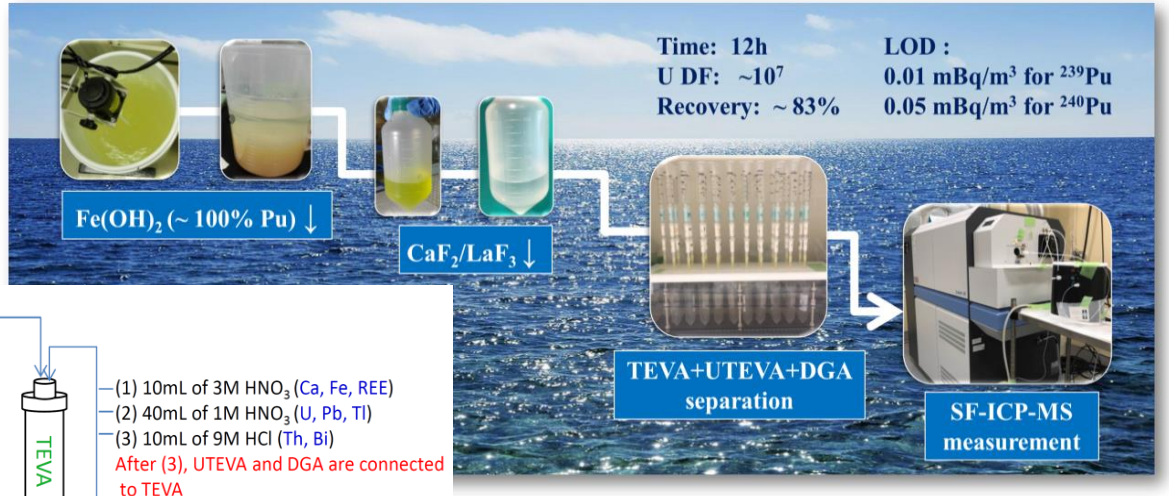
Rapid analysis
High sample throughput
20 samples/12 hours





Pu separation based on extraction chromatography
For small volume seawater samples (10-20 L)

Seawater
Pu(V) or Pu(VI)
↓
Pu(III)
favorable under-go co-precipitation



~15L of pre-filtered seawater (pH=2)

- Add 125mg Fe^{3+}
- Add 7.5 ml of 20% $TiCl_3$
- Add NH_3H_2O to pH=8.8-9.0

(under stirring)

- Settle for several hours
- Centrifuge, 3000rpm, 15min

$Fe(OH)_2$ co-precipitation

- Dissolve with 20mL of cocn. HNO_3
- Add 0.57pg ^{242}Pu spike
- Add 100mg Ca^{2+} and 100mg La^{3+}
- Add 7mL of conc. HF
- Centrifuge, 3000rpm, 15min

CaF_2/LaF_3 co-precipitation

- Add 0.5g of H_3BO_3
- Add 20mL of 3M HNO_3
- Add 0.3g of $NaNO_2$

Pu(IV)-3M HNO_3 solution

TEVA
- (1) 10mL of 3M HNO_3 (Ca, Fe, REE)
- (2) 40mL of 1M HNO_3 (U, Pb, Tl)
- (3) 10mL of 9M HCl (Th, Bi)

After (3), UTEVA and DGA are connected to TEVA

- (4) Pu elution: 20mL of 3M HNO_3-0.1M VC-0.02M Fe^{2+}

Remove U

UTEVA

After (4), TEVA and UTEVA are removed from DGA

DGA
- (5) 30mL of 0.1M HNO_3 (U, Th, Pb, Tl, Fe)
- (6) Pu elution: 20mL of 0.5M HCl-0.1M NH_3OHCl

Pu(III)-0.5M HCl-0.1M NH_3OHCl solution

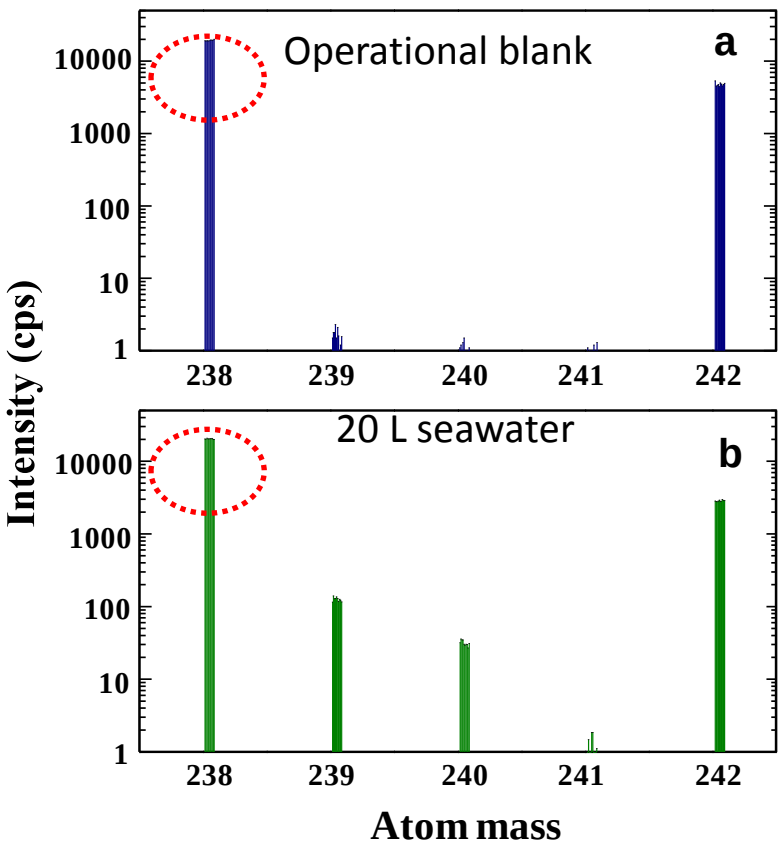
- Heat to dryness, dissolve in 4mL aquq regia
- Heat to dryness, dissolve in 1mL of ultrapure HNO_3
- Heat to dryness, dissolve in 0.7mL of 4% HNO_3

SF-ICP-MS measurement

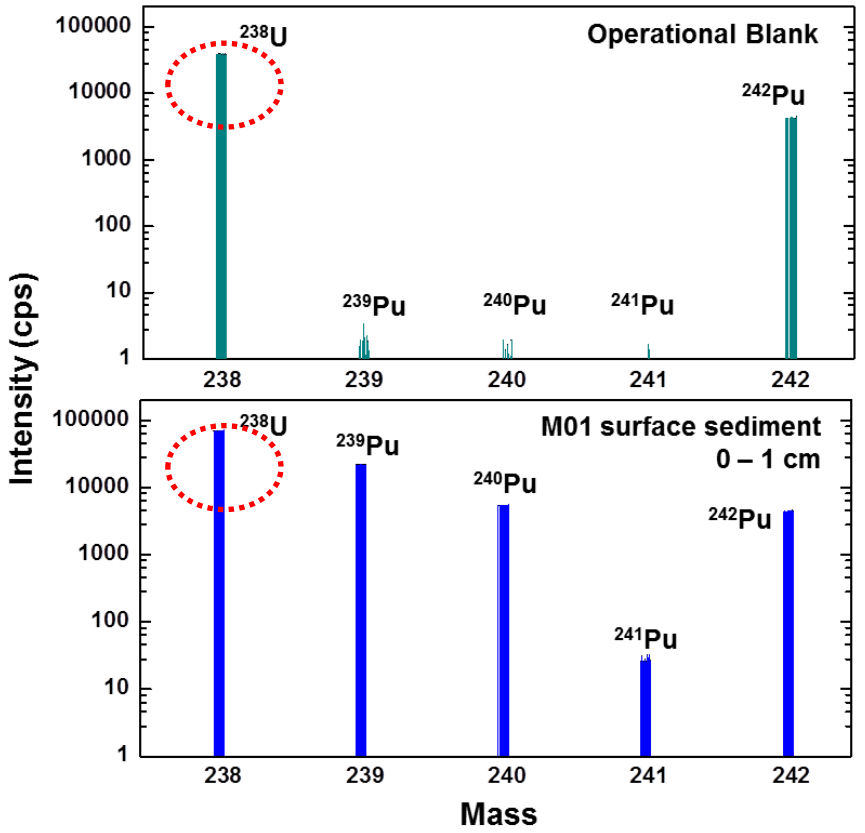
High Pu concentration efficiency of $Fe(OH)_2$ (ca. 100%), Pu-242 can be added after the $Fe(OH)_2$ co-precipitation.

Making it possible: on-boat Co-precipitation without adding Pu-242

Extremely high U DF: interference free Pu measurement



Mass spectrum of 20 L seawater



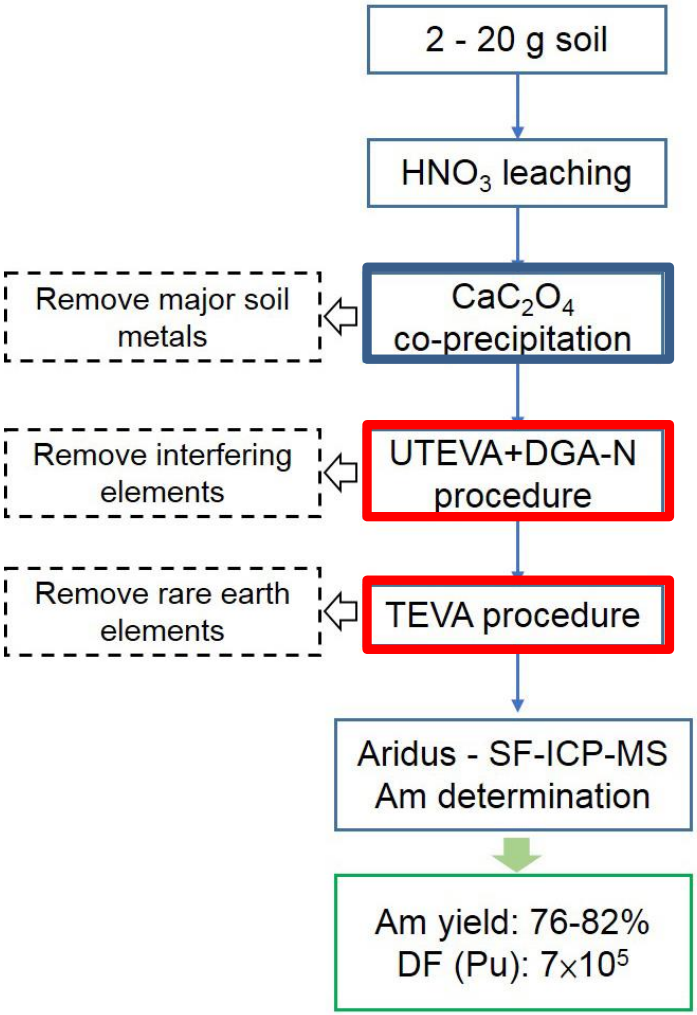
Mass spectrums for sediment (30g)

U decontamination factors:
Sediment method: 2×10^6
Seawater method: 1×10^8

UH^+/U ratio for our system: $1\sim3 \times 10^{-5}$
Desolvation system

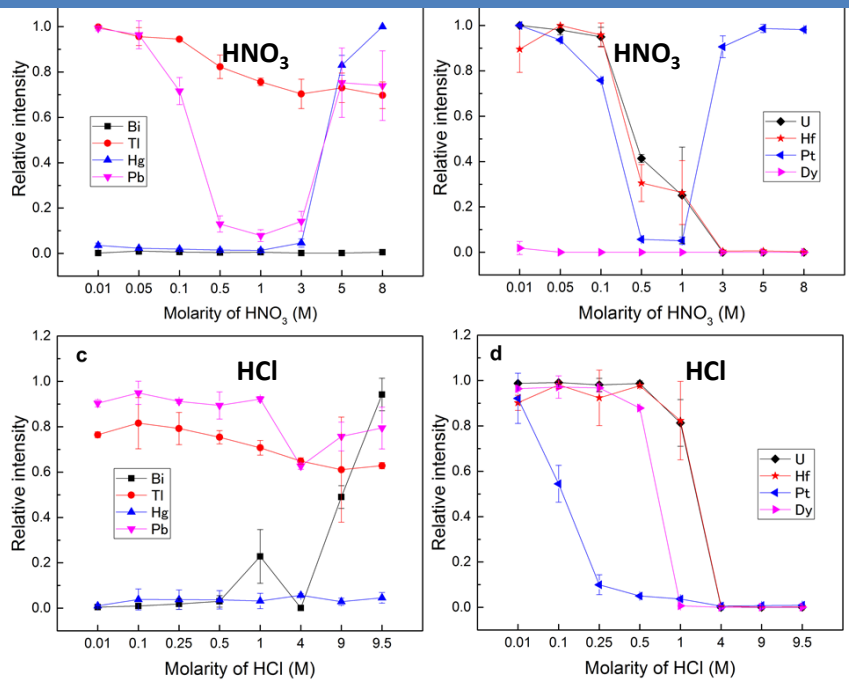
Contribution of UH^+ to ^{239}Pu intensity: **< 1 cps**
No math correction!

Separation chemistry for ^{241}Am analysis by SF-ICP-MS

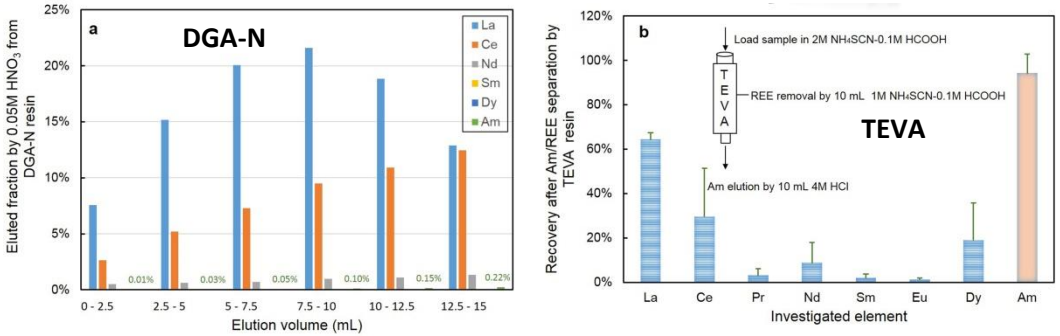


For large size soil samples,
REEs cause matrix effect for ICP-MS!

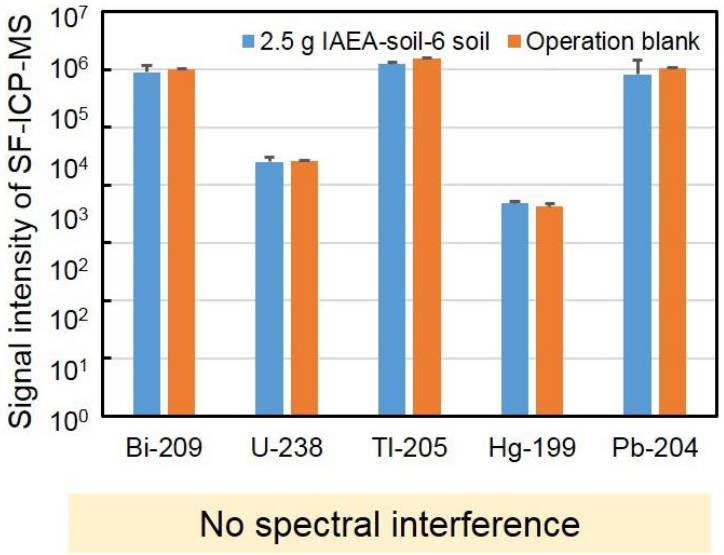
The behaviors of interfering elements on DGA-N resin

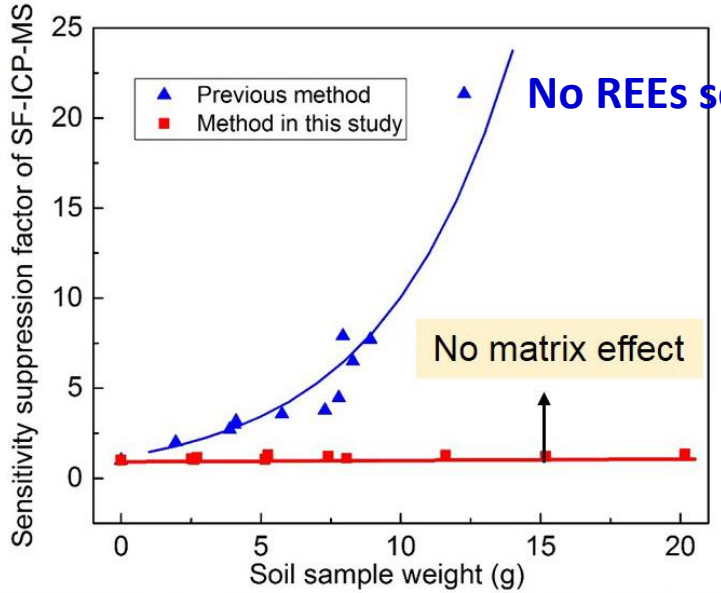


Separation Am from REEs in DGA-N and TEVA resins

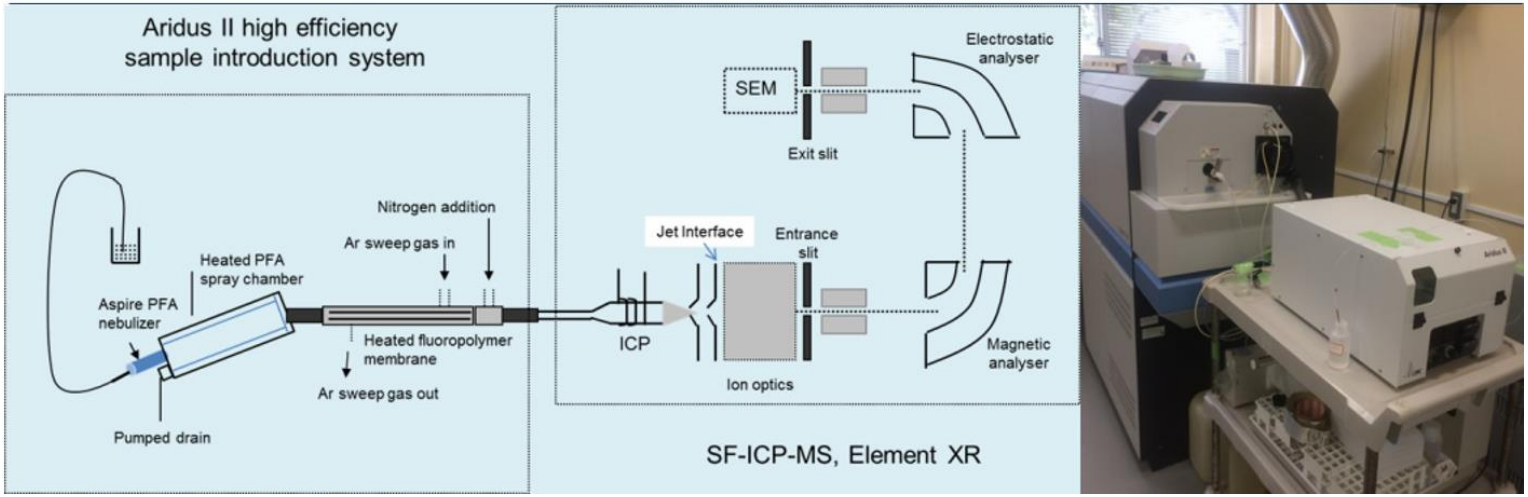


ICP-MS for ultra-trace measurement of ^{241}Am





No REEs separation



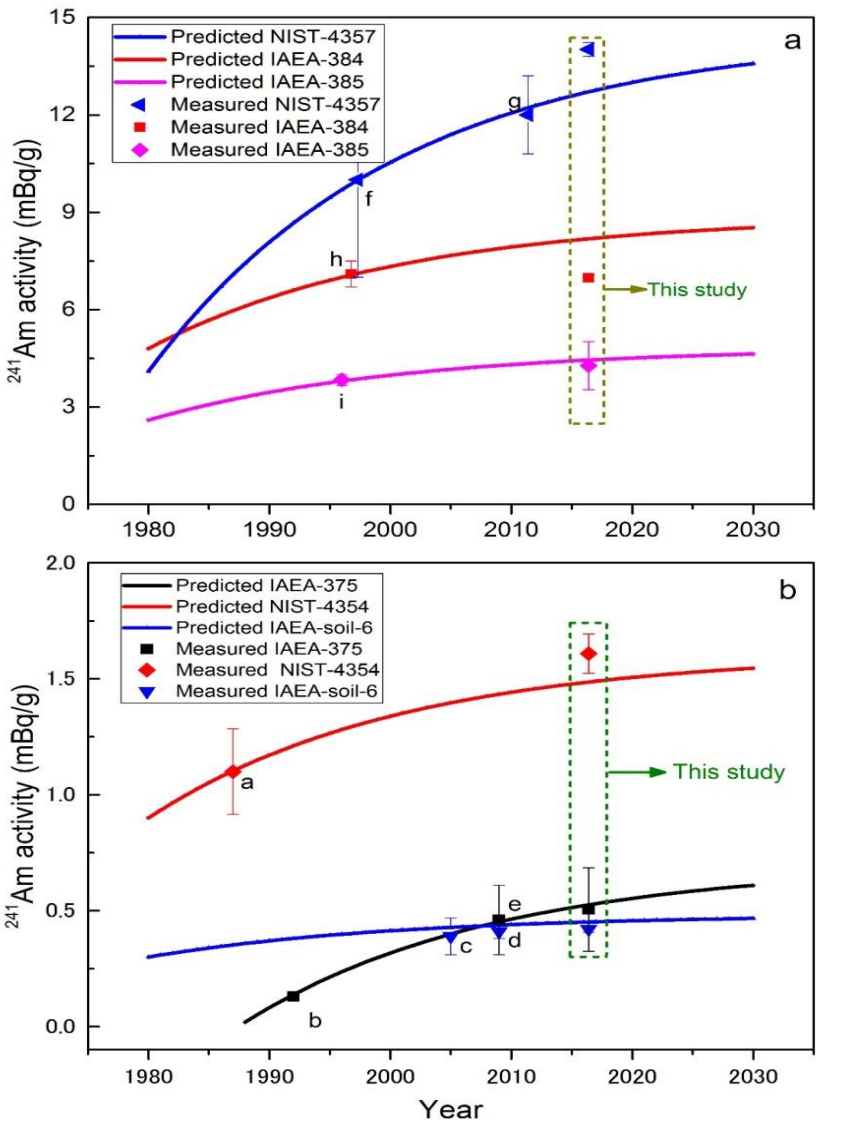
Wang, Zheng, Tagami et al. Anal Chem 2016*

ICP-MS measurement of ^{241}Am: method validation

NIST 4357	**IAEA-375**
IAEA-384	**IAEA-soil-6**
IAEA-385	**NIST-4354**

- The agreement between measured ^{241}Am activities and certified values validated the accuracy of developed method.
- The chemical recovery of Am is steady for soil and sediment samples (**76% to 82%).**
- The low LOD (0.012 mBq/g or **0.024 fg/mL**) makes this method suitable for analysis of ultra-trace level Am in large soil samples **(2-20g**).

^{241}Am analysis in six reference materials

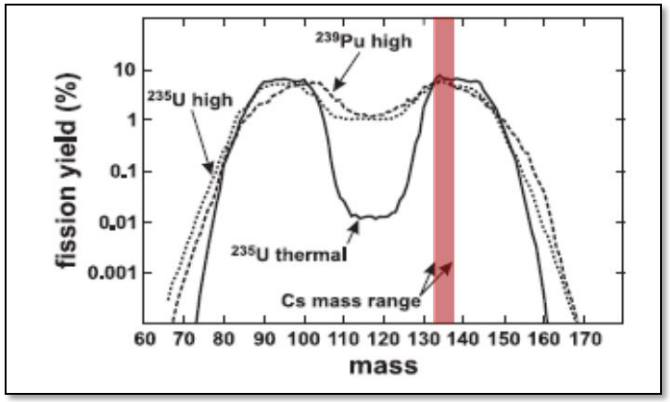


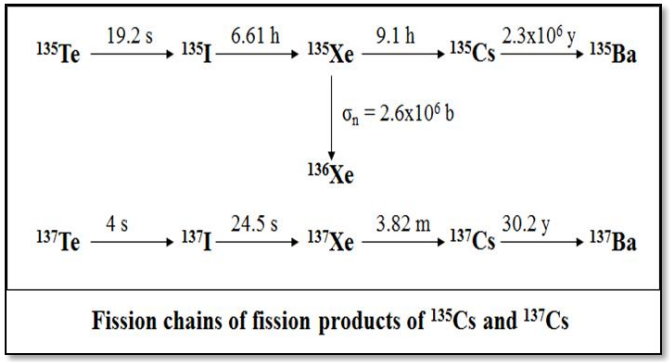
Sources of radiocesium isotopes in the environment

- High yield fission products 6.535% for ^{135}Cs and 6.236% for ^{137}Cs from thermal neutron fission of ^{235}U.

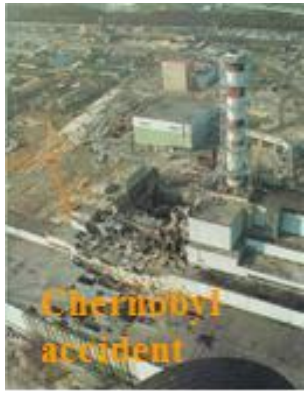
- A shielding of ^{135}Cs occurs due to neutron capture of its precursor, ^{135}Xe, to form ^{136}Xe, whereas production of ^{137}Cs is unaffected. This process causes a high degree of variance of $^{135}Cs/^{137}Cs$ isotope ratio with source.

Chernobyl accident: 0.28-0.32
Global fallout source: *ca*. 2.0-2.7
Fukushima accident: 0.34 (2011/3/11)





Fission chains of fission products of ^{135}Cs and ^{137}Cs



Challenge for ^{135}Cs and ^{137}Cs analysis

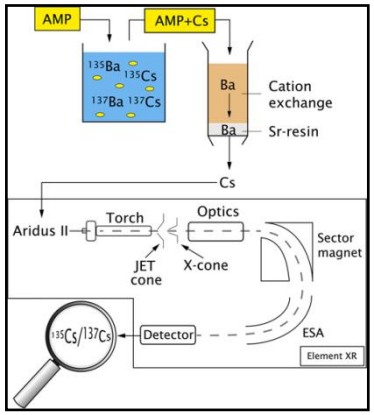
- **Due to the long half life (2.3x10^6 y) and low-energy β-decay (205 keV),**
  the radiometric counting method is impractical for environmental samples

- Only TIMS and ICP-MS with reaction cell realized **^{135}Cs and ^{137}Cs analysis in environmental samples**.

  TIMS: Lee et al., GCA, 1993; Snow et al. IJMS, 2015; Snyder et al., JER, 2012; Shibahara et al., JNST, 2014

  ICP-MS: Taylor et al., JER, 2008, **ICP-QMS**; Russell et al., AC, 2014, **SF-ICP-MS**;
  Zheng et al., AC, 2014, **ICP-MS/MS**; Ohno et al., JAAS, 2014, **ICP-MS/MS**

Russell et al., AC, 2014, **SF-ICP-MS**



Difficulties of ^{135}Cs analysis using ICP-MS

- **Polyatomic interferences**

  ^{135}Cs ^{95}Mo^{40}Ar ^{119}Sn^{16}O

  ^{137}Cs ^{97}Mo^{40}Ar ^{121}Sb^{16}O

- **Isobaric interferences**

  ^{135}Cs ^{135}Ba (abundance 6.592 %)

  ^{137}Cs ^{137}Ba (abundance 11.232 %)

  Ba conc. in soil ca. 550 ppm

- **Interferences from stable ^{133}Cs: peak tailing**

  In environmental samples, global fallout source:

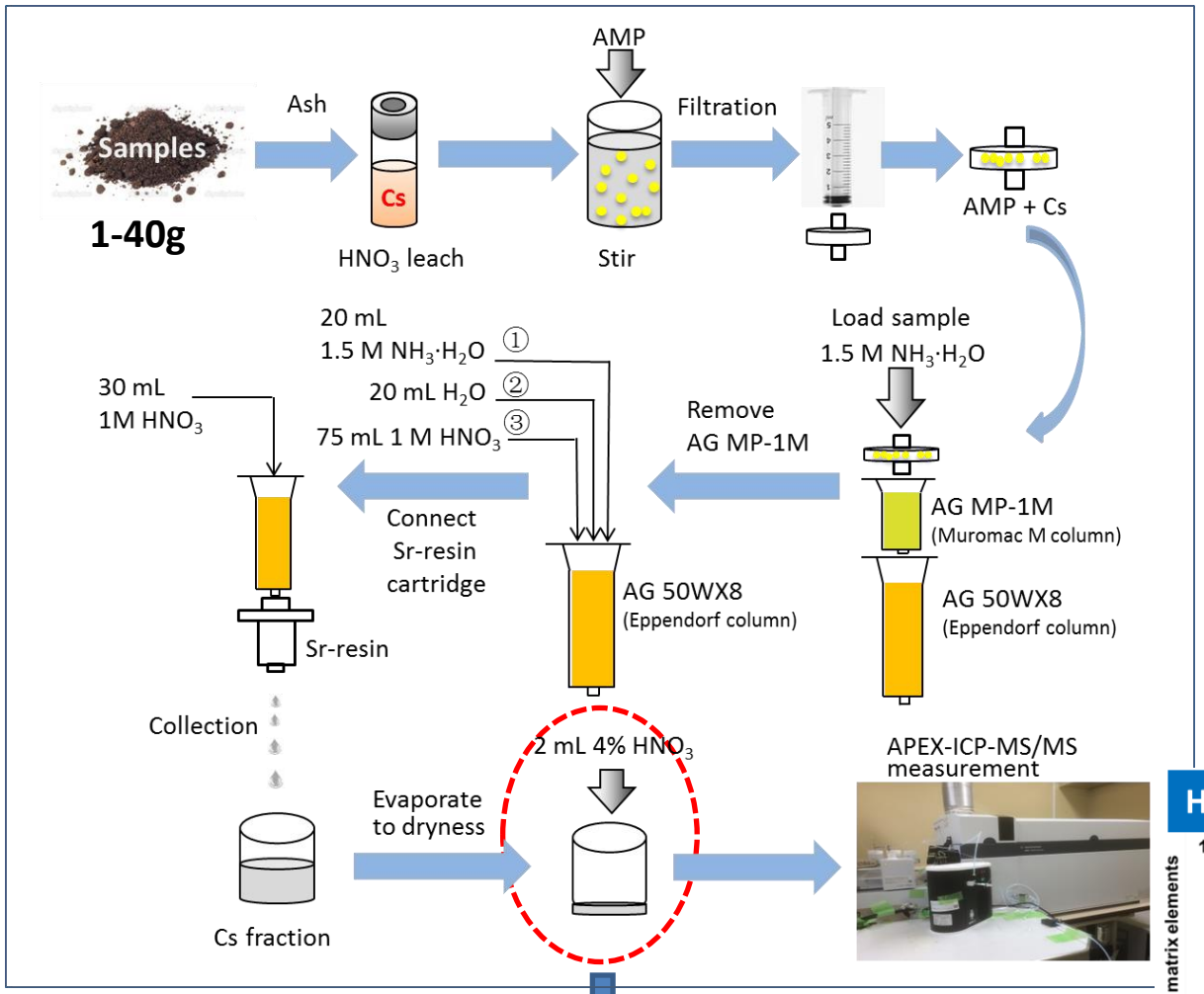
  ^{133}Cs/^{135}Cs ⇒ 10^9

  Need high abundance sensitivity!

- **Sample matrix effect: Na, K, Ca, Mg**

  Salts deposition in cones, sensitivity suppression

Chemical separation for environmental samples



AMP Cs selective adsorption

↓

AG MP-1 M Anion-exchange resin

Separation Mo, Sb, Sn

↓

AG 50W-x8 Cation-exchange resin & Sr resin

Separation major matrix and Ba

High decontamination factors for interfering elements

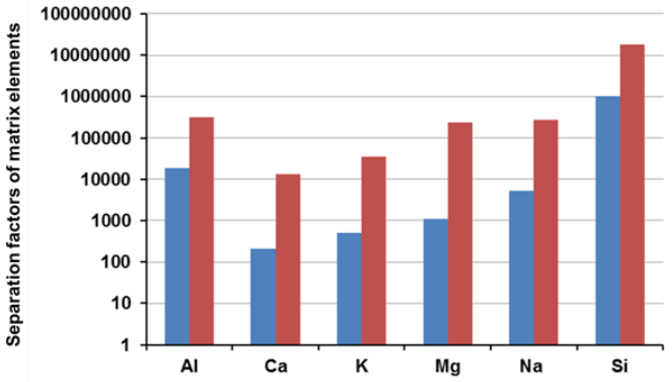
Ba	10^5 - 10^6
Mo	10^6 - 10^7
Sb	10^4 - 10^5
Sn	10^4 - 10^5

Ba, Mo < 5 ppb

Sn, Sb < 0.5 ppb

Cs recovery: 95 %

High decontamination factors for matrix



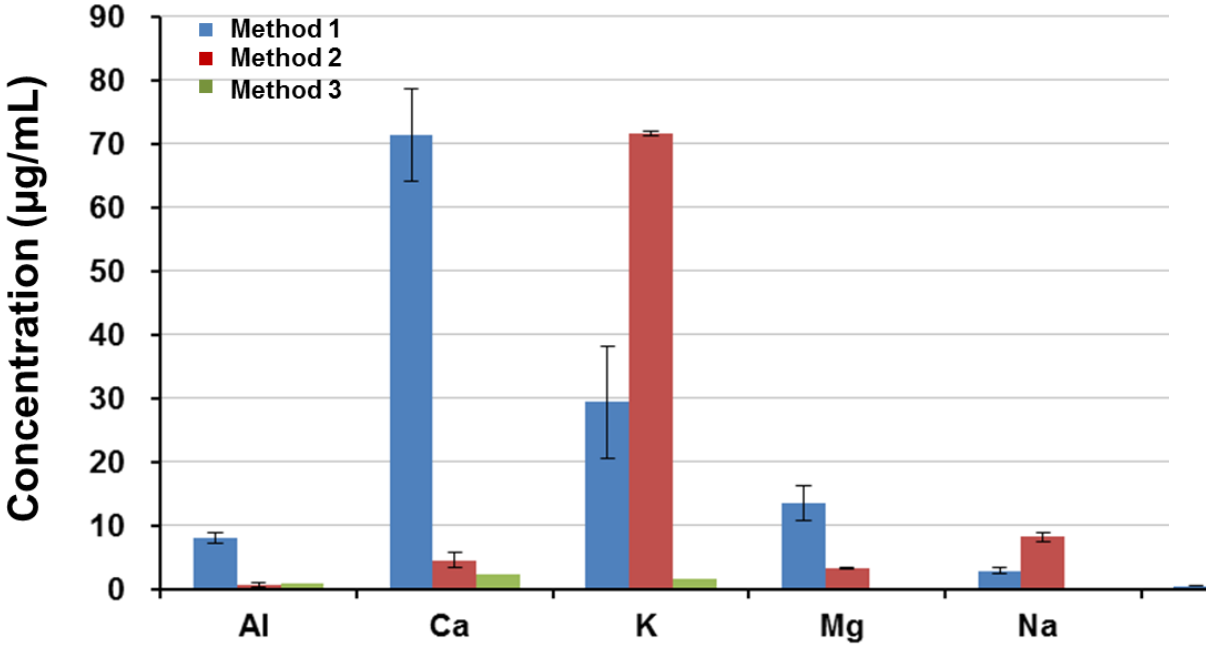
Matrix elements separation

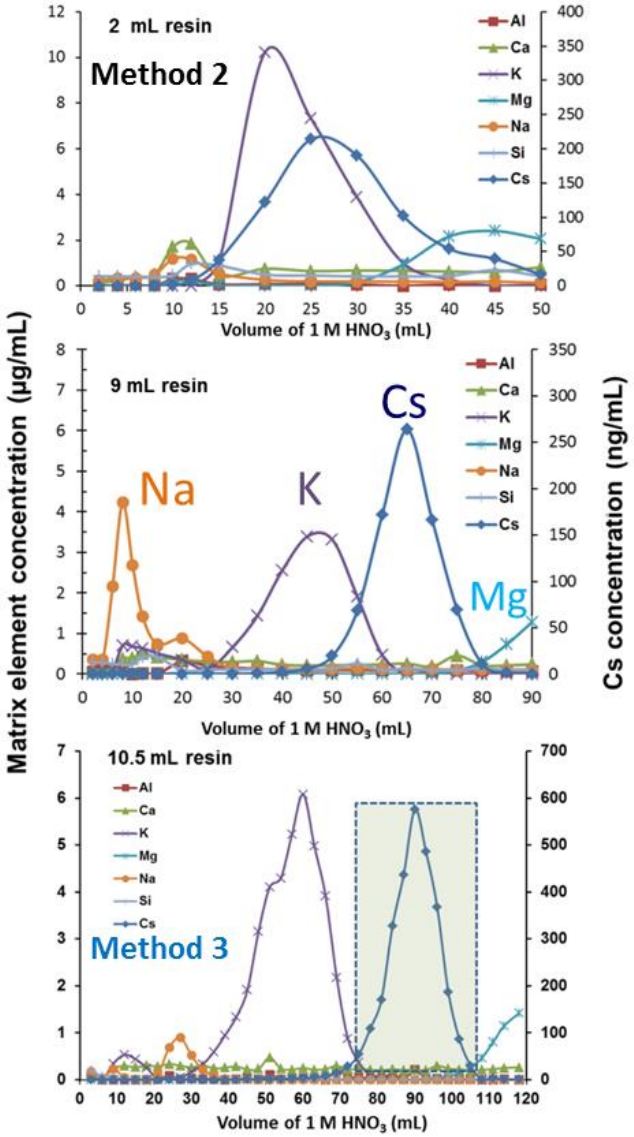
AG 50W-X8 Cation-exchange column

Method 1: Muromac M , 1.5 M HCl

Method 2: Muromac M, 1 M HNO_3 with Sr resin

Method 3: Eppendorf column, 1 M HNO_3 with Sr resin





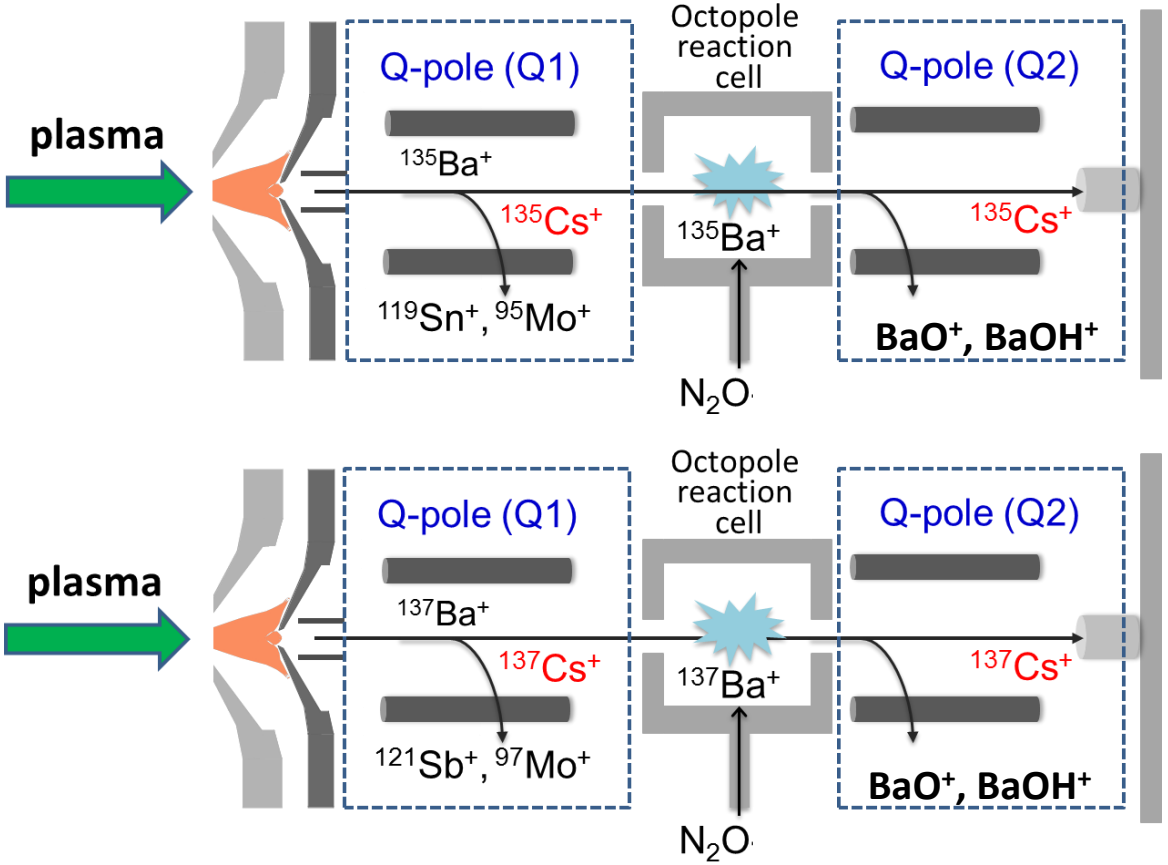
Concentrations of matrix elements (Al, Ca, K, Mg, Na and Si) in the final 2 mL Cs fraction sample for APEX-ICP-MS/MS analysis.

Zheng et al., Anal Chem., 2016b

^{135}Cs and ^{137}Cs analysis using ICP-MS/MS

Chemical resolution

Finally, Q2 is set to measure the desired ^{135}Cs and ^{137}Cs



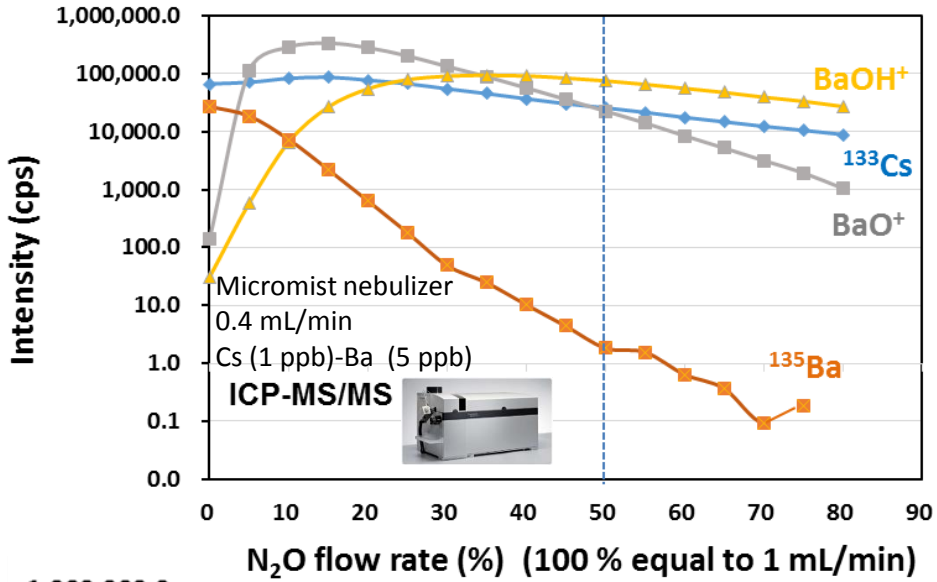
Target ions are separated from matrix ions by Q1 set at *m/z* 135 and 137, respectively, and they enter the collision/reaction cell where

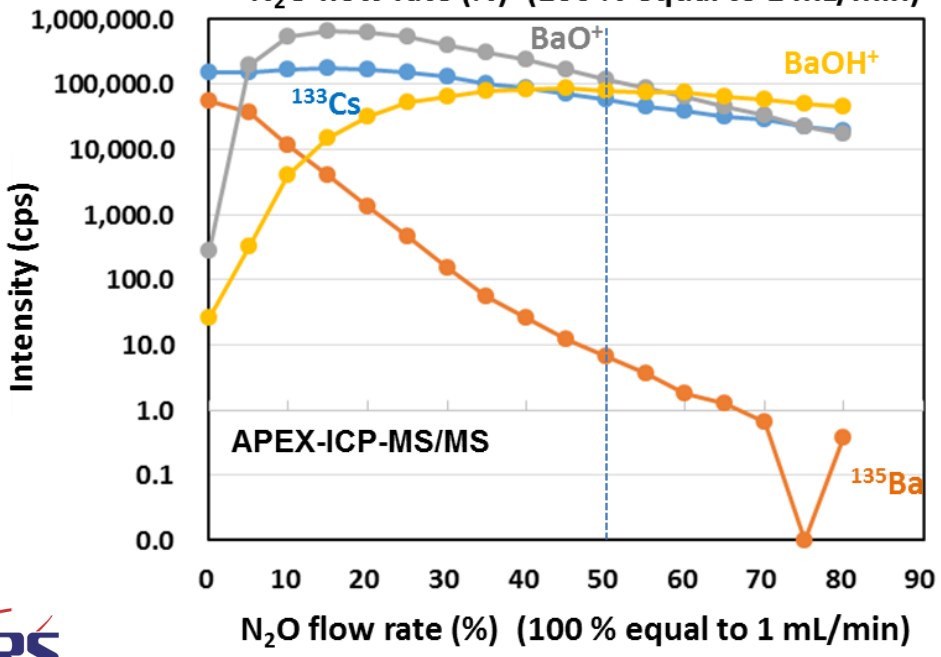
- **they react with N_2O to separate Cs/Ba,**
- **eliminate $MoAr^+$ polyatomic interference,**
- **suppress formation of SbO^+ and SnO^+.**

Zheng et al., Anal Chem., 2014

Chemical resolution of Cs from interfering Ba in ICP-MS/MS

APEX desolvation system for sensitivity increase





ion-molecule reaction

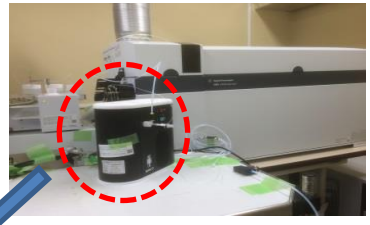
$Ba^+ + N_2O \Rightarrow BaO^+, BaOH^+$

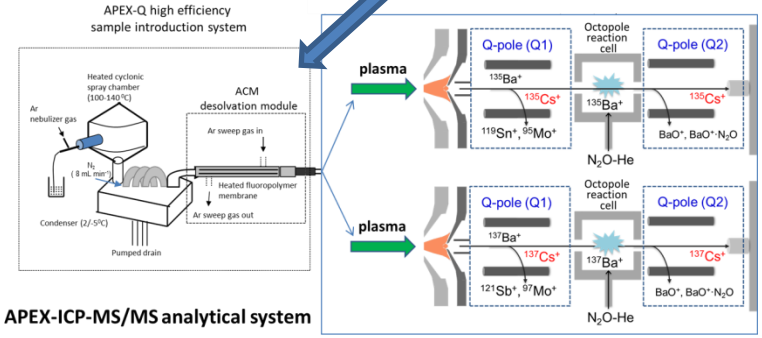
Cs^+ remains unreactive

APEX-ICP-MS/MS,

Micromist nebulizer 0.4 mL/min, Cs (0.2 ppb)-Ba (1 ppb)

Sensitivity enhancement 11 times





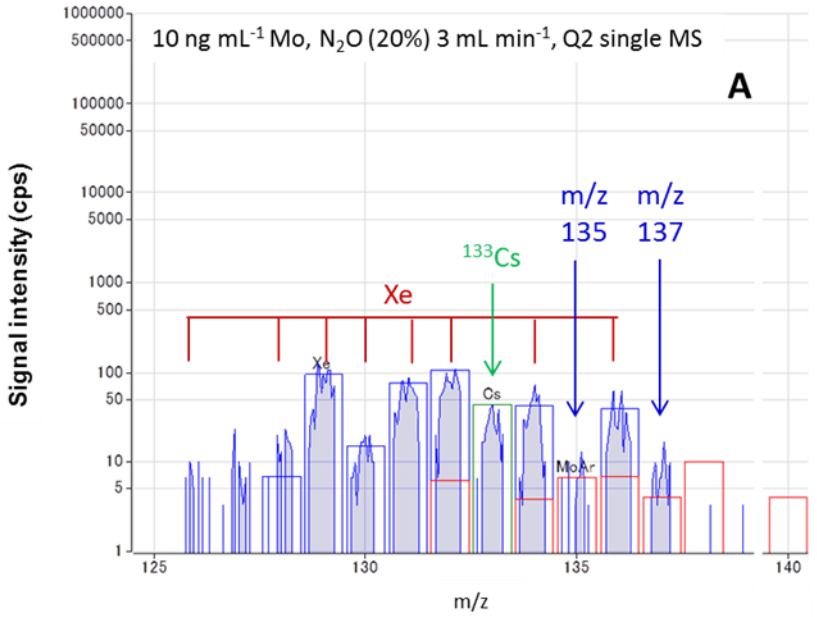
APEX-ICP-MS/MS analytical system

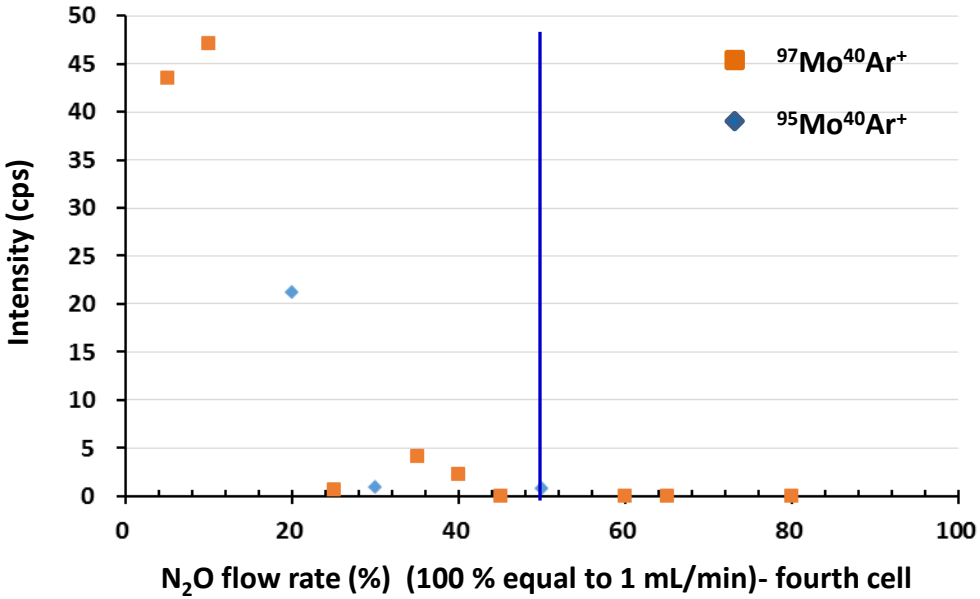
Eliminate/reduce polyatomic interferences in ICP-MS/MS

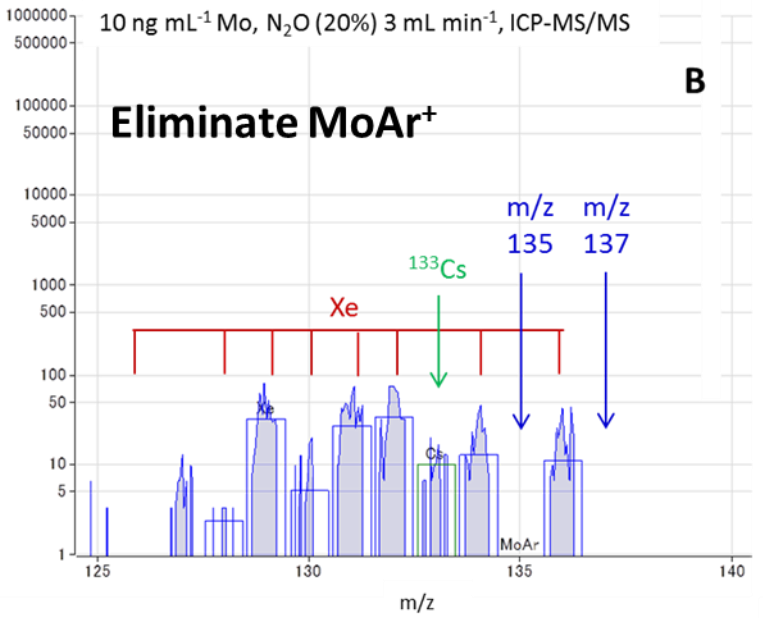
$^{95,97}Mo^{40}Ar$ interference

Best condition:
N_2O Flow rate 50%
(0.5 mL/min)

Interferences from $^{95}Mo^{40}Ar^+$ and $^{97}Mo^{40}Ar$ were negligible

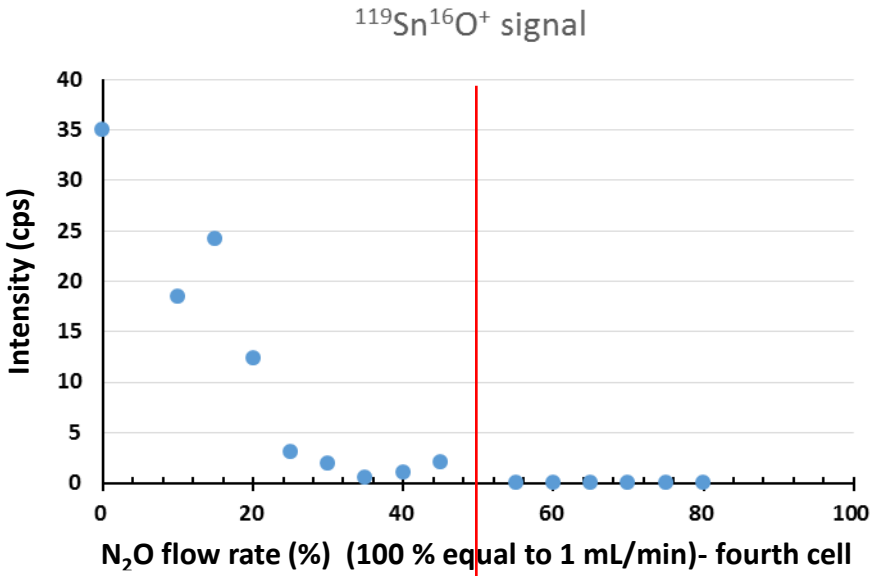


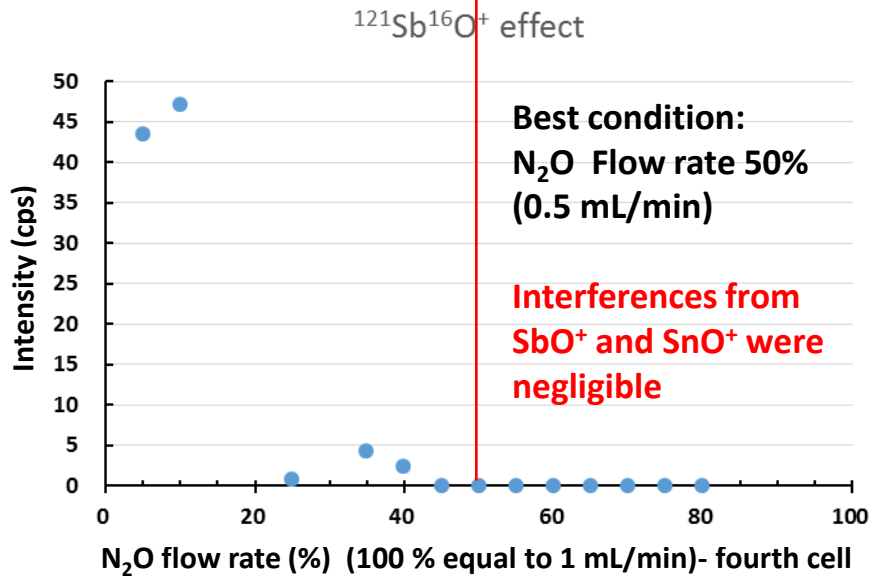




Eliminate/reduce polyatomic interferences in ICP-MS/MS

$^{119}Sn^{16}O$ and $^{121}Sb^{16}O$ interferences

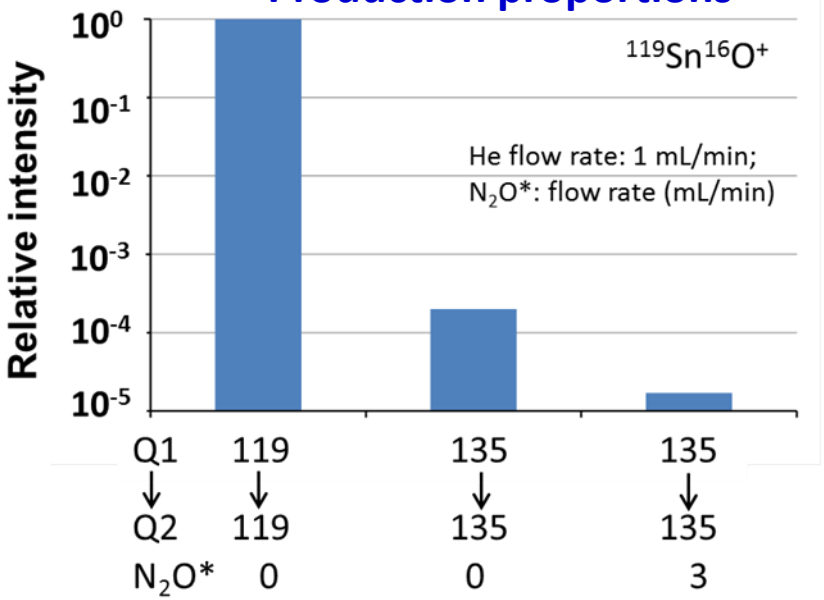




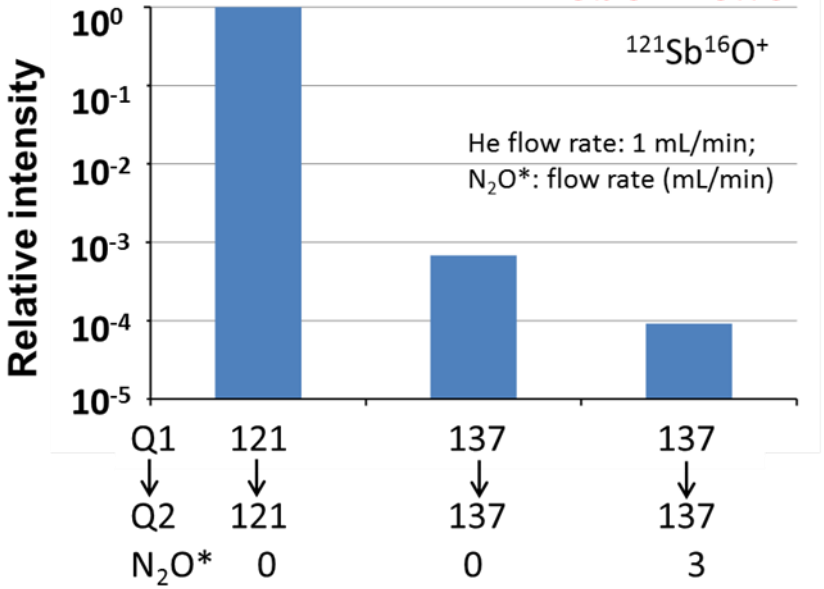
Best condition:
N_2O Flow rate 50%
(0.5 mL/min)

Interferences from SbO^+ and SnO^+ were negligible

Production proportions

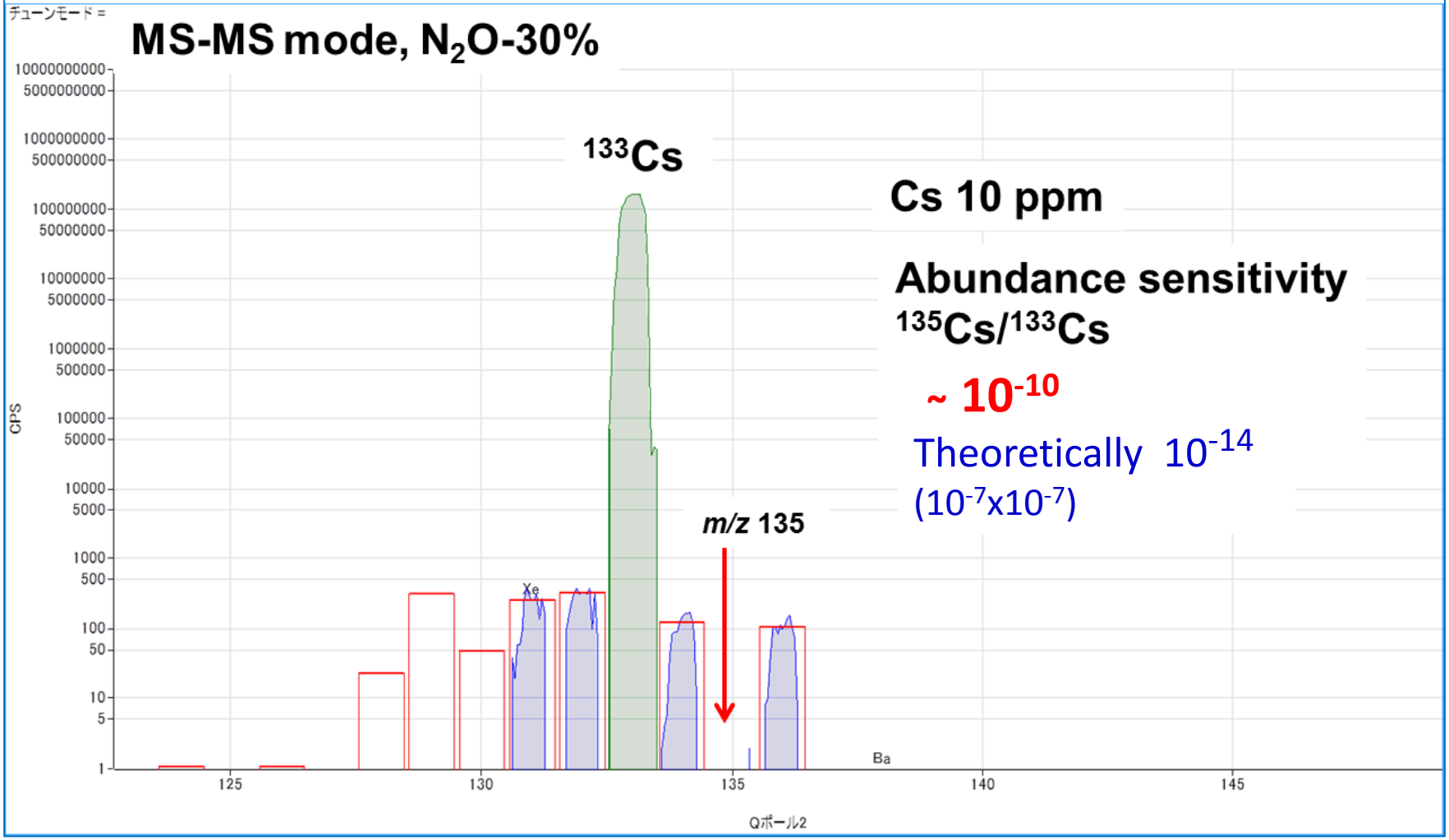


$SbO^+ > SnO^+$

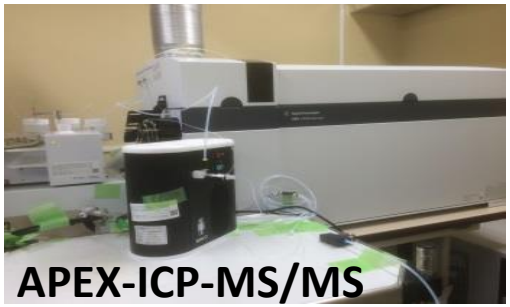


^{135}Cs and ^{137}Cs analysis using ICP-MS/MS

QQQ-ICP-MS 8800 abundance sensitivity



^{135}Cs and ^{137}Cs analysis using ICP-MS/MS



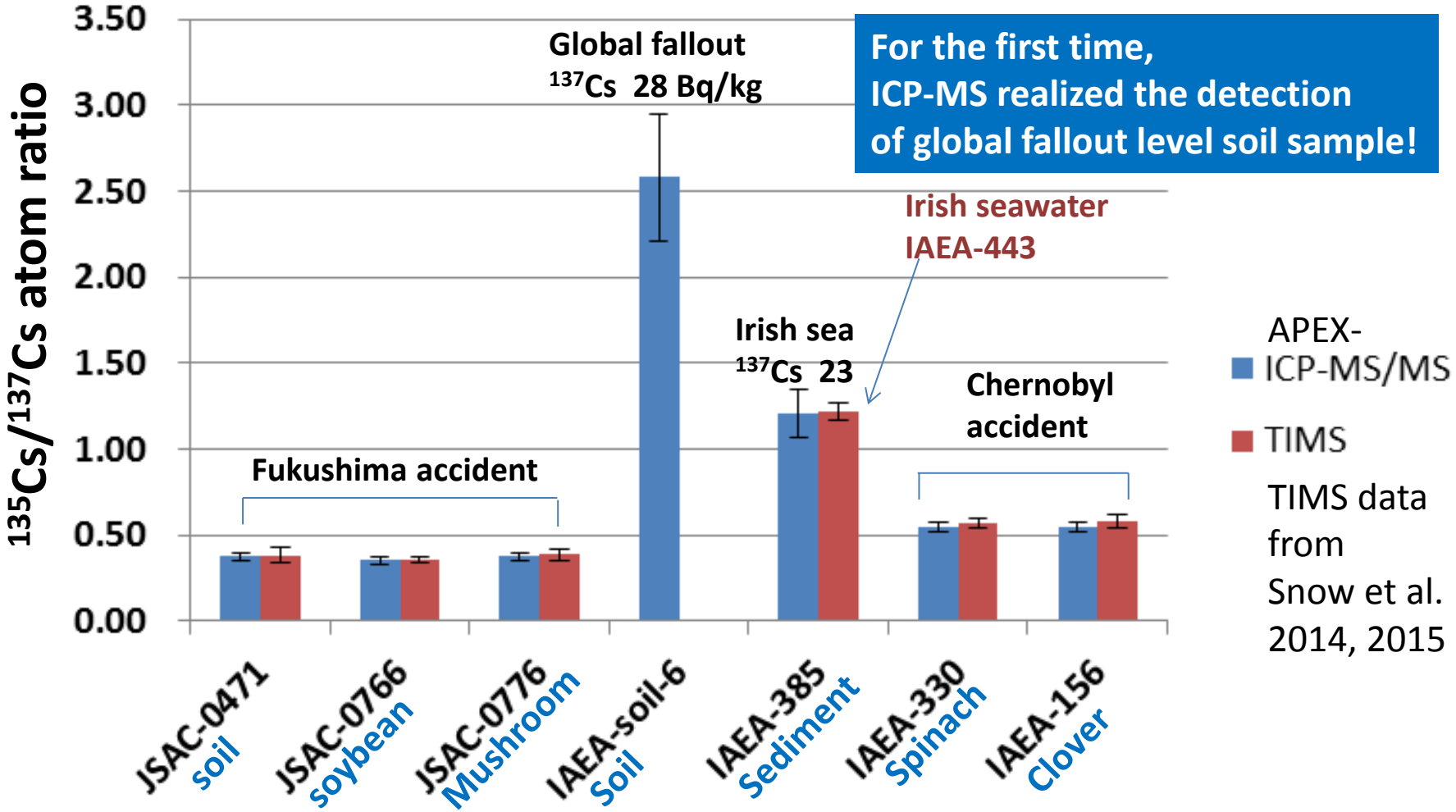
Detection limit (calculated based on 1 g solid sample)

	Mass unit (pg/g)	ICP-MS method
^{133}Cs	0.9	ICP-MS/MS
	0.36	APEX-ICP-MS/MS
^{135}Cs	0.01	ICP-MS/MS
	0.002	APEX-ICP-MS/MS
	0.05	Aridus-SF-ICP-MS
^{137}Cs	0.006	ICP-MS/MS
	0.002	APEX-ICP-MS/MS
	0.05	Aridus-SF-ICP-MS

Aridus SF-ICP-MS data cited from Russell et al. 2014

Analytical method validation: reference materials

^{137}Cs activity: 23 – 1142 Bq/kg



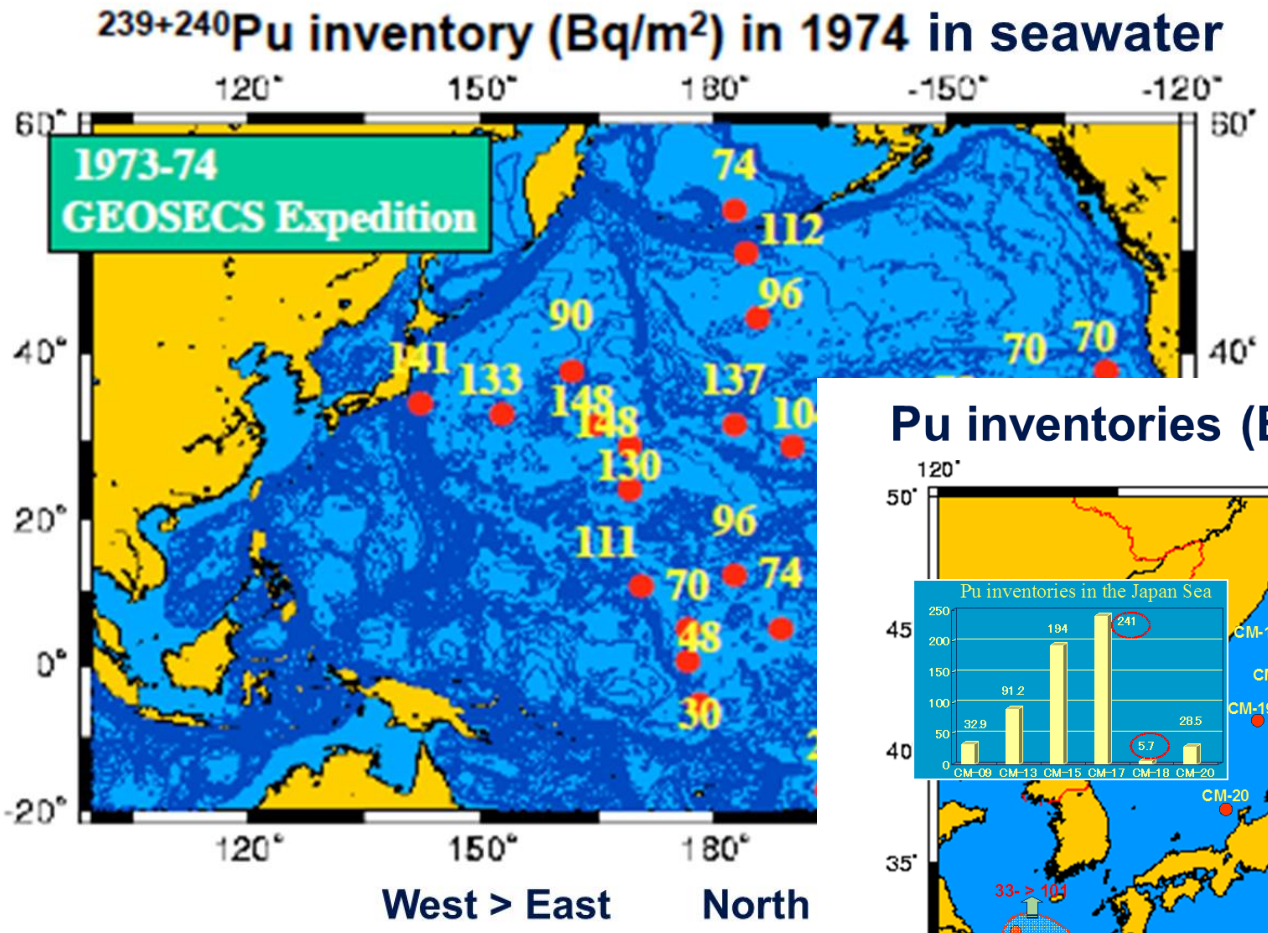
Contents

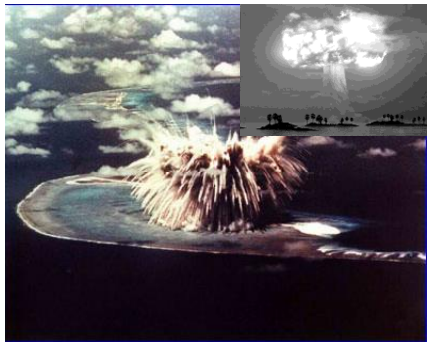
- Development of advanced mass spectrometric techniques for radionuclide (actinides, Cs) analysis
  - Sensitivity improvement
  - Chemical separation development

- **Pu isotopes as geochemical tracer: transport process in the ocean**

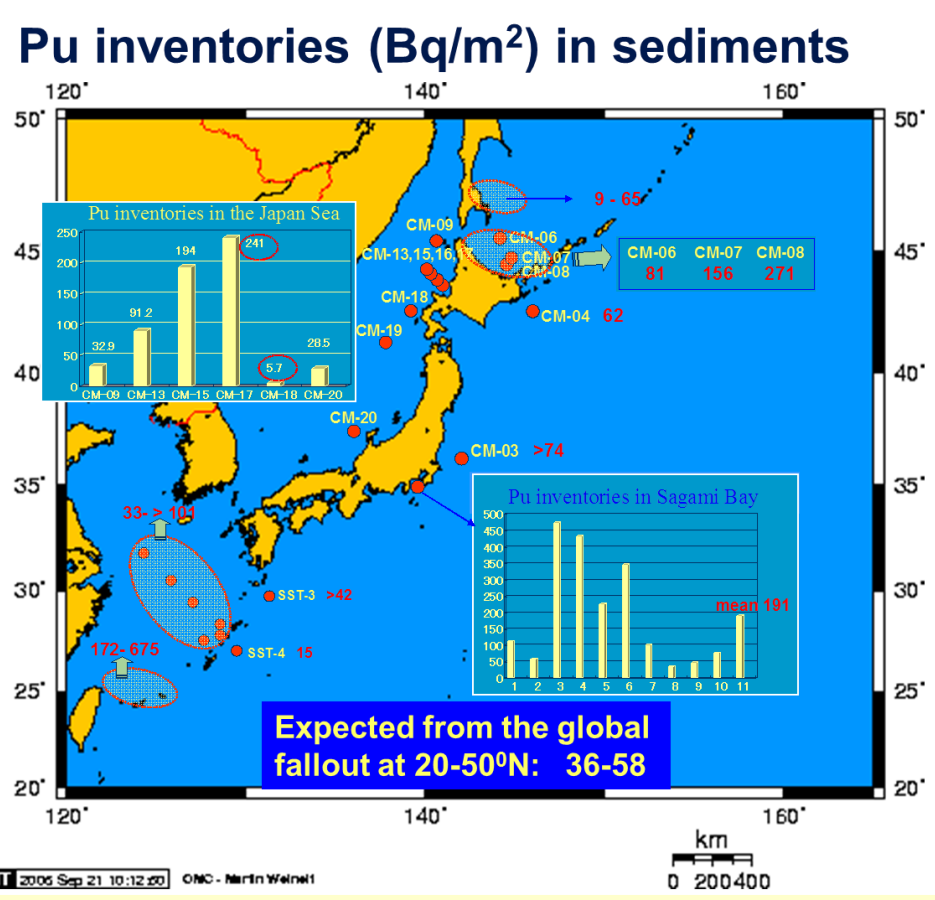
- Tracing Fukushima nuclear accident released Pu and Cs isotopes in the environment

Pu isotopes as geochemical tracer: transport process in the ocean





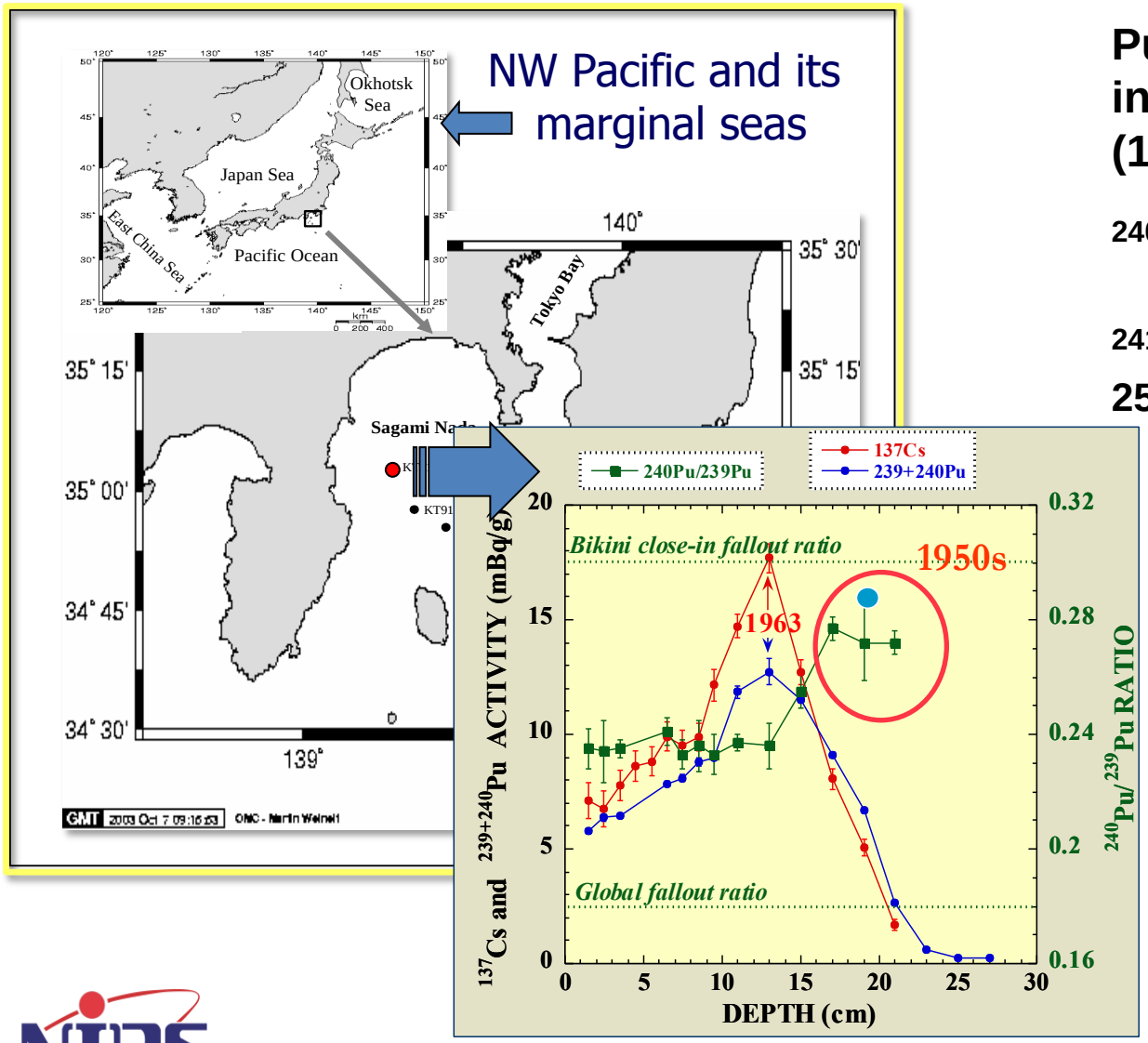
Nuclear Weapons testing in Bikini Atoll in 1954
(Bravo thermonuclear detonation, 15 MT)



Sources of Pu isotopes in the NW Pacific?

Global fallout
Pacific Proving Ground close-in fallout

Isotopic signature of plutonium in Sagami Nada



Pu isotopic compositions in the deep layer sediment (18-20 cm), we found:

$^{240}Pu/^{239}Pu$ ratio 0.27-0.30

$^{241}Pu/^{239+240}Pu$ activity ratio 25.0 (in the 1950s)

PPG (Marshall Islands Tests)
$^{240}Pu/^{239}Pu$ ratio 0.30-0.36

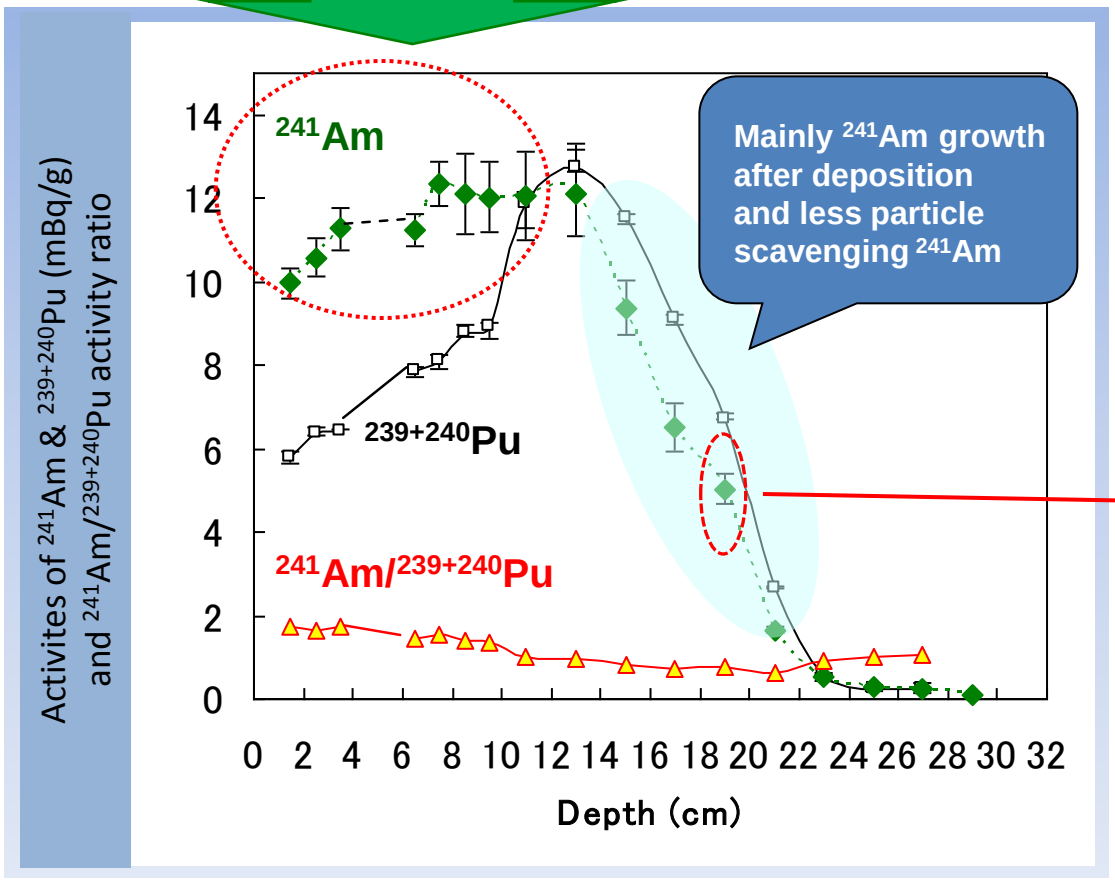
$^{241}Pu/^{239+240}Pu$ activity ratio ~ 27 (Koide et al., 1981)

Sedimentation rate: 0.4 cm/y
^{210}Pb dating

Pu isotopes as geochemical tracer: transport process in the ocean

Continuous supply seawater with higher Am/Pu ratio
Enhanced particle scavenging
^{241}Am increase after deposition

Vertical profiles between Pu and ^{241}Am in Sagami Nada



Estimate the release date of Pu

$$T = \frac{1}{\lambda_1 - \lambda_2} \ln\left[1 + \frac{(\lambda_1 - \lambda_2)\, A_2(t)}{\lambda_2\, A_1(t)}\right]$$

λ1 (0.0483), λ2 (0.0016)
A2(t) (^{241}Am, 5.03 ± 0.37)
A1(t) (^{241}Pu, 9.72 ± 1.88)

Release date: 1949 ±4 y

Zheng and Yamada, ES & T, 2004; J. Oceanogr. 2008

Transport of PPG close-in fallout Pu in the NW Pacific

Direct atmospheric deposition ???

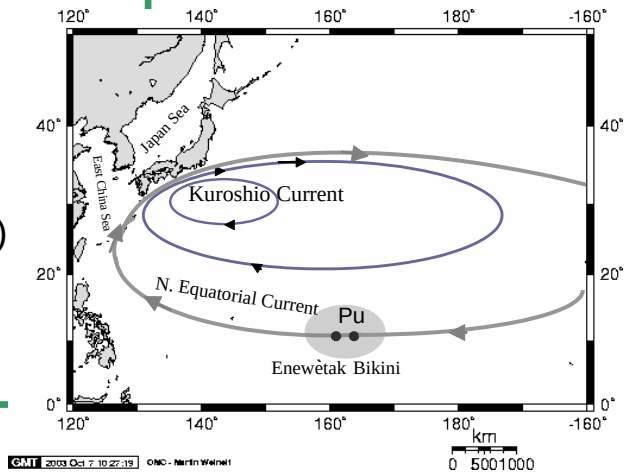
$^{240}Pu/^{239}Pu$ atom ratio in soils in Japan:
(*Muramatsu et al., JAAS, 1999; JRNC, 2003*)

0.168 — 0.181 surface soils
0.168 --- 0.194 0-30 cm vertical profile

$^{240}Pu/^{239}Pu$ atom ratio in lake sediments in Japan:

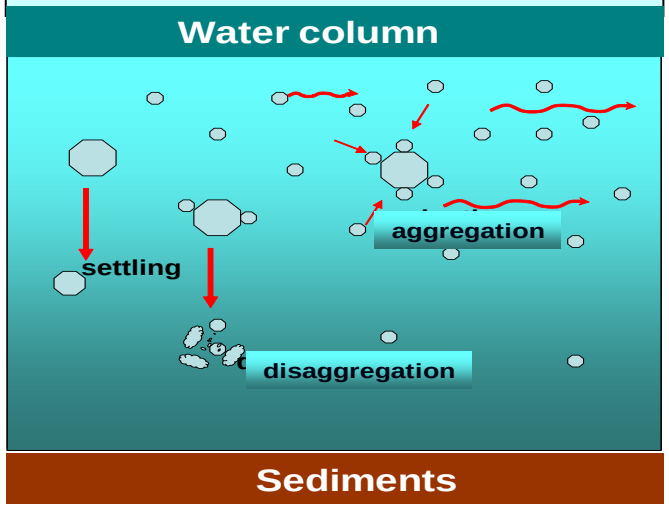
0.186 ± 0.016 Lake Obuchi
(*Zheng & Yamada, JEM. 2005*)

0.182 ± 0.005 Lake Towada
(*Otsuka et al., JRNC, 2004*)



Hypothesis

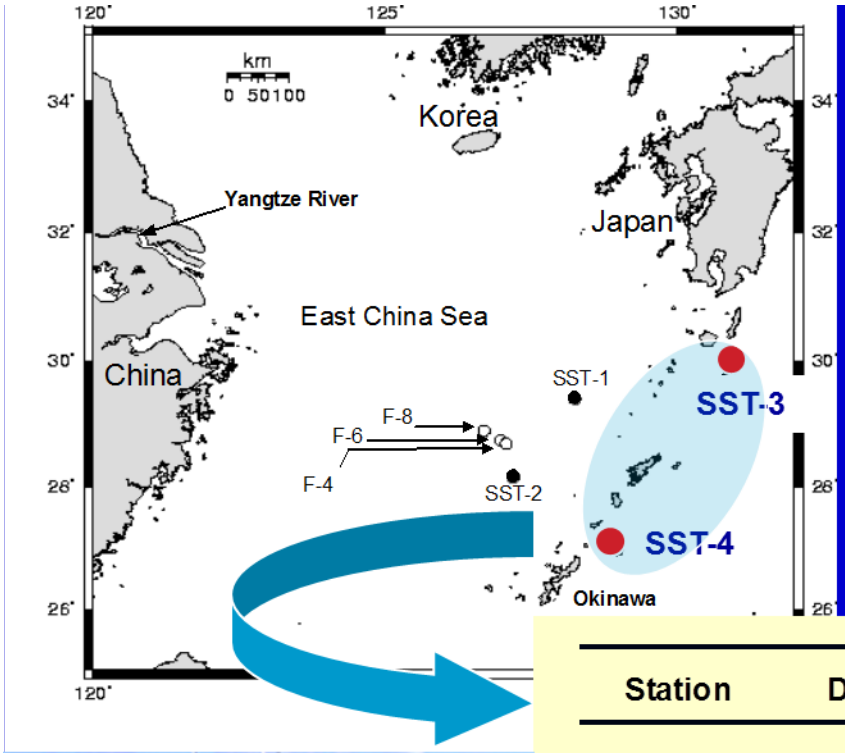
Transportation via Oceanic process,
Advective lateral transportation,
boundary scavenging???



Highly sensitive analytical technique is required for trace level Pu isotope ratio measurement in:
Settling particles **seawater**

Pu isotopes as geochemical tracer: transport process in the ocean

First dataset on Pu isotopic composition in setting particles in the world



Mean Pu activities and $^{240}Pu/^{239}Pu$ ratios on annual basis at the open ocean stations

- Tracing particle scavenging
- Tracing sediment resuspension

More details on particle scavenging of Pu, ^{241}Am and ^{210}Pb, Please visit our poster OS23B-191

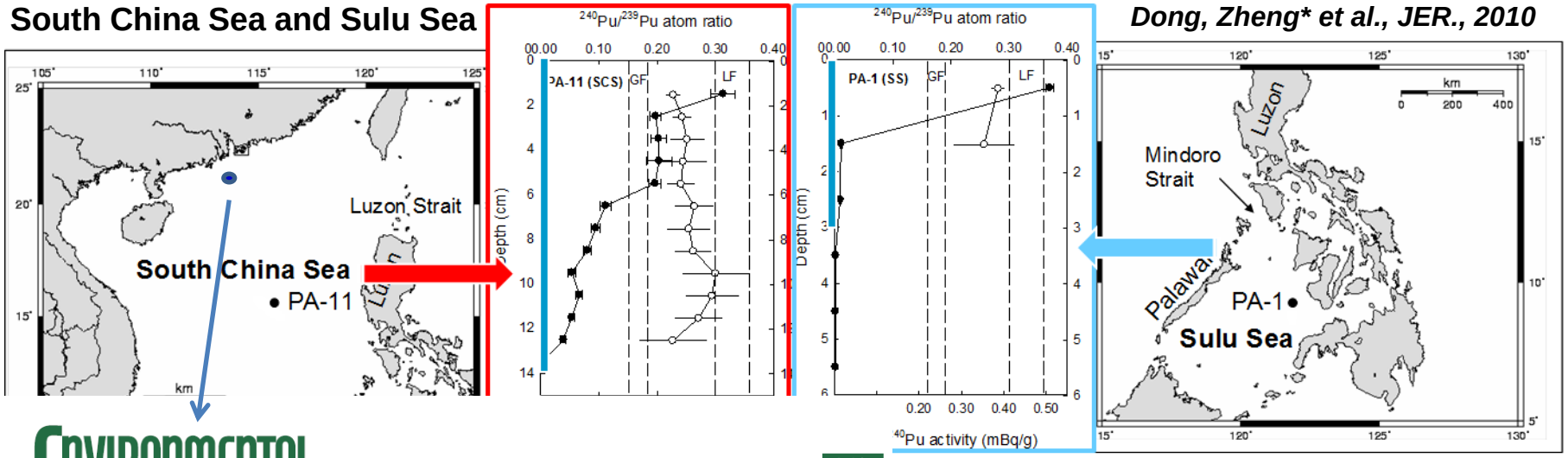
Station	Depth (m)	$^{239+240}Pu$ activity	$^{240}Pu/^{239}Pu$	Pu flux
SST-3	707	1.99 ± 0.07	0.233 ± 0.009	0.11
Scavenging	1413	2.96 ± 0.11	0.240 ± 0.015	0.61
	1819	3.44 ± 0.09	0.244 ± 0.009	1.80
SST4	667	2.83 ± 0.15	0.238 ± 0.020	0.03
Scavenging Resuspension	1373	5.41 ± 0.17	0.226 ± 0.010	0.36
	1779	3.38 ± 0.08	0.227 ± 0.007	0.62

Zheng and Yamada, ES & T, 2006

Pu isotopes as geochemical tracer: transport process in the ocean

South China Sea and Sulu Sea

Dong, Zheng et al., JER., 2010*



ENVIRONMENTAL Science & Technology

Article

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2014

Isotopic Composition and Distribution of Plutonium in Northern South China Sea Sediments Revealed Continuous Release and Transport of Pu from the Marshall Islands

Junwen Wu,[†,‡] Jian Zheng,[*,‡] Minhan Dai,[*,†] Chih-An Huh,[§] Weifang Chen,[†] and Shigeo Uchida[‡]

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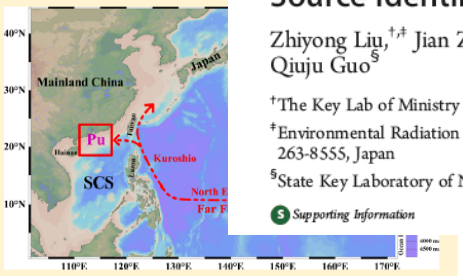
[‡]Research Center of Radiation Protection, National Institute of Radiological Sciences, 4-9-1 Anagawa,
[§]Institute of Earth Sciences, Academia Sinica, P.O. Box 1-55, Nankang, Taipei 11529, Taiwan

Supporting Information

ABSTRACT: The $^{239+240}Pu$ activities and $^{240}Pu/^{239}Pu$ atom ratios in sediments of the northern South China Sea and its adjacent Pearl River Estuary were determined to examine the spatial and temporal variations of Pu inputs. We clarified that Pu in the study area is sourced from a combination of global fallout and close-in fallout from the Pacific Proving Grounds in the Marshall Islands where above-ground nuclear weapons testing was carried out during the period of 1952–1958. The latter source dominated the Pu input in idenced by elevated $^{240}Pu/^{239}Pu$ atom ratios sediment core. Even after the 1950s, the Pacific was still a dominant Pu source due to continuous pilized Pu from the Marshall Islands, about 4500 he North Equatorial Current followed by the



Okhotsk Sea Sediments
Japan Sea sediments

Zheng and Yamada, Sci. Total Environ. 2006
Zheng and Yamada, JRNC, 2006

ENVIRONMENTAL Science & Technology

Yangtzer River Estuary Sediments

ARTICLE

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2011

Pu and ^{137}Cs in the Yangtze River Estuary Sediments: Distribution and Source Identification

Zhiyong Liu,[†,‡] Jian Zheng,[*,‡] Shaoming Pan,[*,†] Wei Dong,[§] Masatoshi Yamada,[‡] Tatsuo Aono,[‡] and Qiuju Guo[§]

[†]The Key Lab of Ministry of Education of Coast and Island Development, Nanjing University, Nanjing 210093, China
[‡]Environmental Radiation Effects Research Group, National Institute of Radiological Sciences, 491 Anagawa, Inage-ku, Chiba-shi, 263-8555, Japan
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Supporting Information

NIRS

Pu isotopes as geochemical tracer: transport process in the ocean

$^{239+240}$Pu inventory and increasing ratio of $^{239+240}$Pu inventory in each depth interval of the water columns in the Japan Sea.

Depth interval (m)	Yamato Basin			Tsushima Basin		
	$^{239+240}$Pu inventory (Bq m^{-2})		Increasing ratio[c]	$^{239+240}$Pu inventory (Bq m^{-2})		Increasing ratio[c]
	1984[a]	1993[b]		1984[d]	1993[b]	
0–300	4.2 ± 0.2	5.2 ± 0.1	1.23 ± 0.06	5.3 ± 0.1	5.9 ± 0.2	1.11 ± 0.04
300–1000	14.8 ± 0.5	25.4 ± 0.3	1.72 ± 0.07	17.8 ± 0.3	24.9 ± 0.3	1.40 ± 0.03
1000–2000	12.7 ± 0.6	30.7 ± 1.1	2.43 ± 0.14	16.6 ± 0.3	32.4 ± 0.5	1.95 ± 0.05
2000–bottom	11.2 ± 0.5	25.2 ± 1.3	2.26 ± 0.16	9.1 ± 0.2	22.0 ± 0.4	2.42 ± 0.07
0–bottom (total)[e]	42.8 ± 0.9	86.6 ± 1.4	2.02 ± 0.06	48.9 ± 0.5	85.2 ± 0.6	1.74 ± 0.02

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Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

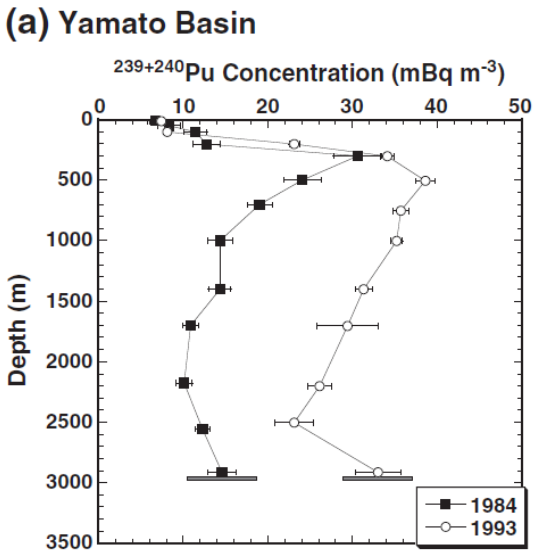
Increase of Pu inventory in water column

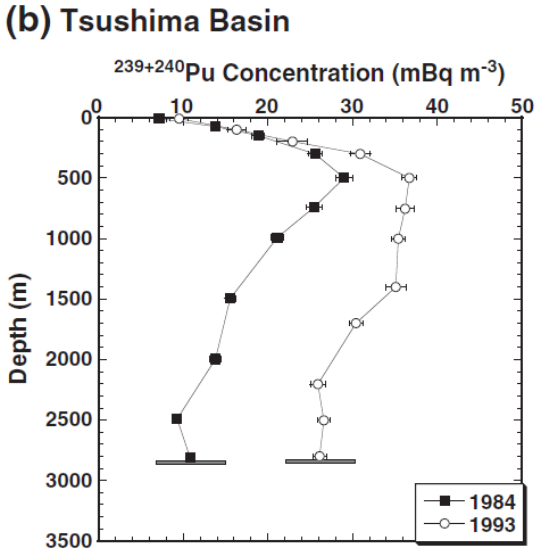
Temporal variation of ^{240}Pu/^{239}Pu atom ratio and $^{239+240}$Pu inventory in water columns of the Japan Sea

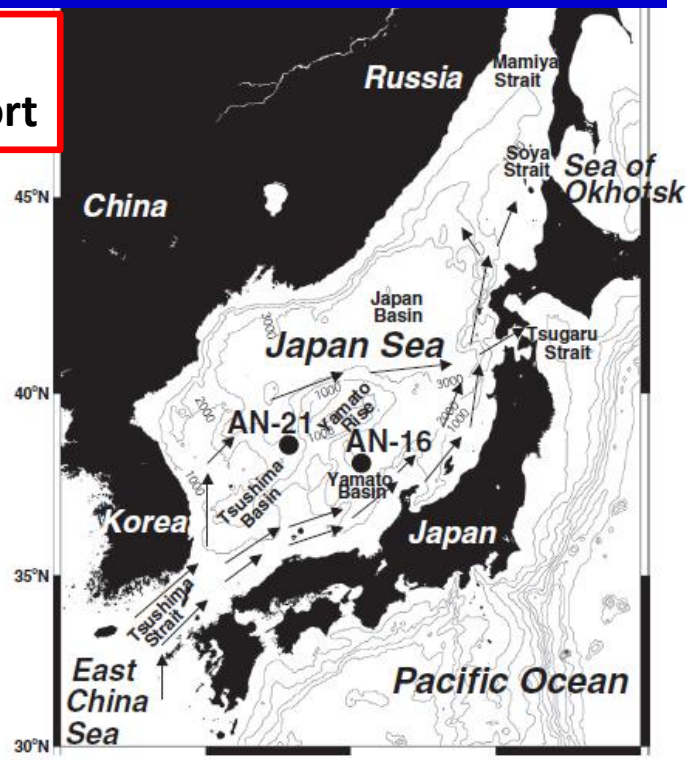
Masatoshi Yamada *, Jian Zheng

M. Yamada, J. Zheng / Science of the Total Environment 408 (2010) 5951–5957

Evidence of PPG Pu transport





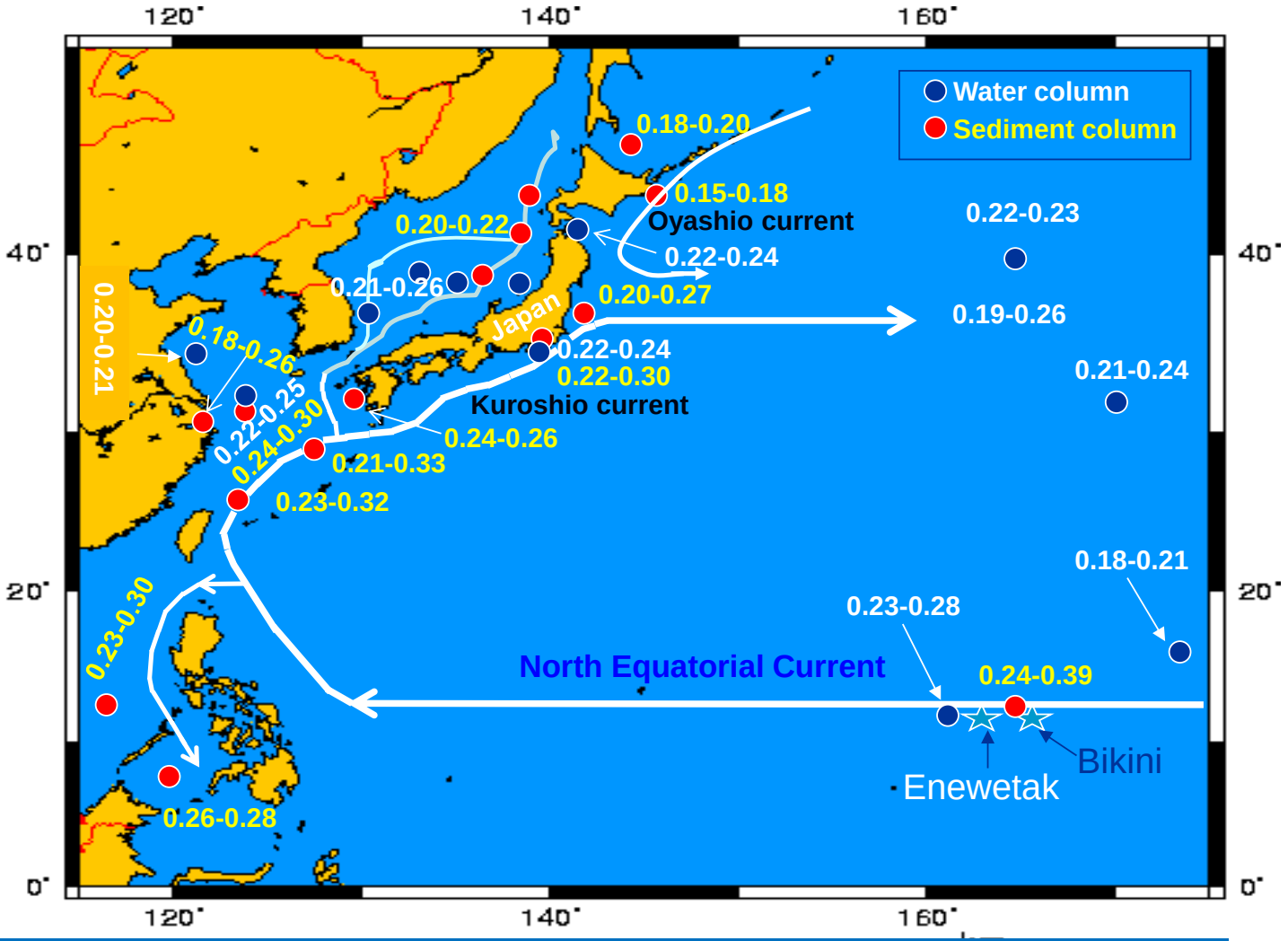


Pu isotopes as geochemical tracer: transport process in the ocean

Distribution of Pu in the western NW Pacific Before the Fukushima DNPP accident

Baseline $^{240}Pu/^{239}Pu$ ratio

0.150-0.281
NW Pacific

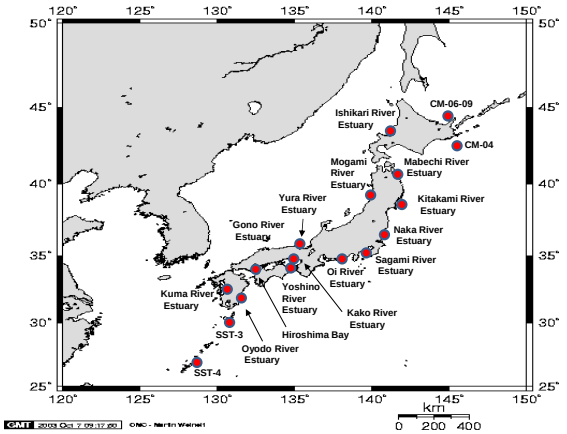


Sources of Pu in the North Pacific: Global fallout and PPG fallout
$^{240}Pu/^{239}Pu$ atom ratio: 0.18 0.30-0.36

Zheng et al., Geochem. J., 2012

Pu isotopes as geochemical tracer: transport process in the ocean

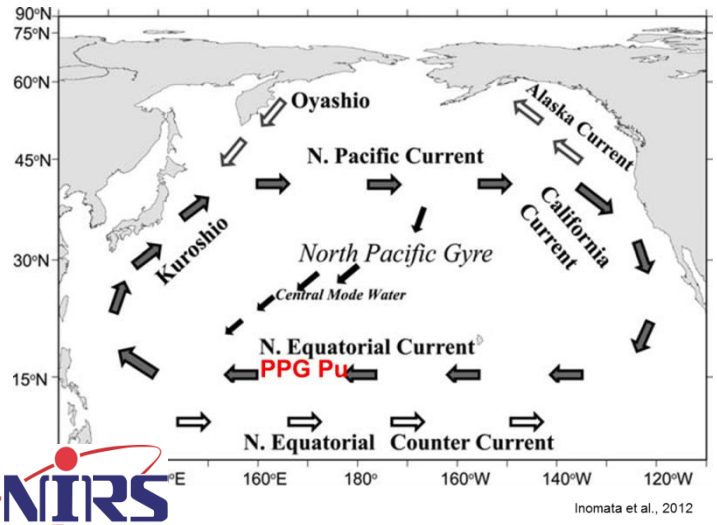
Pu atom ratios in the surface sediments for the Japanese estuaries

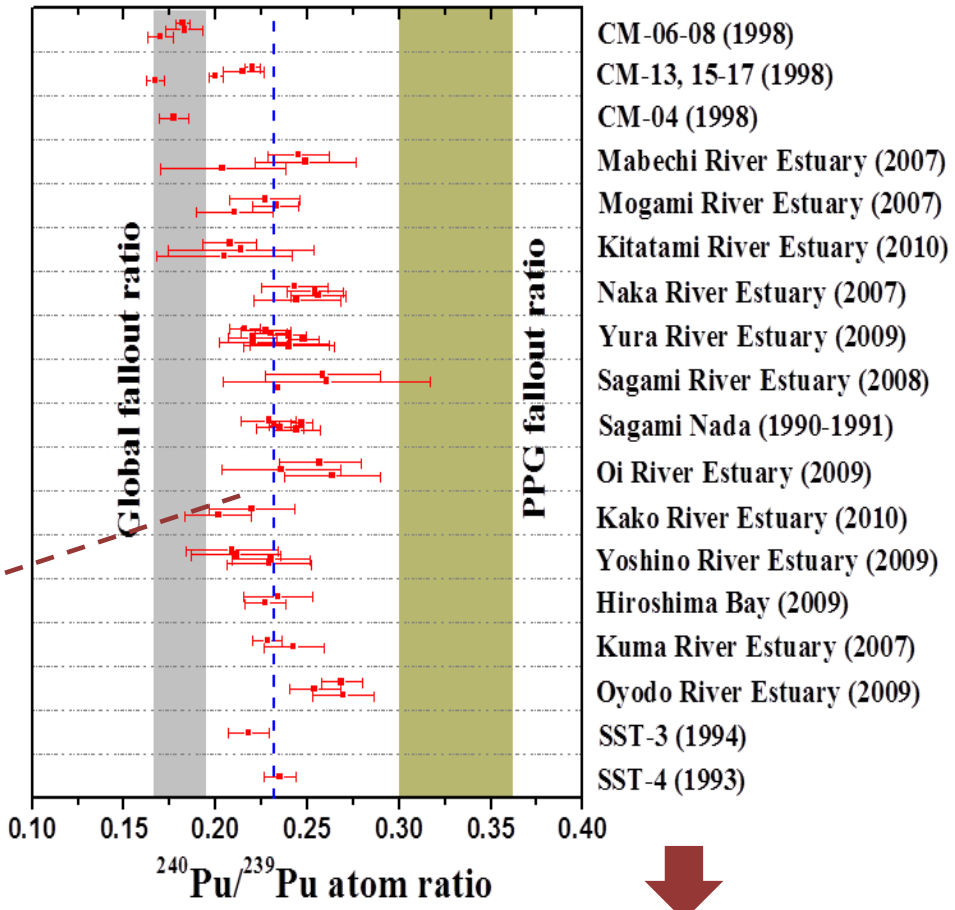


$^{240}Pu/^{239}Pu$ atom ratio range:

0.170-0.270

Mean $^{240}Pu/^{239}Pu$ atom ratio in the Pacific side: **0.231**





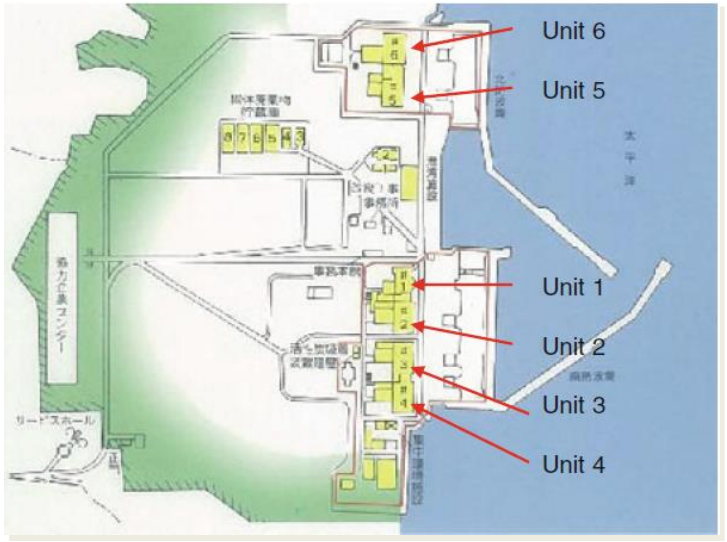
Important baseline data of Pu isotopes for radiological assessment of the impact of Fukushima nuclear accident in the marine environment

Bu, Zheng et al., Biogeosci., 2014*

Contents

- Development of advanced mass spectrometric techniques for radionuclide (actinides, Cs) analysis
  - Sensitivity improvement
  - Chemical separation development
- Pu isotopes as geochemical tracer: transport process in the ocean
- **Tracing Fukushima nuclear accident released Pu and Cs isotopes in the environment**

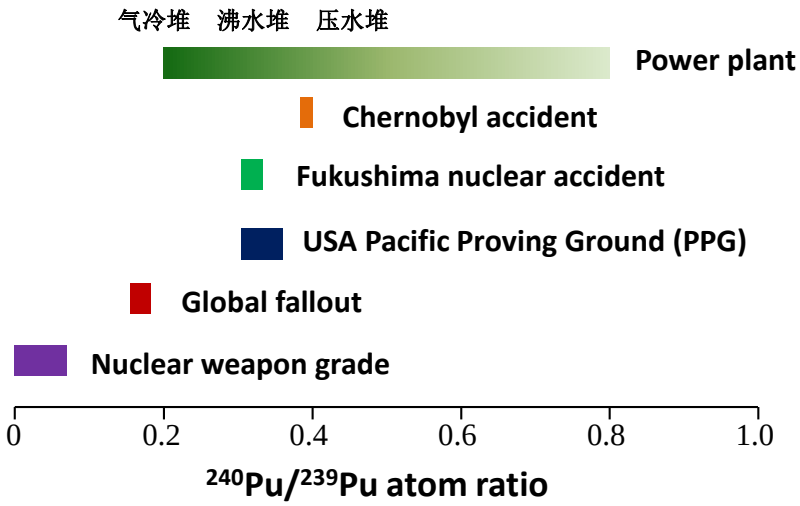
Fukushima Daiichi Nuclear Power Plant



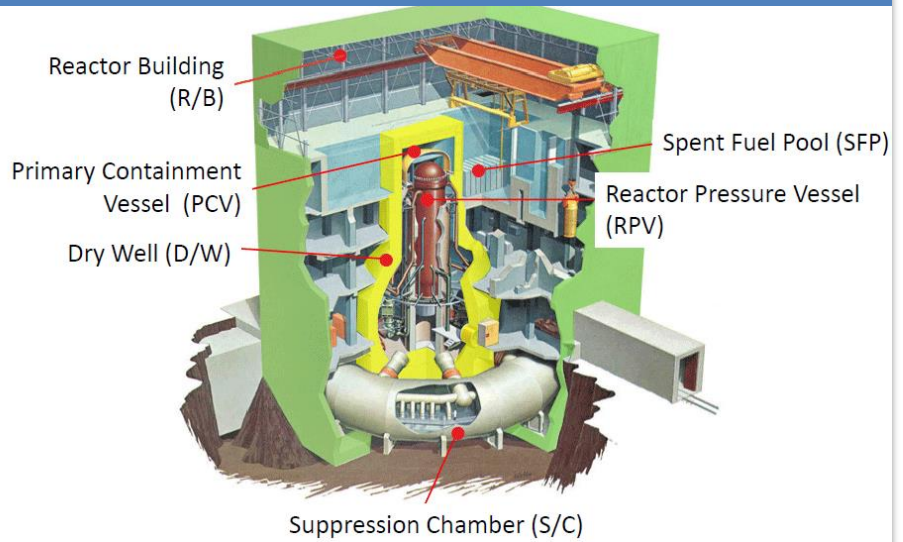
Six boiling water reactors in FDNPP
Four reactors (U1-U4) were destroyed by the accident

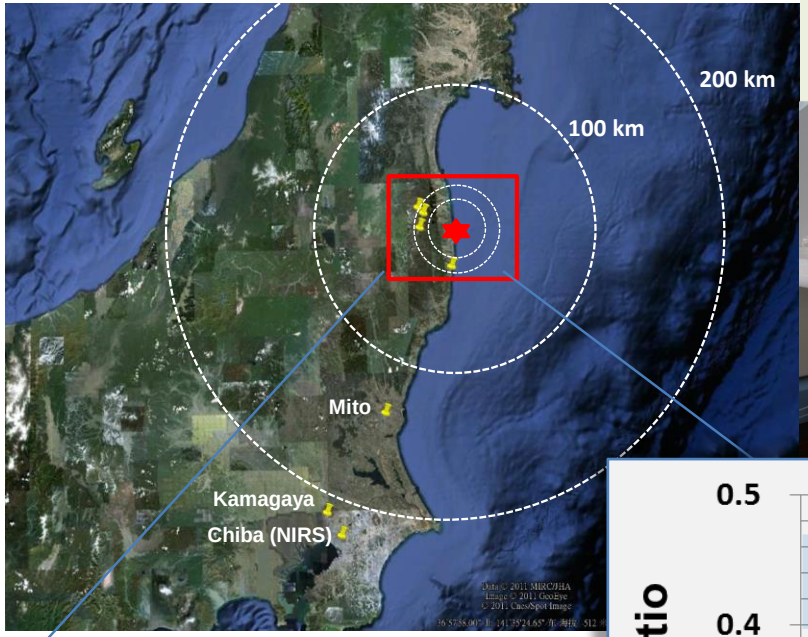
U1-U3 operating at the time of the earthquake and tsunami U4 fuel had been removed and stored in cooling pools

U1-U3 nuclear fuel 256 metric tons which includes 5.5 tons MOX fuel
Spent fuel pools (SFP) in the four destroyed reactor buildings contained additional 461 metric tons fuel

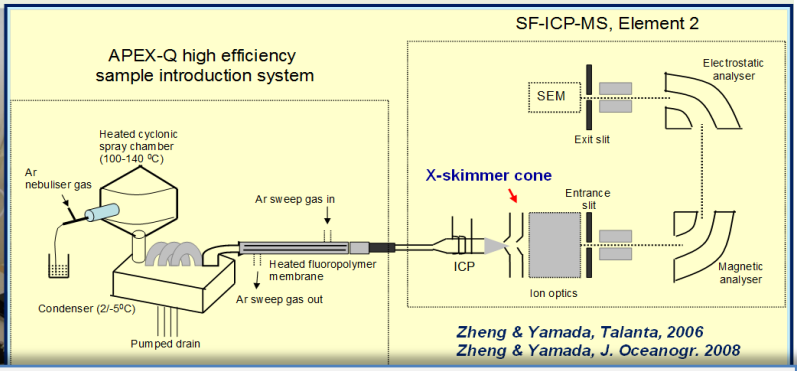


Release sources
1. **Fuel in the damaged reactor core**
2. **Fuel in the spent fuel pool (SFP)**



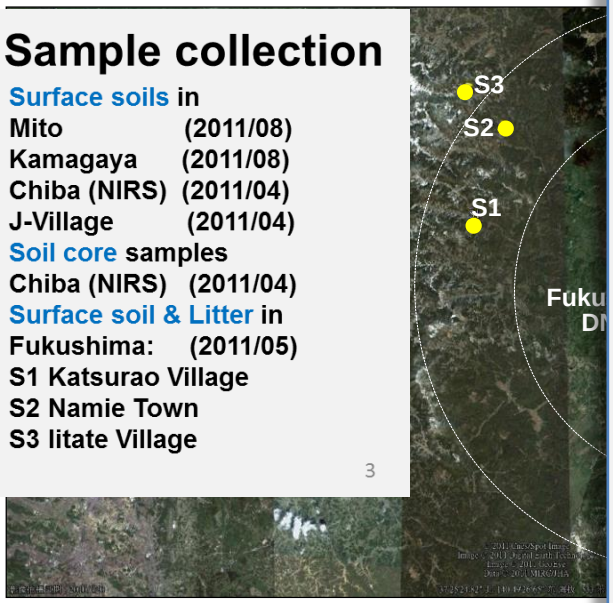


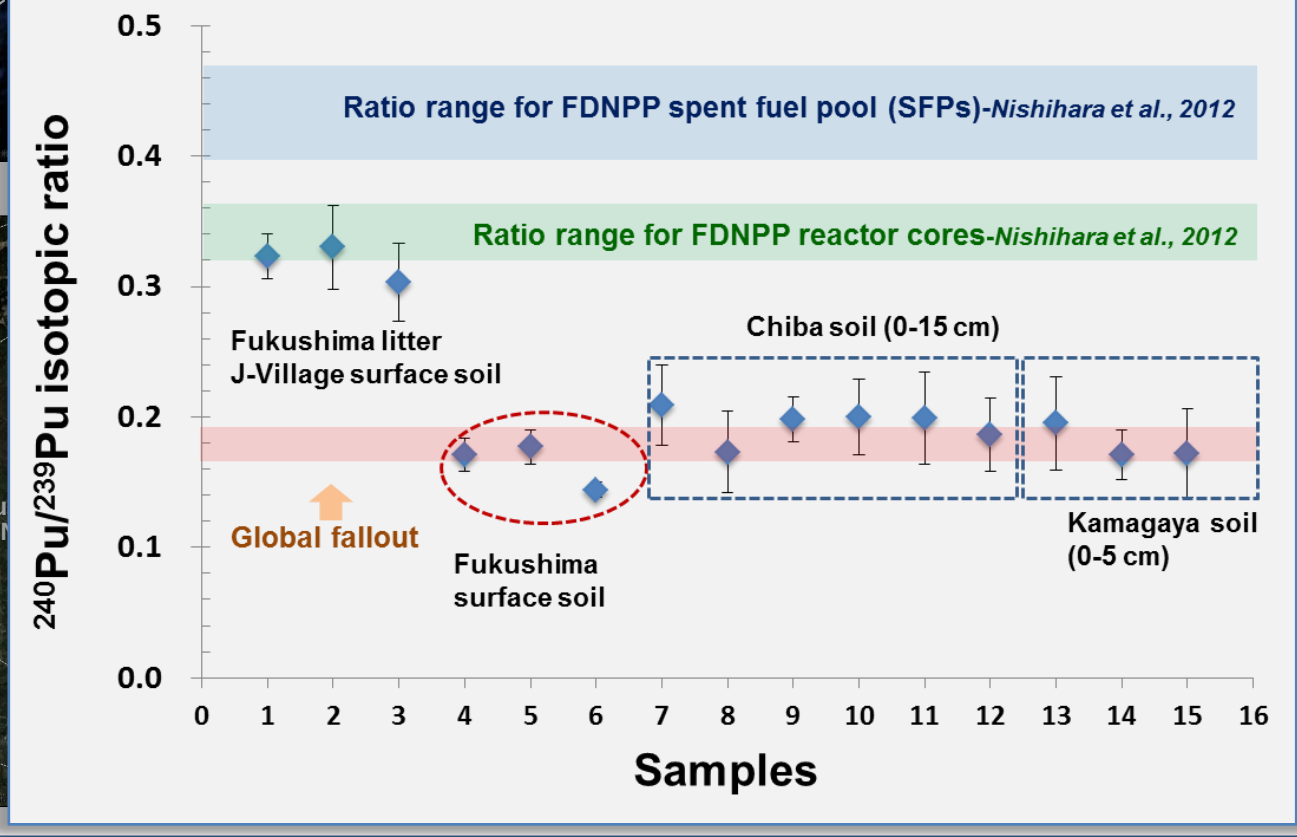
APEX-Q-SF-ICP-MS analytical system



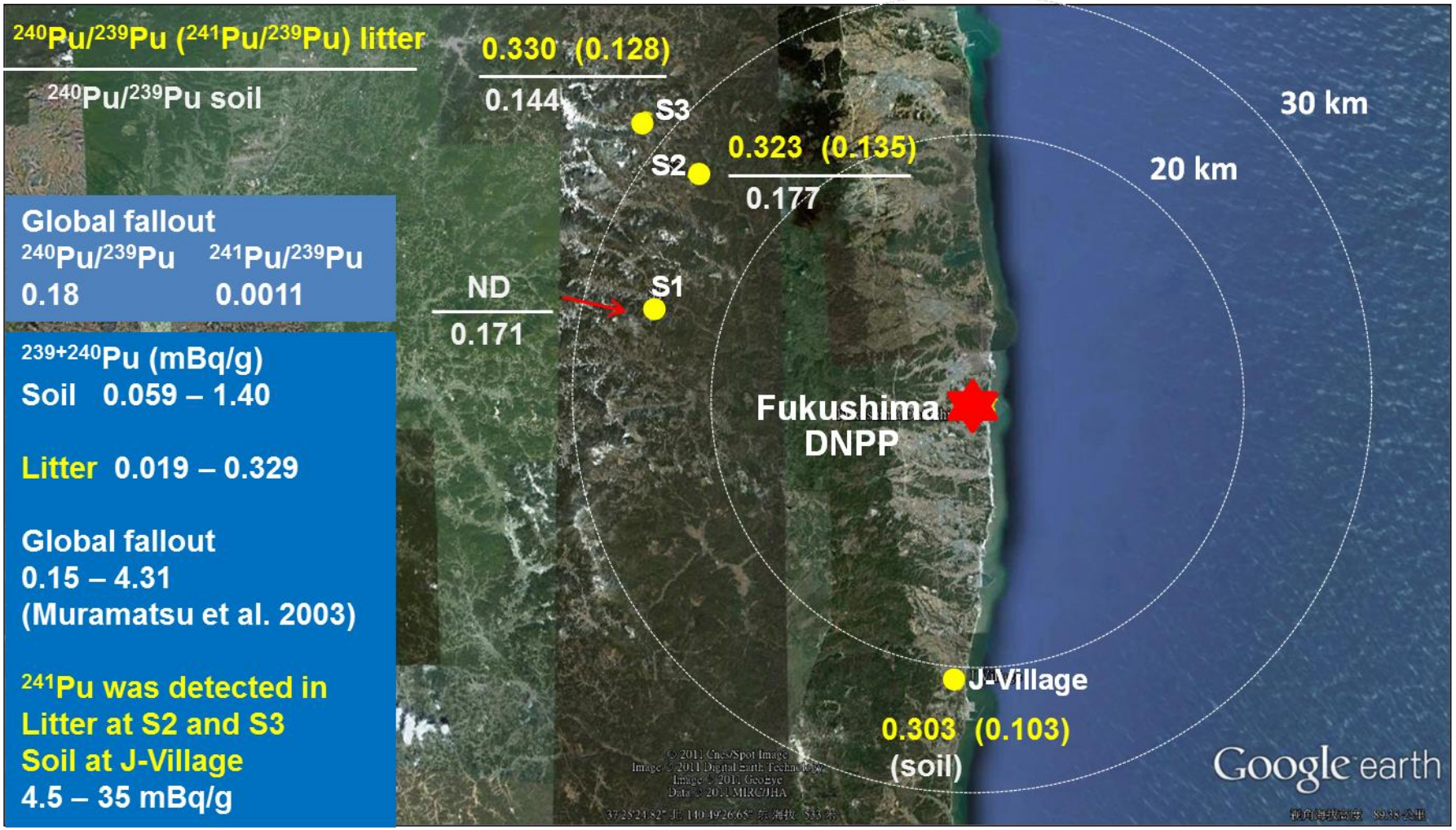
Sample collection

Surface soils in
Mito (2011/08)
Kamagaya (2011/08)
Chiba (NIRS) (2011/04)
J-Village (2011/04)
Soil core samples
Chiba (NIRS) (2011/04)
Surface soil & Litter in
Fukushima: (2011/05)
S1 Katsurao Village
S2 Namie Town
S3 Iitate Village





Isotopic evidence of Pu release from the FDNPP

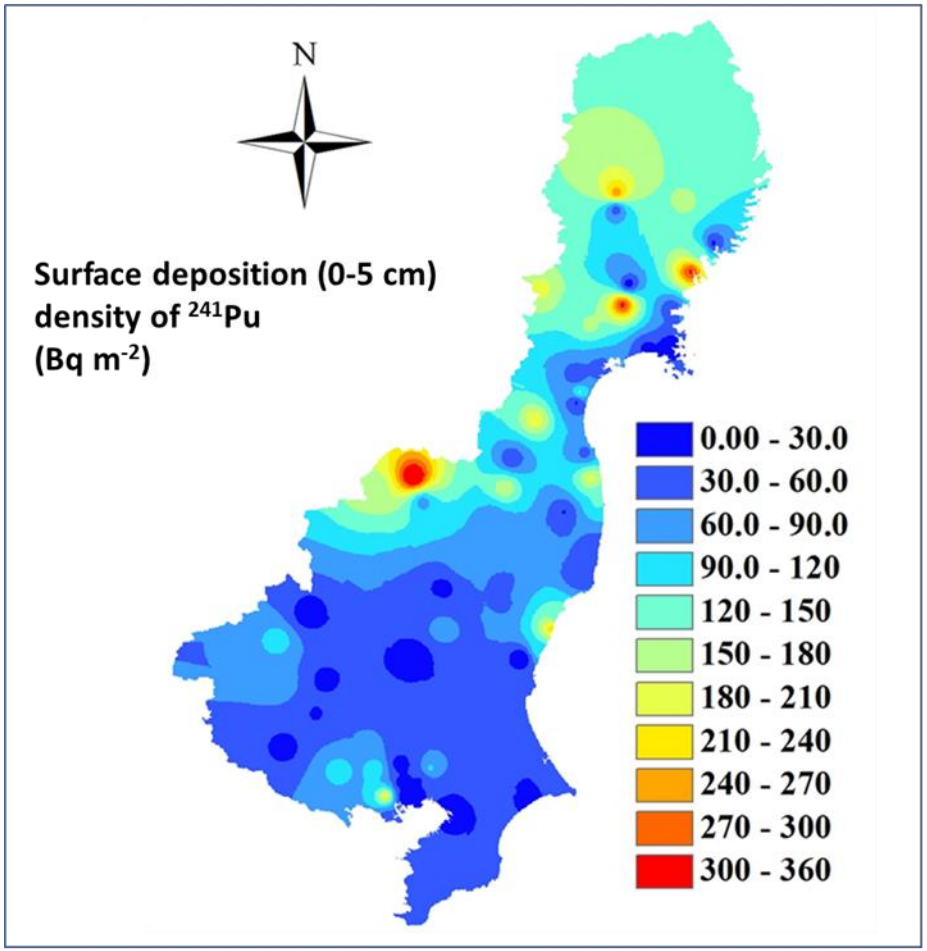


Fukushima DNPP source Pu was found not only in Northwest but also South of the plant

Zheng et al., Sci. Rep. 2012

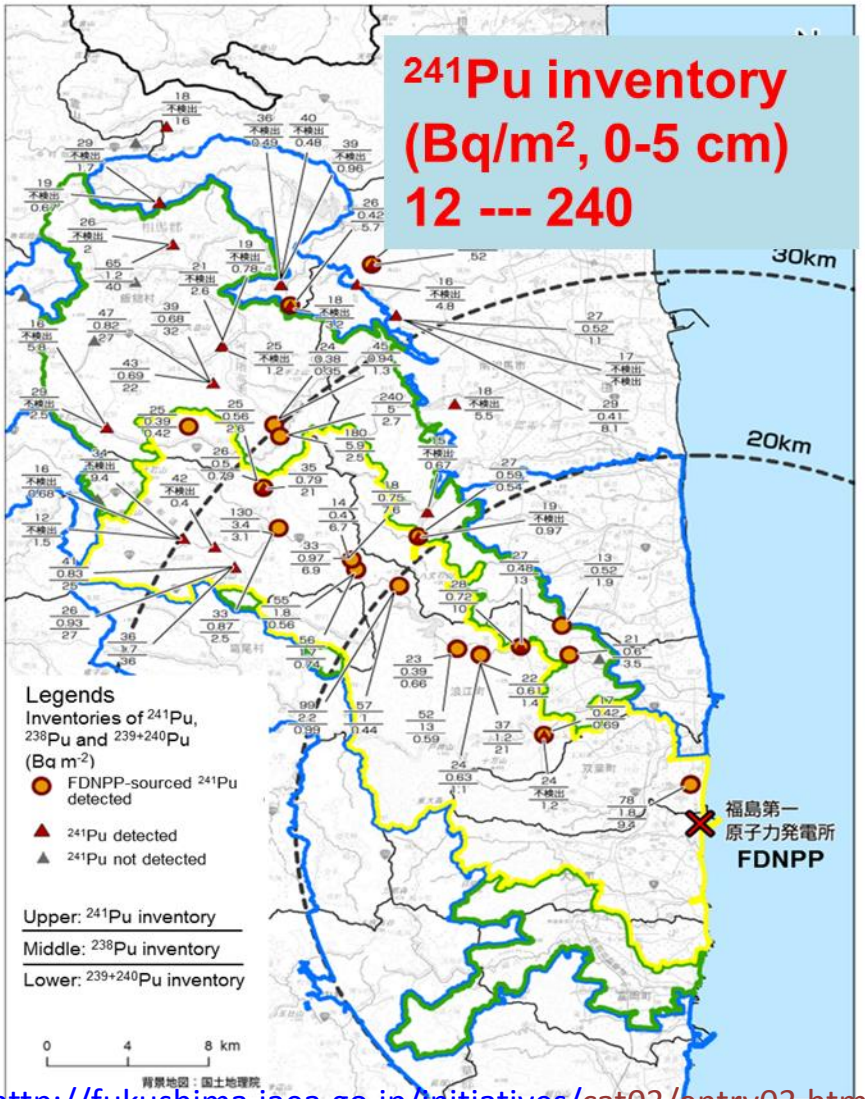
Comparison of ^{241}Pu inventory in surface soils

in the 1970s



Yang, Zheng et al., Sci. Rep. 2015*

after the FDNPP accident



http://fukushima.jaea.go.jp/initiatives/cat03/entry03.html

Pu isotopic fingerprint for source identification

	$^{240}Pu/^{239}Pu$ atom ratio	$^{241}Pu/^{239}Pu$ atom ratio	$^{241}Pu/^{239+240}Pu$ activity ratio	$^{238}Pu/^{239+240}Pu$ activity ratio
Global fallout	0.180±0.007	0.00194±0.00014	1.2 (2011/3/15)	0.026
Atmospheric fallout 1963-1979 in Japan	0.1922±0.0044	0.00287±0.00056	1.86 (2000/1/1)	0.037
Nagasaki A-bomb	0.028 – 0.037	0.00073	1.21 (1945/8/9)	0.074±0.001
Pacific Proving Ground	0.30 – 0.36	0.0057 (2005)	27 (1952-1954)	0.001 – 0.014
Chernobyl accident	0.408±0.003	0.123±0.007	83 (1986/5/1)	0.5
FDNPP accident	0.323-0.330	0.128-0.135	108 (2011/3/15)	1.07-2.89

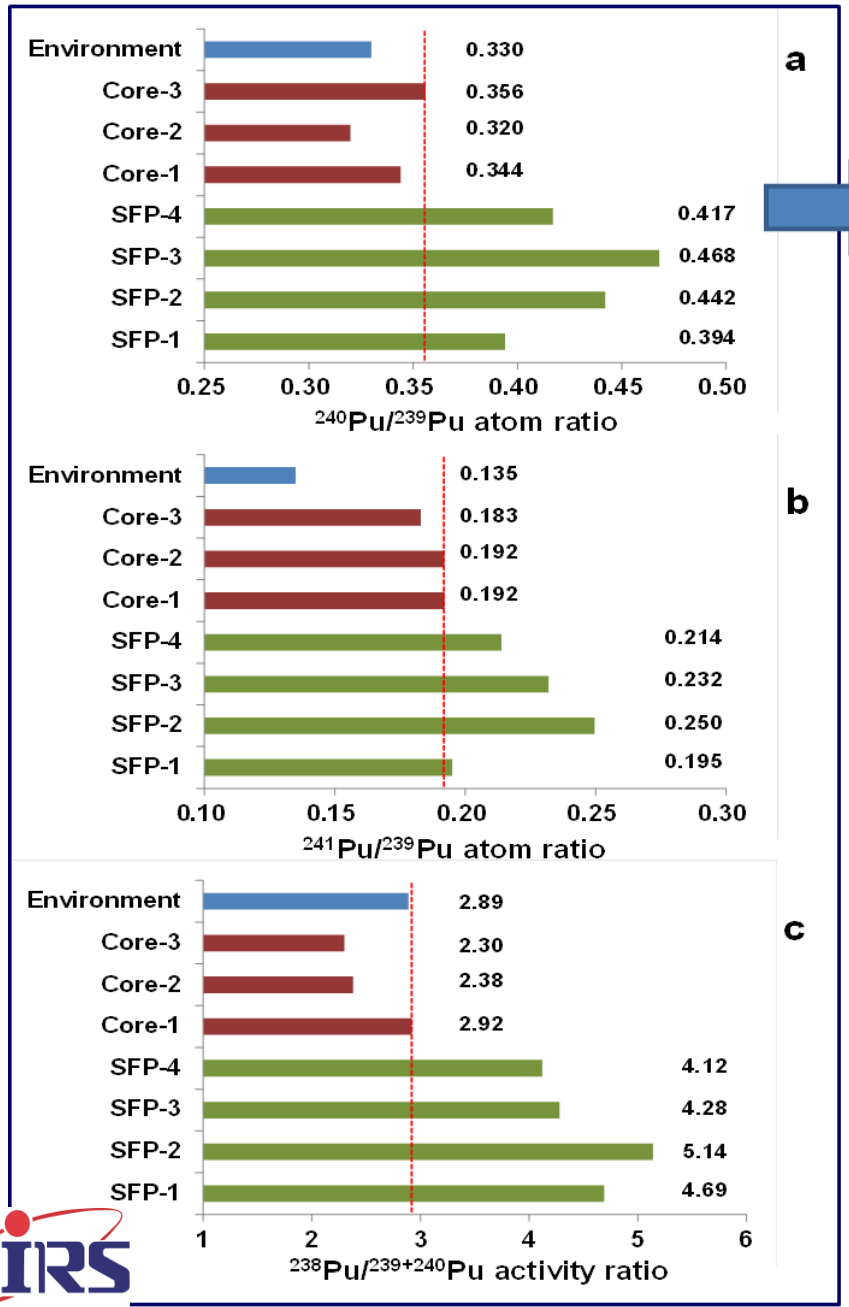
Data for global fallout are cited from *Kelley et al. 1999; Holm, 1988.* Data for atmospheric fallout in Japan (1963-1979) are cited from *Zhang et al. 2010 and Otsuji-Hatori et al. 1996.* Data for Nagasaki A-bomb are cited from *Yamamoto et al. 1983.* Data for Chernobyl accident are cited from *Muramatsu et al. 2000; Ketterer et al. 2004; IAEA, 1986; Hirose et al., 2001.* Data for the Pacific Proving Ground are cited from *Muramatsu et al. 2001; Diamond et al. 1960; Koide et al. 1985; Lee et al. 2005.* Data for Fukushima accident are cited from *Zheng et al., 2012.; TEPCO, 2012.*

New FDNPP Pu isotope ratio measurements:

$^{240}Pu/^{239}Pu$ ratio — Yamamoto et al., J. Environ. Radioact. 2014

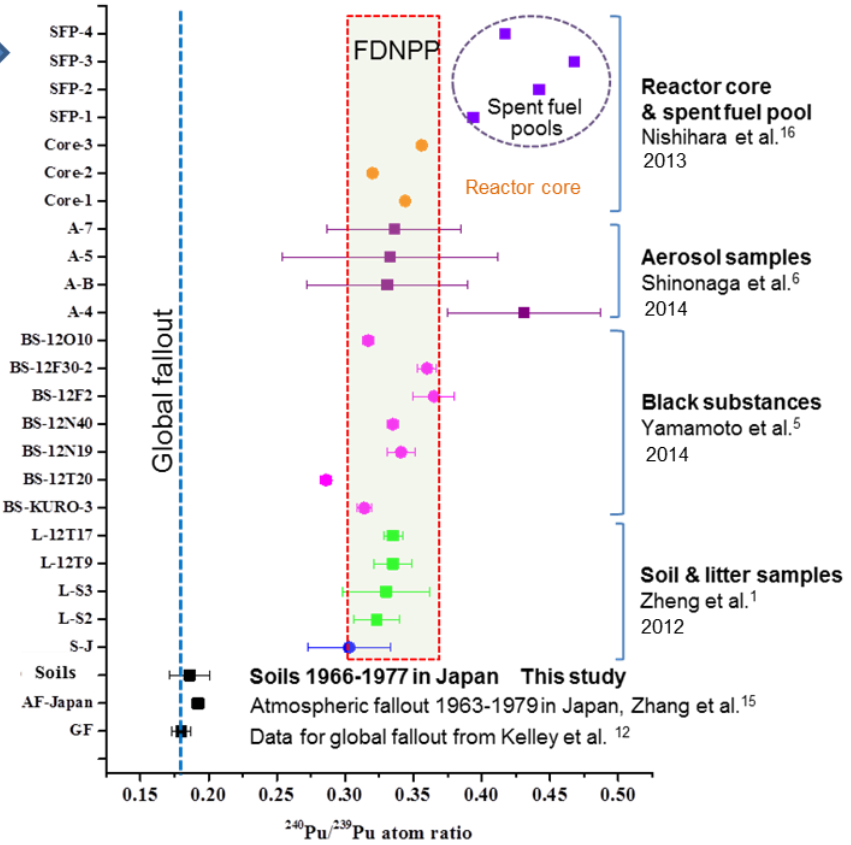
$^{241}Pu/^{239}Pu$ ratio — Schneider et al., Sci. Rep., 2013; Shinonaga et al., ES&T, 2014; Evrard et al., ES&T, 2014

Tracing Fukushima nuclear accident released Pu and Cs isotopes in the environment



Pu release sources

Damaged reactors or spent fuel pools?



Pu was released from the damaged reactors, not the spent fuel pools!

Zheng et al., EST Critical review, 2013

Estimation of the amounts of Pu isotopes released

		FDNPP accident	
	Chernobyl	METI calculated	Estimation of this study
Amount of released (Bq)			
Pu-239+240	8.7×10^{13}	6.4×10^{9}	1.0×10^{9} – 2.4×10^{9}
Pu-241	7.2×10^{15}	1.2×10^{12}	1.1×10^{11} – 2.6×10^{11}
Pu-238	3.5×10^{13}	1.9×10^{10}	2.9×10^{9} – 6.9×10^{9}
Pu inventories at reactors (Bq) at the time of accident initiation			
Pu-239+240	2.4×10^{15}	---	8.3×10^{15}
Pu-241	1.9×10^{17}	---	7.0×10^{17}
Pu-238	1.0×10^{15}	---	1.1×10^{16}
Percentage of core inventory released (%)			
Pu-239+240	3.5	---	1.2×10^{-5} – 2.9×10^{-5}
Pu-241	3.5	---	1.6×10^{-5} – 3.7×10^{-5}
Pu-238	3.5	---	2.0×10^{-5} – 4.7×10^{-5}

A rough estimation on the amounts of atmospheric release of Pu isotopes based on $^{137}Cs/^{239+240}Pu$ activity ratios observed in litter samples in 20-30 km zones

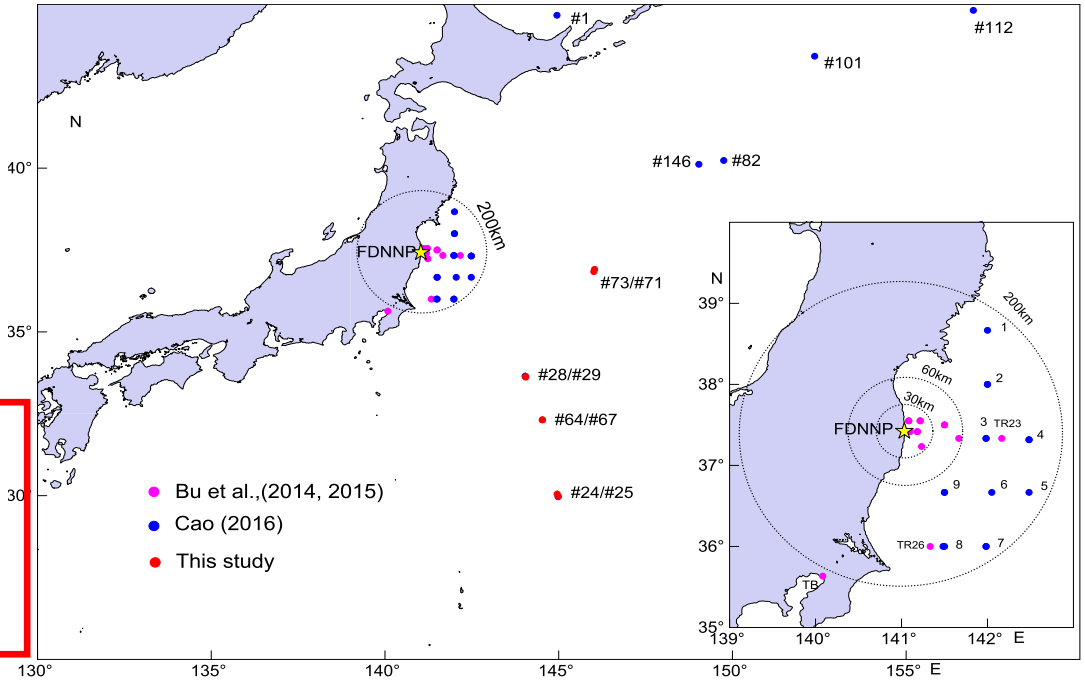
FDNPP released Pu: 4 orders of magnitude lower than Chernobyl accident

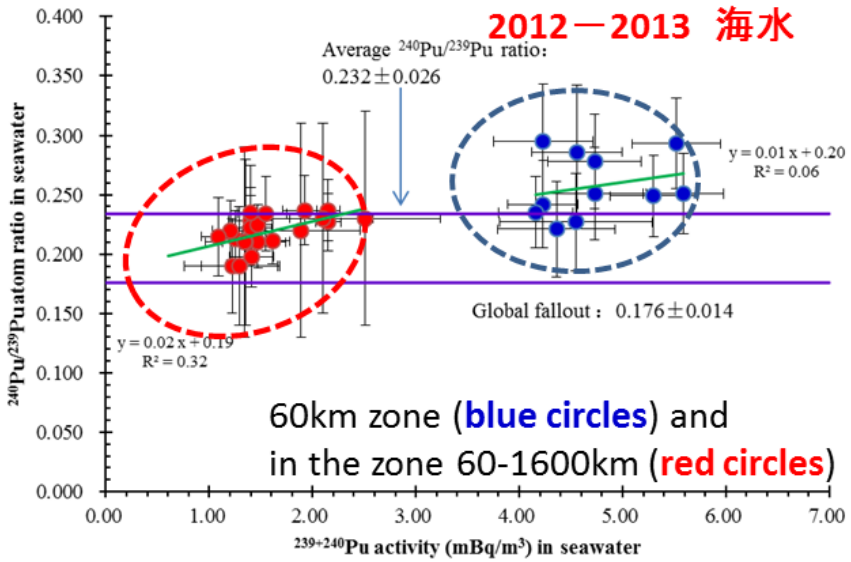
Zheng et al., Sci. Rep., 2012; ES&T 2013

Pu isotopes in seawater samples (5 – 1600 km) off Fukushima coast

Bu, Zheng et al.,*
J. Nucl. Radiochem. Sci.
2015

No observable increase of Pu activity and change of $^{240}Pu/^{239}Pu$ atom ratio





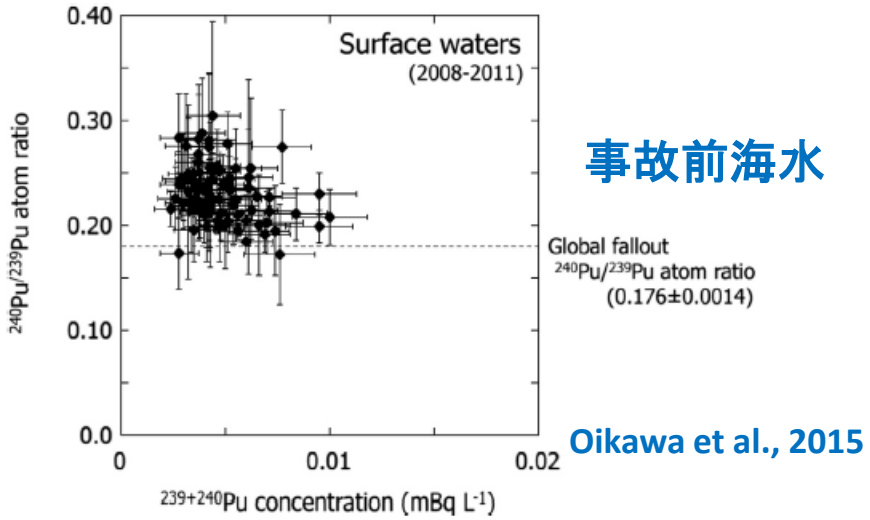
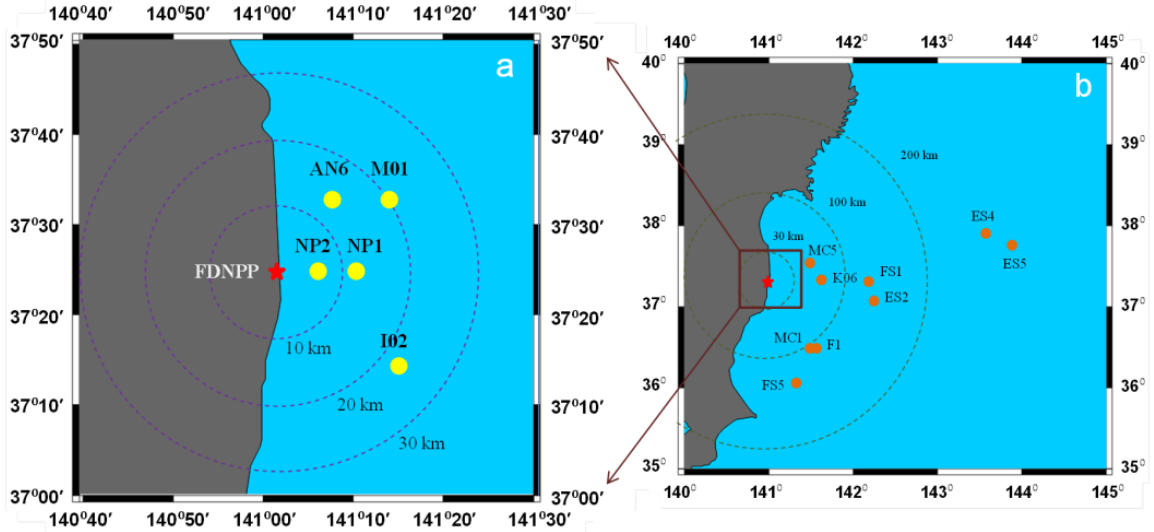


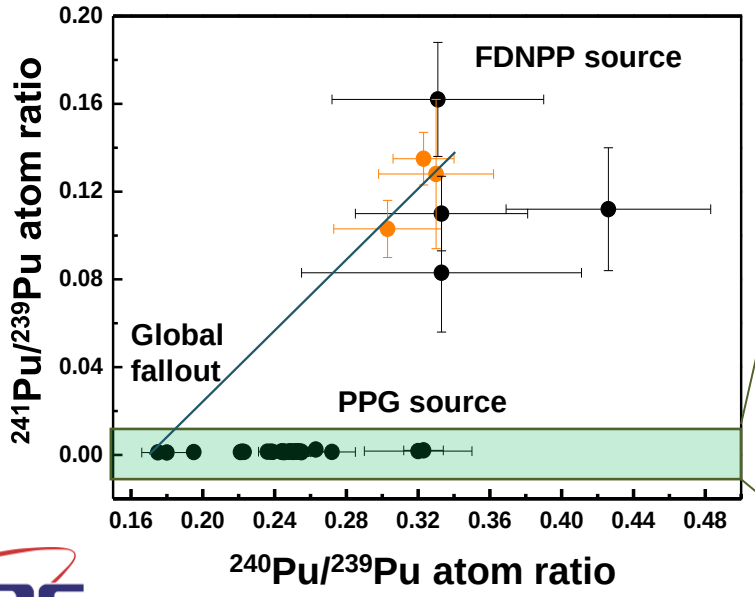
Fig. 3. Relationship between $^{239+240}Pu$ concentration and $^{240}Pu/^{239}Pu$ atom ratio found in the surface waters at the 37 sampling locations during 2008–2011.

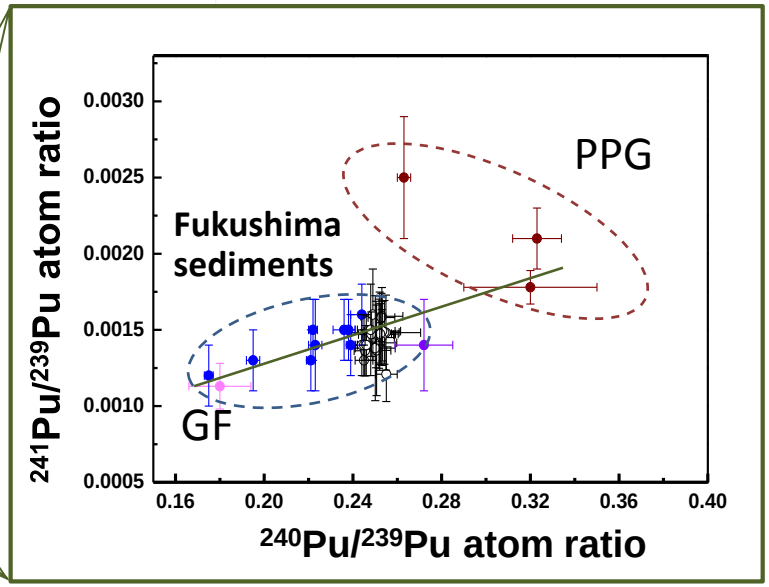
Pu contamination in Ocean was negligible

(2011-2013)
>200 samples

Source identification of Pu in marine sediments off Fukushima coast
5 km--220 km



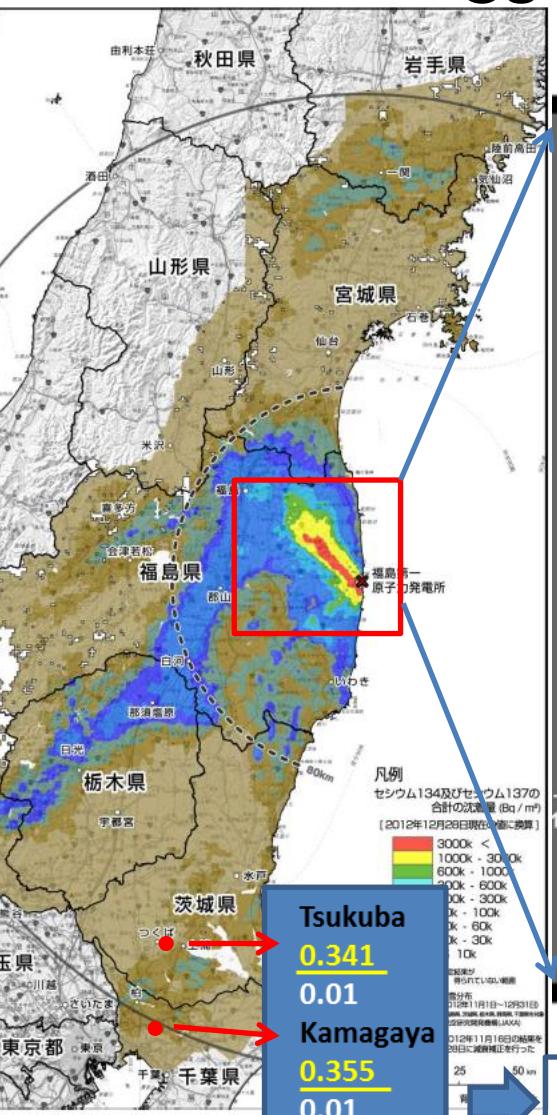




Yaman

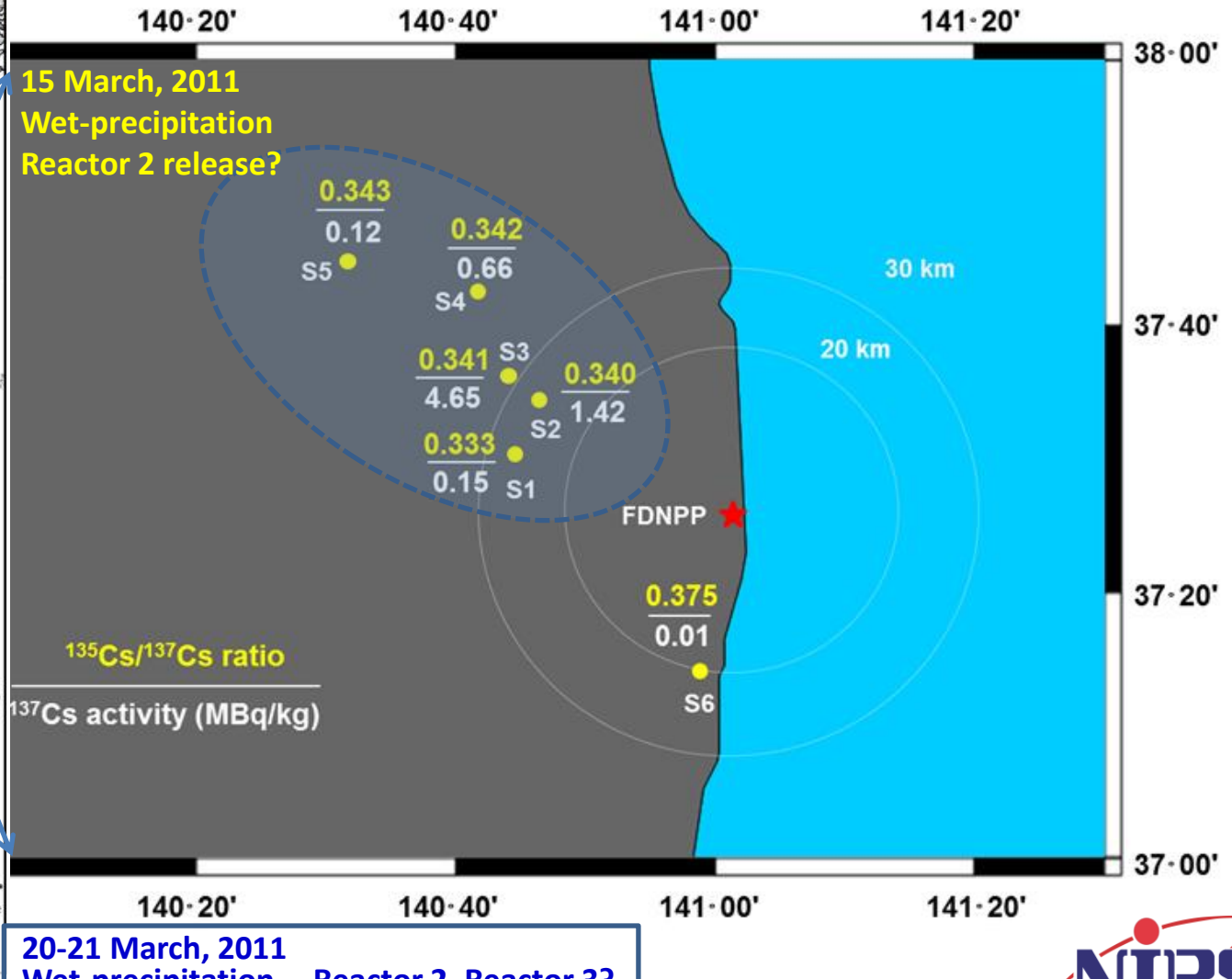
Bu, Zheng et al., ES&T, 2014b*

Further source identification
Cs isotopes ($^{135}Cs/^{137}Cs$) in litter in Fukushima



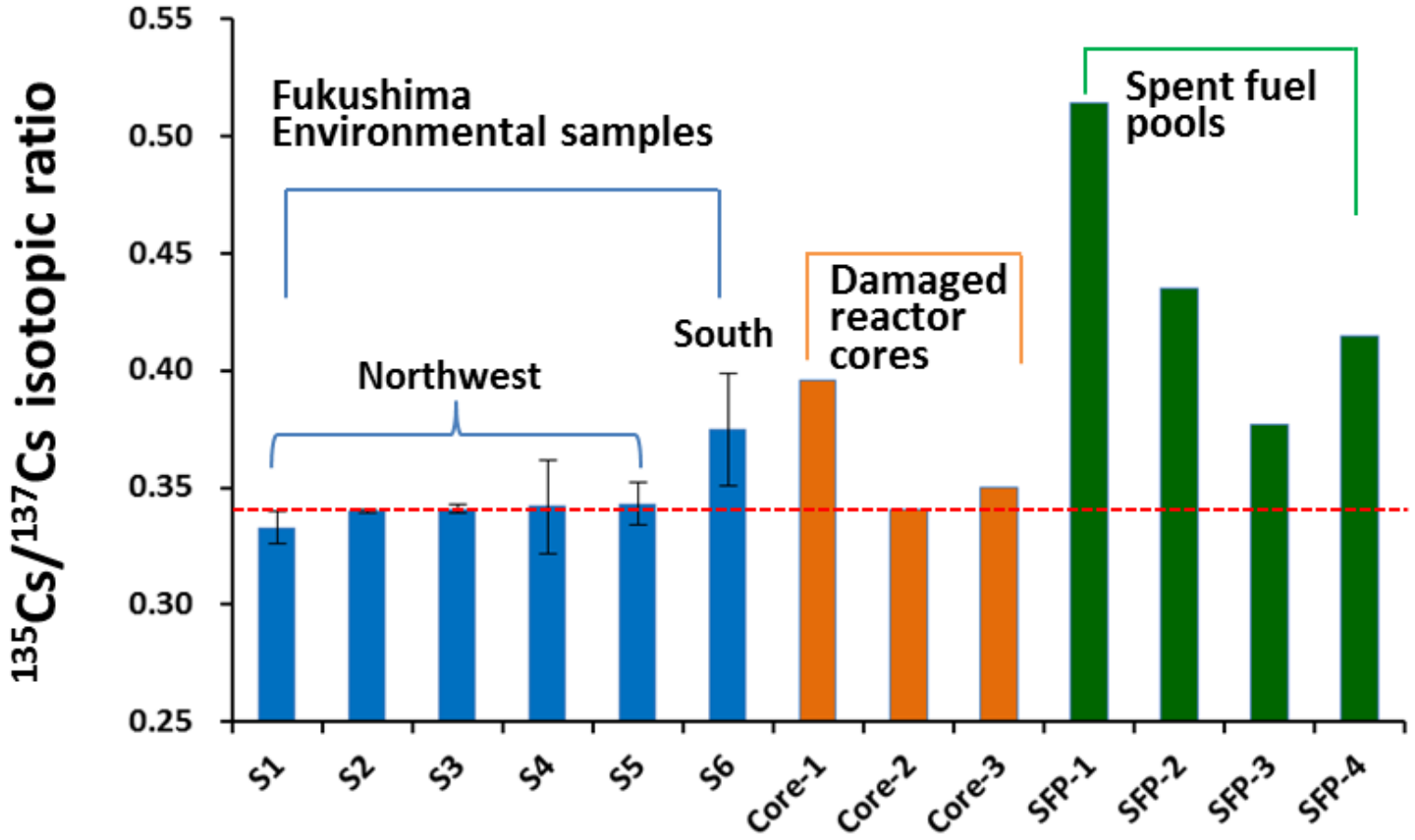
Tsukuba
0.341
0.01

Kamagaya
0.355
0.01



20-21 March, 2011
Wet-precipitation, Reactor 2, Reactor 3?

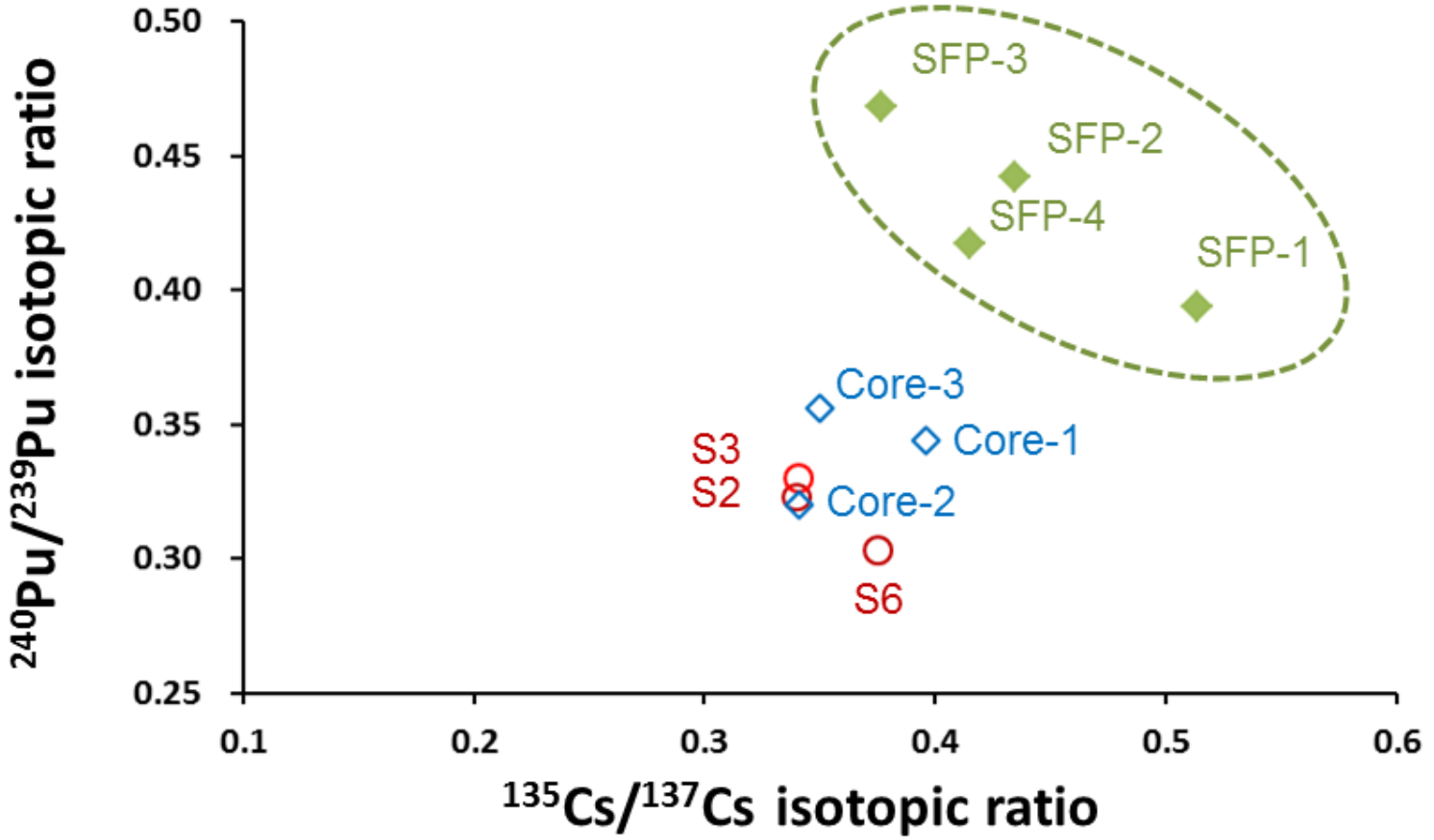
$^{135}Cs/^{137}Cs$ in litter and in reactor core & SFP



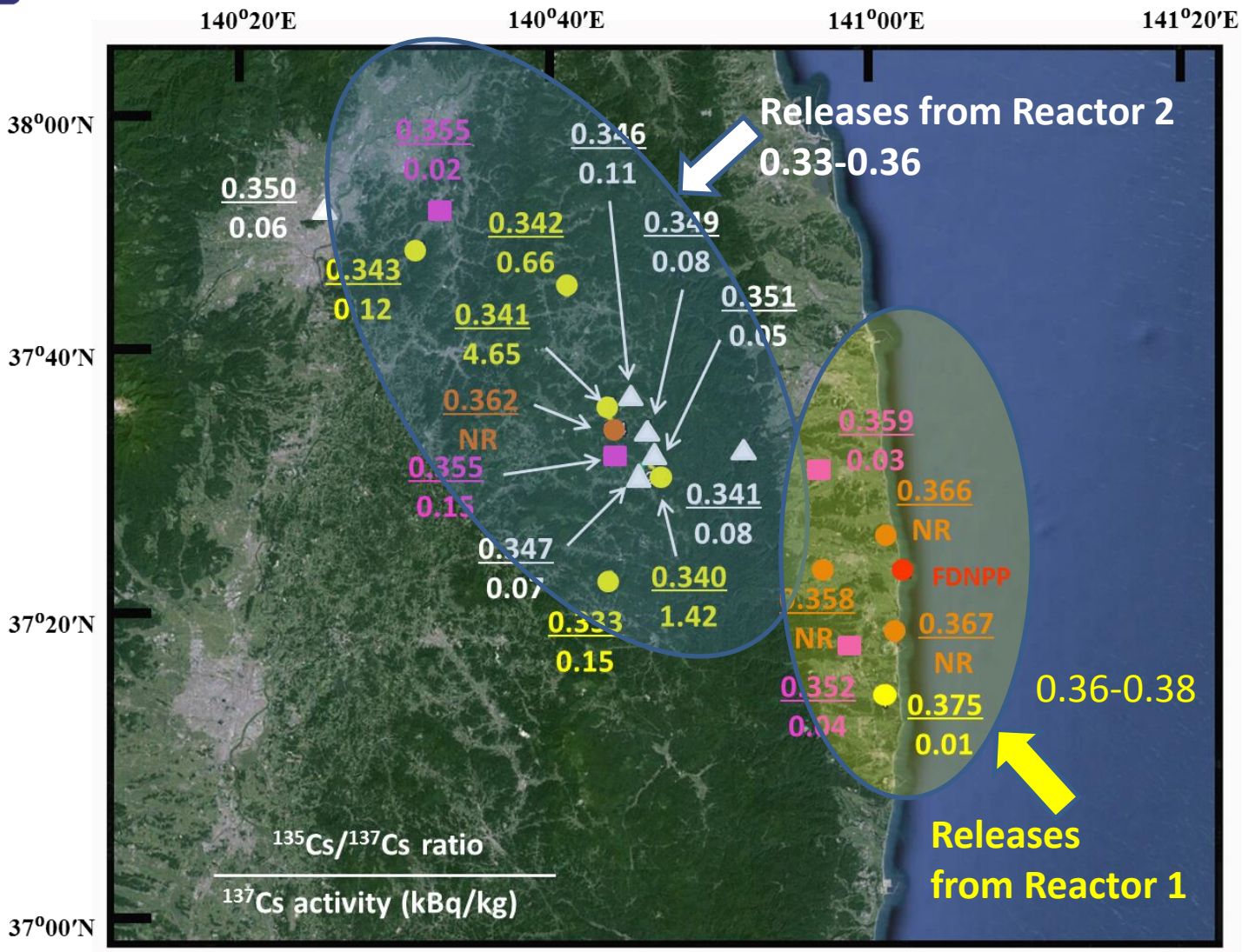
Comparison of $^{135}Cs/^{137}Cs$ isotopic ratios observed in litter and lichen samples and those in nuclear fuels in the damaged reactors (core-1, core-2 and core-3) and in the spent fuel pools (SFPs) based on the model calculation of inventory (*Nishihara et al., 2012*).

Zheng et al. ES&T, 2014

Reactor unit 2 as the major release source for Cs deposition in the NW of the FDNPP

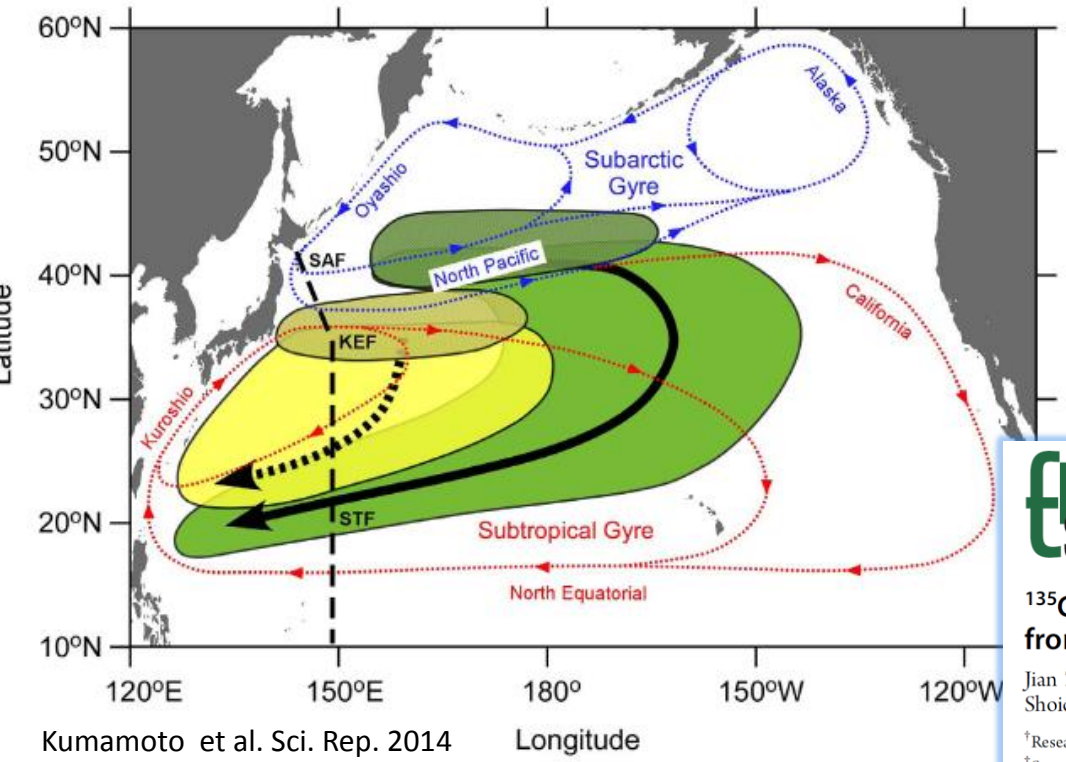


Comparison of Cs and Pu isotopic compositions among litter (S2 and S3) and surface soil (S6) samples, nuclear fuels in the damaged reactors and in the SFPs.



Pink squares represent river suspended particles (*Cao et al. Talanta, 2016*)
Yellow circles represent soil and litter samples (*Zheng et al. ES&T, 2014*)
White triangles represent soil samples (Yang et al., Anal Chim Acta, 2016)
Orange circles represent grass and moss samples (Shibahara et al., JNST, 2014)

Cs isotope ratio as a geochemical tracer



Kumamoto et al. Sci. Rep. 2014

^{134}Cs/^{137}Cs activity ratio as a tracer to understand the transport and fate of Fukushima-sourced ^{137}Cs in the Pacific *courtesy of Dr. M. Aoyama*

^{134}Cs 2.06 year **^{136}Cs 13.2 day**

^{137}Cs 30.2 year **^{135}Cs 2.3E6 year**

^{134}Cs, ^{136}Cs are difficult to be measured in the future
Need new "tracer" to study environmental behavior and fate of the FDNPP-sourced radioactive Cs isotopes:
^{135}Cs/^{137}Cs new tracer

Environmental Science & Technology

Article

pubs.acs.org/

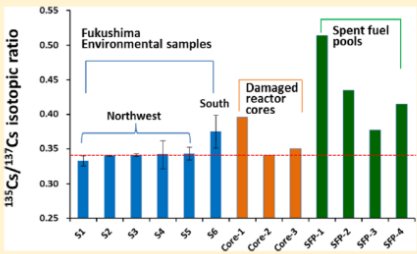
^{135}Cs/^{137}Cs Isotopic Ratio as a New Tracer of Radiocesium Released from the Fukushima Nuclear Accident

Jian Zheng,*[,†] Keiko Tagami,[†] Wenting Bu,[†,‡] Shigeo Uchida,[†] Yoshito Watanabe,[§] Yoshihisa Kubota,[§] Shoichi Fuma,[§] and Sadao Ihara[∥]

[†]Research Center for Radiation Protection, National Institute of Radiological Sciences, 491 Anagawa, Inage, Chiba 263-8555, Jap
[‡]State Key Laboratory of Nuclear Physics and Technology, School of Physics, Peking University, Beijing 100871, China
[§]Project for Environmental Dynamics and Radiation Effects, Fukushima Project Headquarters, National Institute of Radiological Sciences, 491 Anagawa, Inage, Chiba 263-8555, Japan
[∥]Department of Biology, Ohu University, 31-1 Koriyama, Fukushima 963-8611, Japan

Supporting Information

ABSTRACT: Since the Fukushima Daiichi nuclear power plant (FDNPP) accident in 2011, intensive studies of the distribution of released fission products, in particular ^{134}Cs and ^{137}Cs, in the environment have been conducted. However, the release sources, that is, the damaged reactors or the spent fuel pools, have not been identified, which resulted in great variation in the estimated amounts of ^{137}Cs released. Here, we investigated heavily contaminated environmental samples (litter, lichen, and soil) collected from Fukushima forests for the long-lived ^{135}Cs (half-life of 2×10^6 years), which is usually difficult to measure using decay-counting techniques. Using a newly developed triple-quadrupole inductively coupled plasma tandem mass spectrometry method, we analyzed the ^{135}Cs/^{137}Cs isotopic ratio of the



Thank you very much!

ご清聴ありがとうございました

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