



ICMGP 2024
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Use of Environmental Reference Materials (RMs) for Quality Control of Precise Hg Isotopic Measurements

Session 25: Special Session Advancing Metrological Practices

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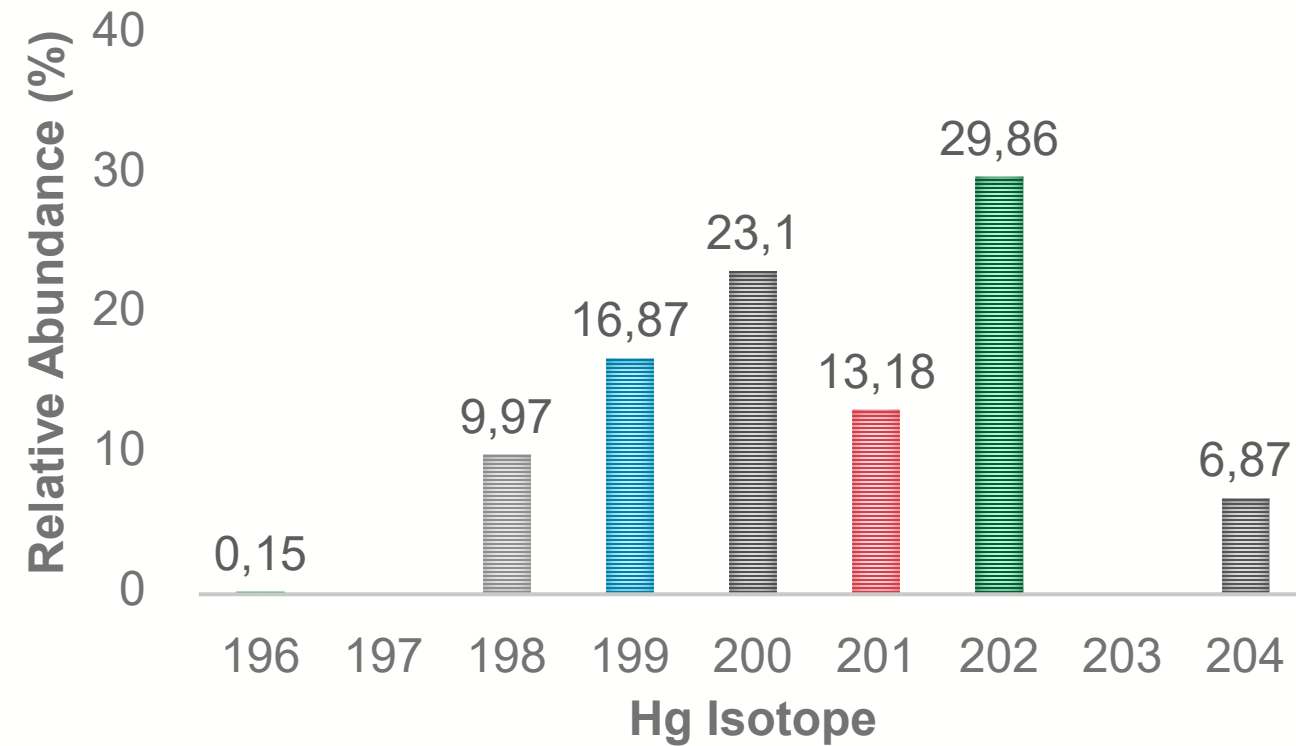


Today's Talk

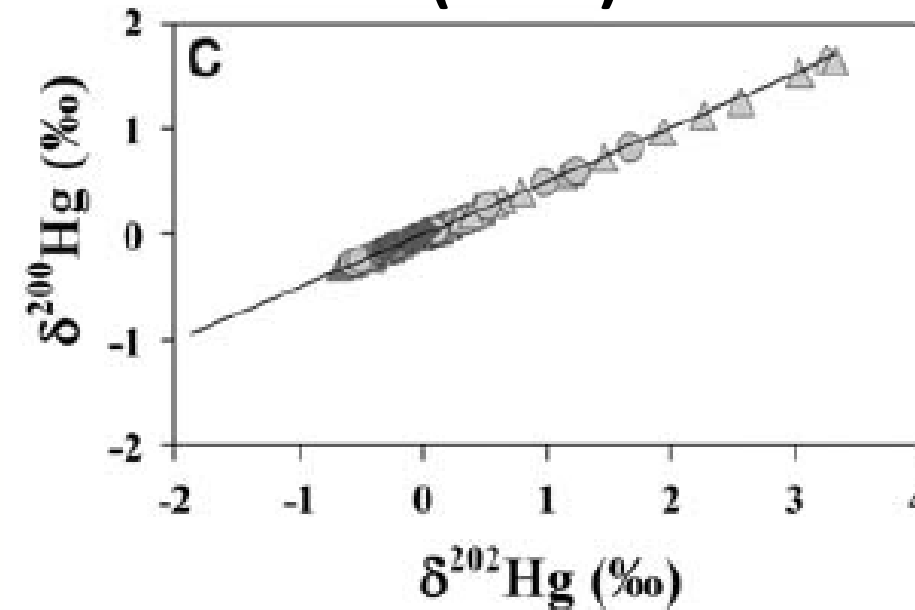
1. Characteristics of Hg isotope
2. Contribution to accuracy control of Hg isotope analysis using NIES Reference Materials



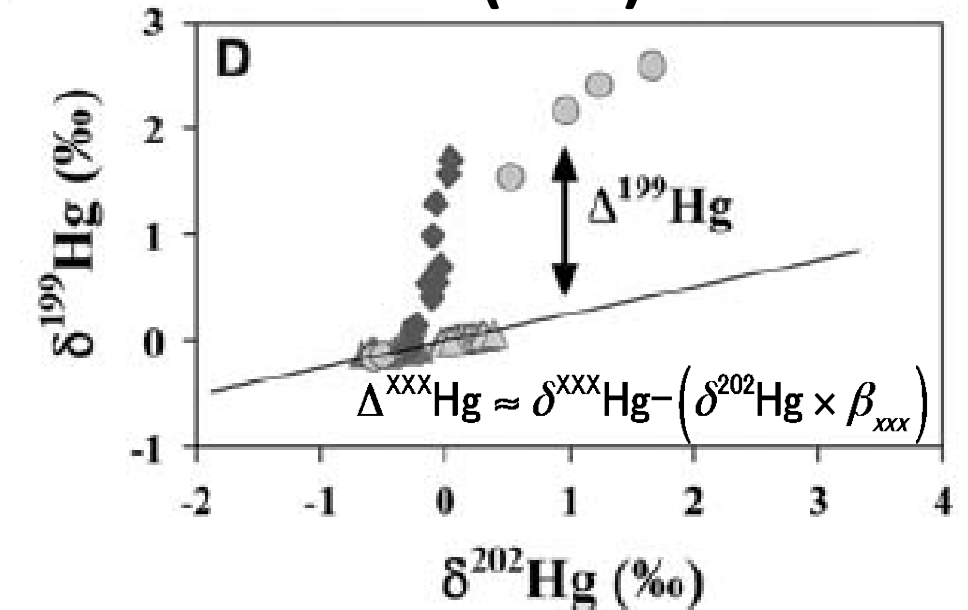
1. Characteristics of Hg isotopes



Mass Dependent Fractionation (MDF)



Mass Independent Fractionation (MIF)



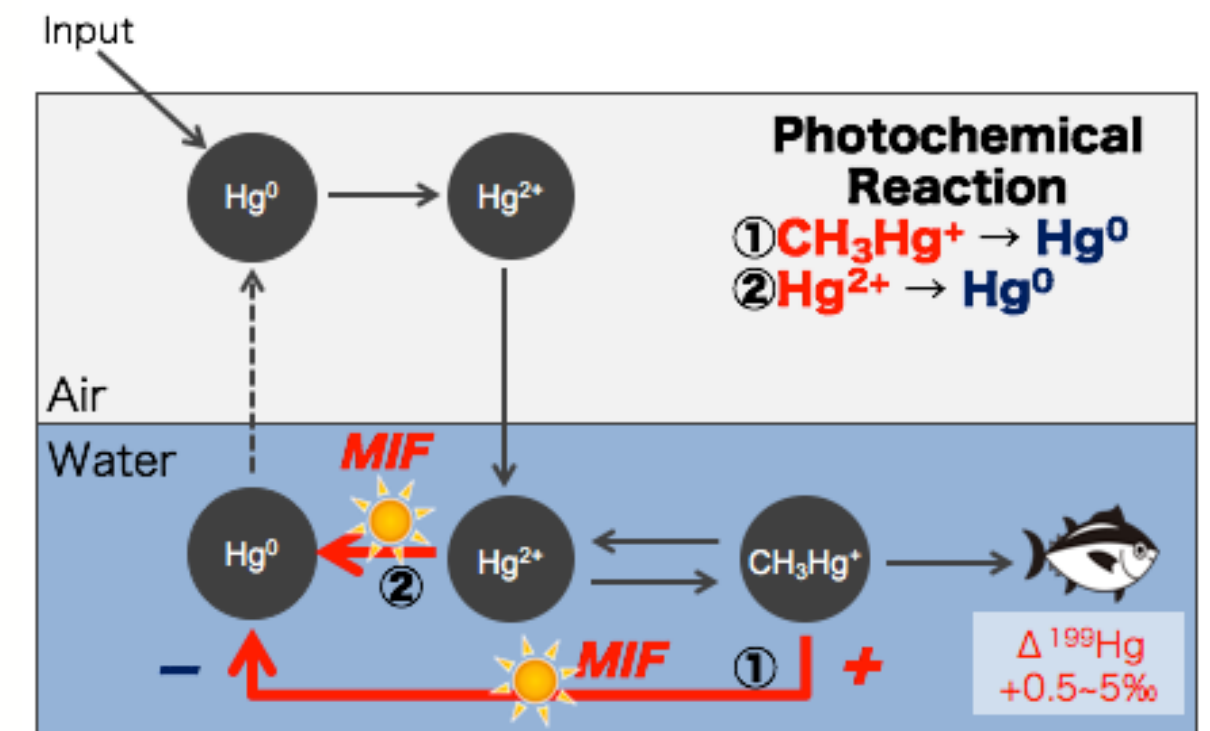
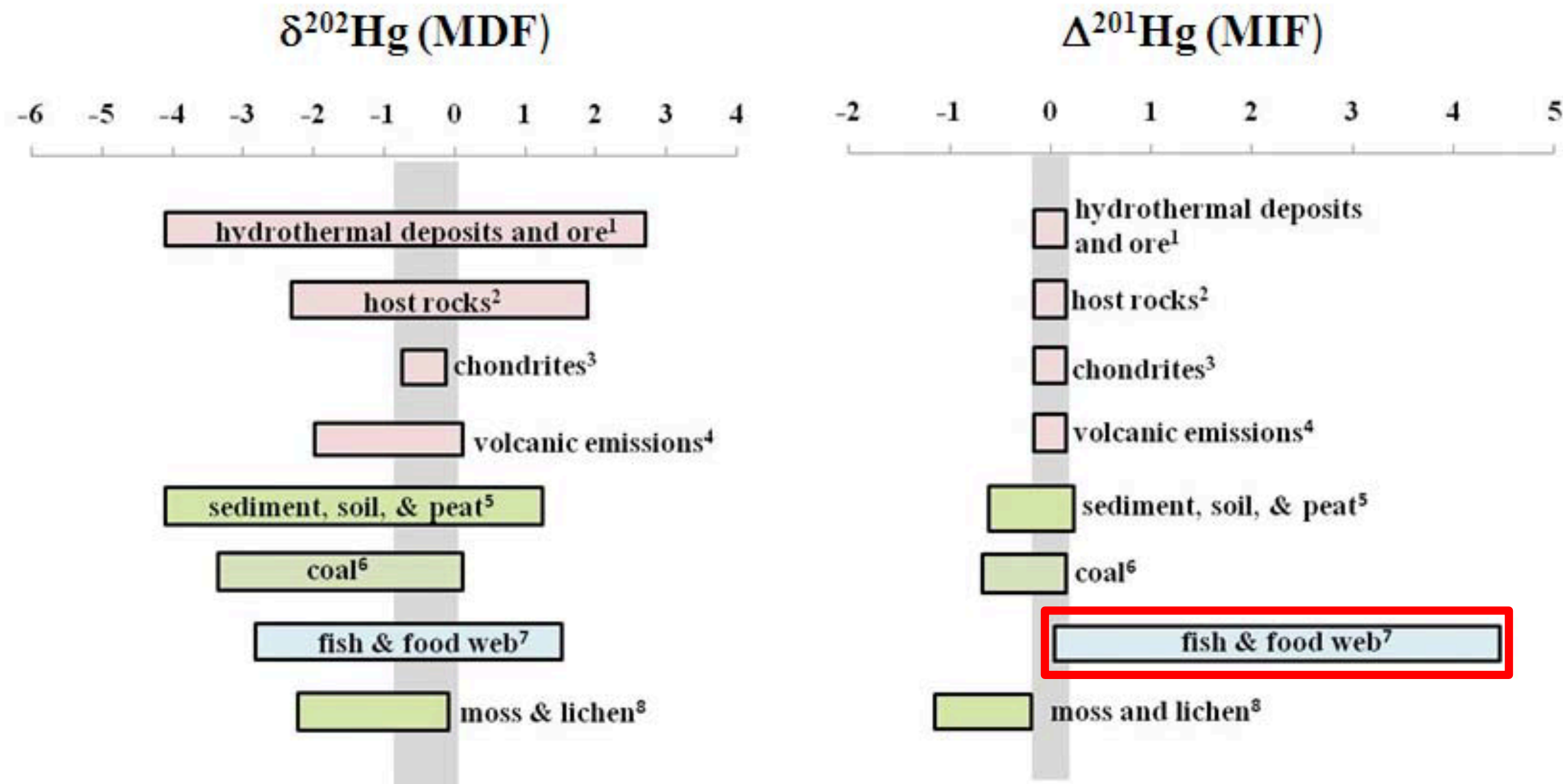
- Isotopic composition is reported in delta notation (δ) relative to a NIST SRM 3133 Hg standard:

$$\delta^{XXX}\text{Hg} \left[\text{‰} \right] = \left\{ \left[\frac{\left(\frac{XXX\text{Hg}}{^{198}\text{Hg}} \right)_{\text{Sample}}}{\left(\frac{XXX\text{Hg}}{^{198}\text{Hg}} \right)_{\text{NIST3133}}} \right] - 1 \right\} \times 1000$$

XXX = 199, 200, 201, 202, 204

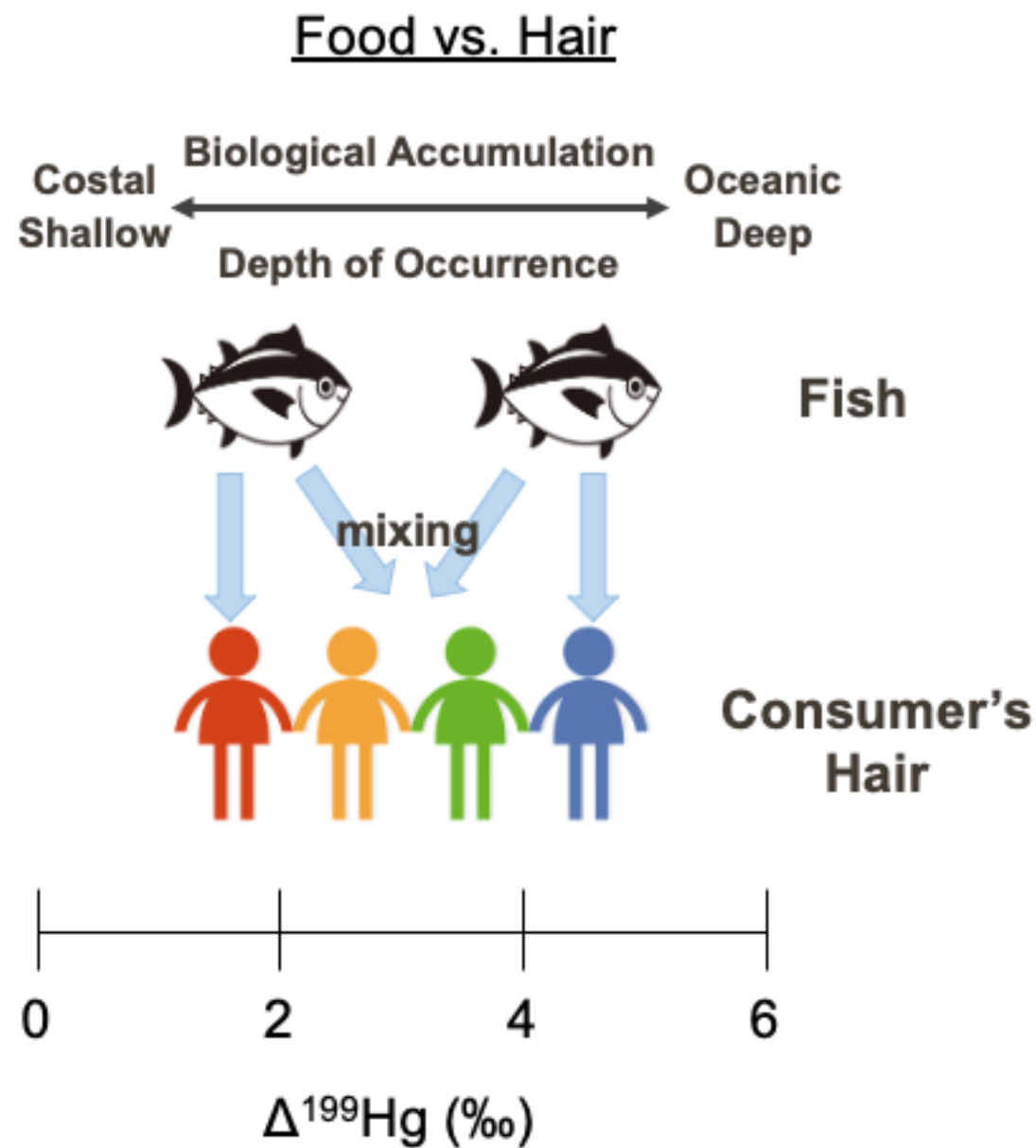
- Isotope fractionation is the process of changing isotope ratios by physical and chemical processes, and those that fractionate according to mass are called **mass-dependent fractionation (MDF)**.
- Hg isotopes are known to exhibit **mass-independent fractionation (MIF)** with odd-isotopes ($\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$), and the fractionation occur due to **photochemical reactions**.

Hg isotope ratios can track its sources and transformation

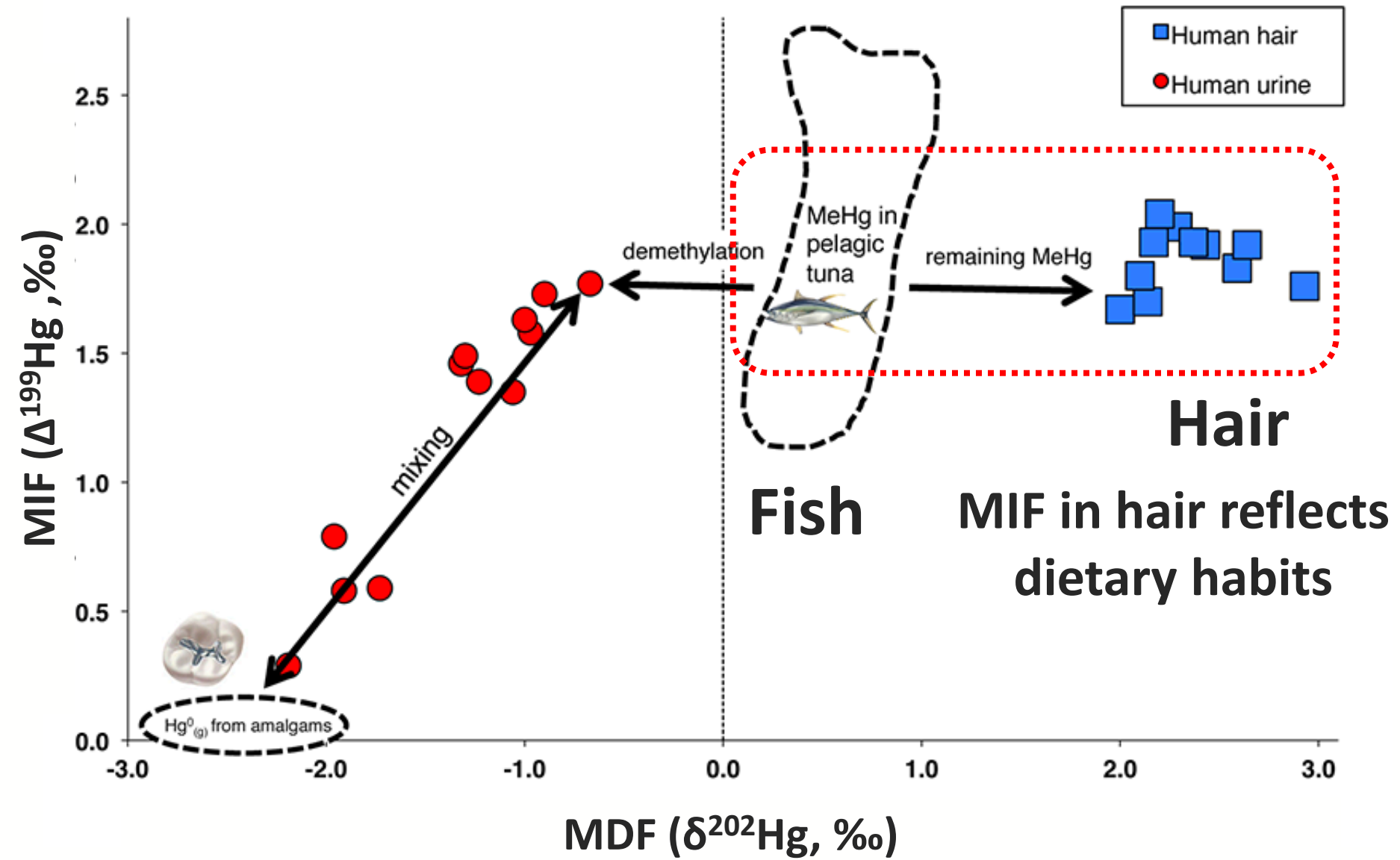


(Bergquist and Blum, 2009)

Estimation of mercury exposure routes by MIF

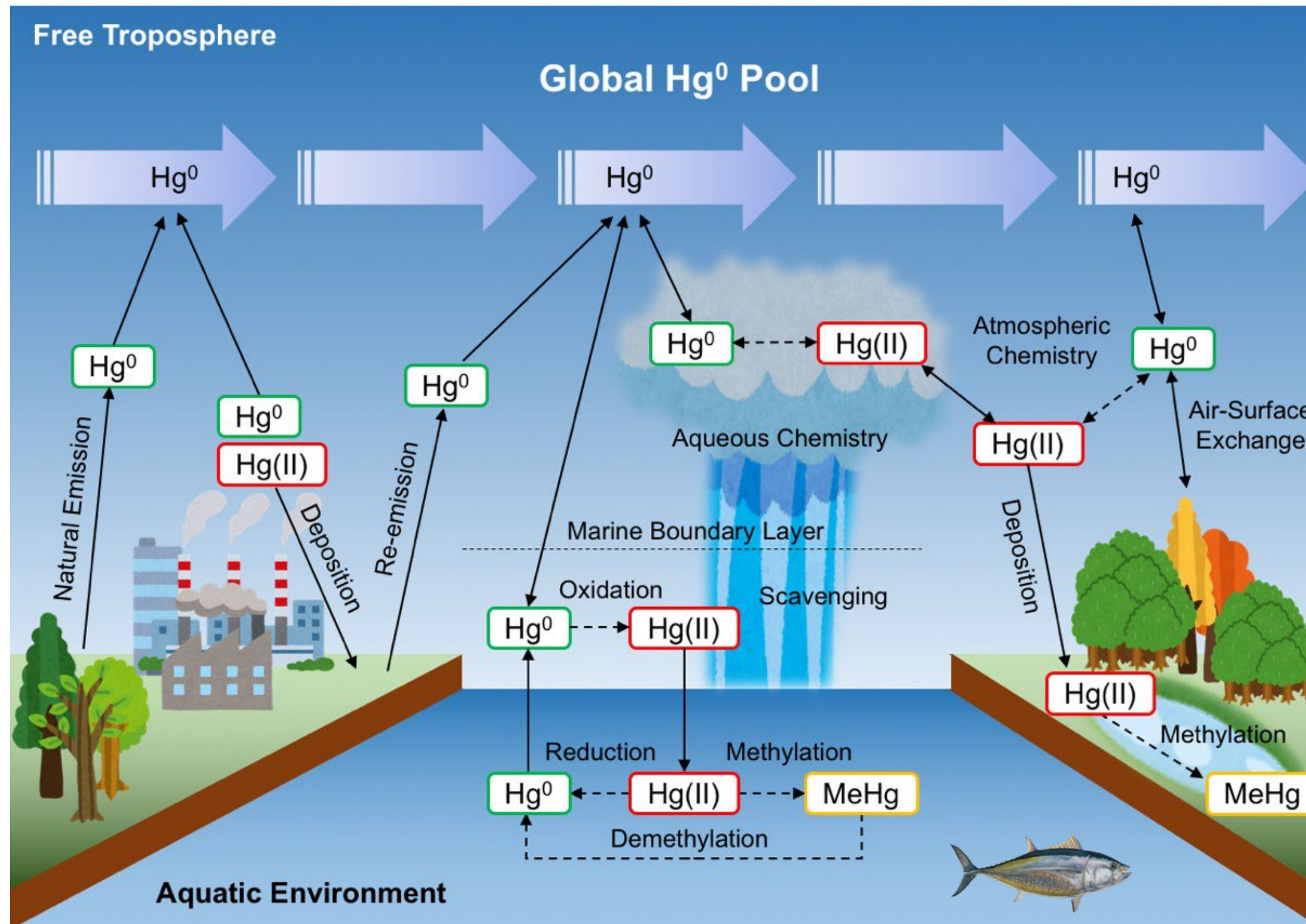


(Sherman et al., 2013)



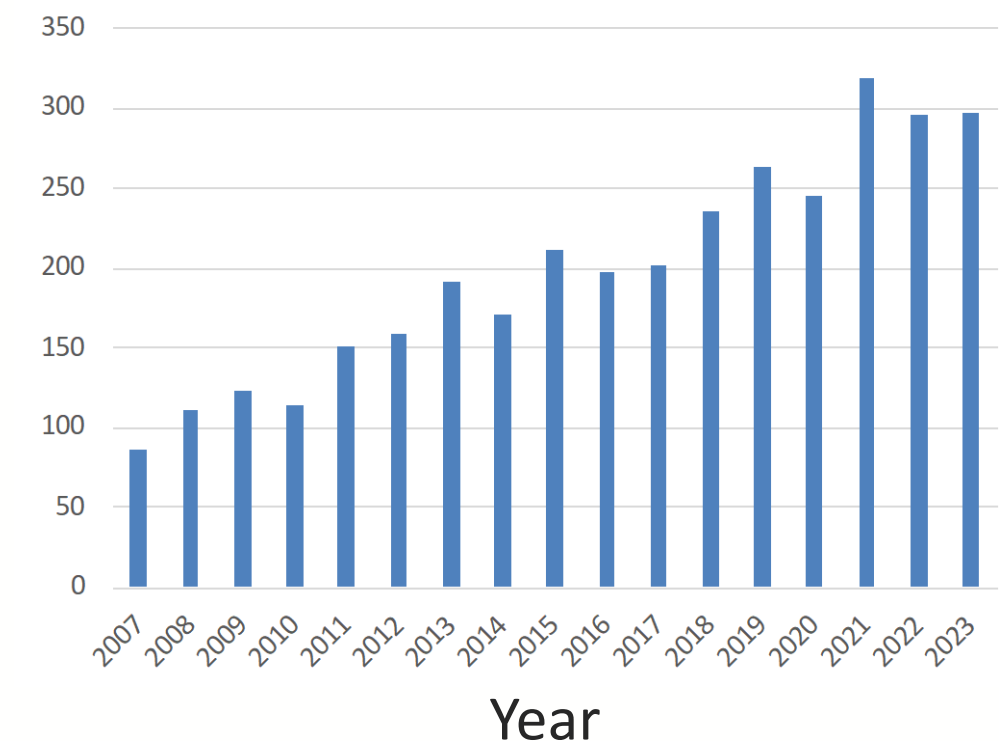
Environmental Studies Using Hg Isotopes

Improvements in analytical techniques have revealed small variations in other environmental samples.



- Hg isotopes are used to
- estimate emission sources (natural/anthropogenic), and
 - understand atmospheric chemistry (wet/dry deposition, etc),
 - air-surface exchange,
 - aquatic environment (methylation/demethylation), etc.

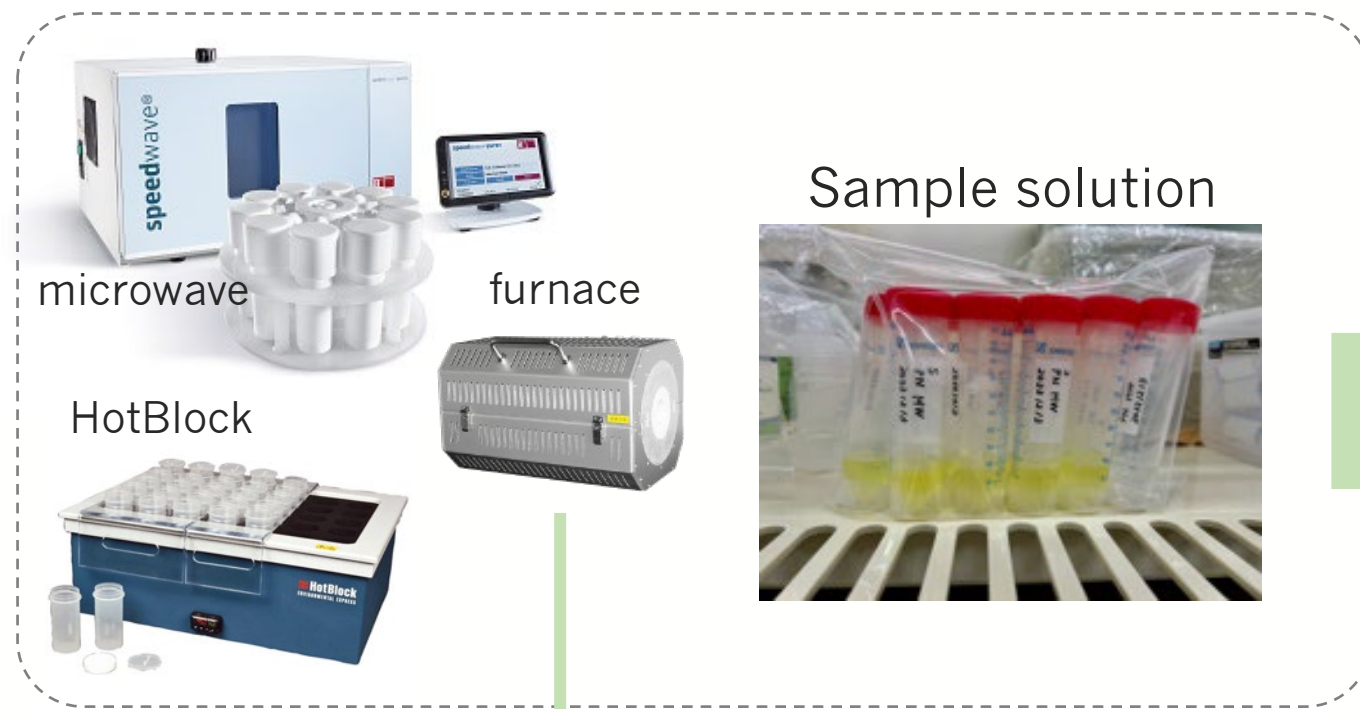
“Hg isotope” (Web of Science)



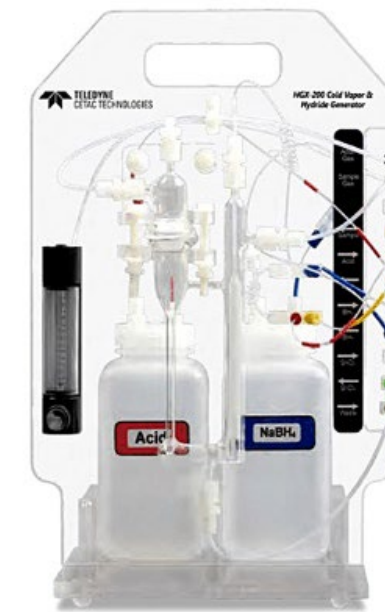
(Travnikov, 2012)

Hg isotopic measurement using MC-ICP-MS

Pretreatment (Preconcentration)

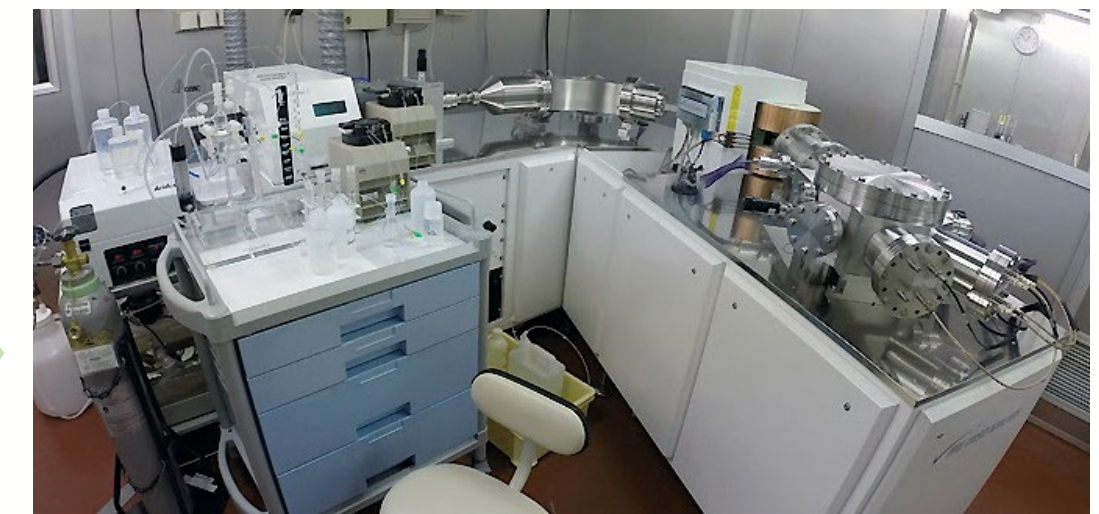


Sample Introduction (reducing vaporization)



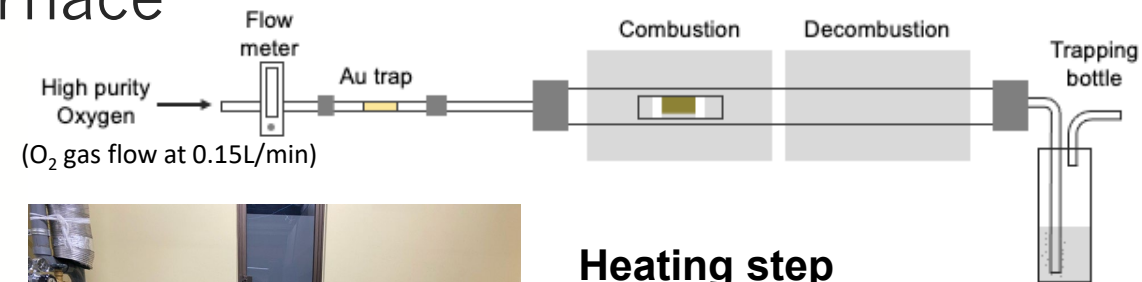
Mixing with SnCl_2 to form $\text{Hg}^{2+} \rightarrow \text{Hg}^0$

Measurement (MC-ICP-MS)



(need ~10ng Hg/measurement)

Furnace



Heating step

Combustion furnace:

1. ambient to 180 °C (12 min)
2. held at 180 °C (20 min)
3. 180 to 600 °C (60 min)
4. 600 to 950 °C (23 min)
5. held at 950 °C (30 min)
6. cooled down from 950 to 25 °C (60 min)

Decombustion furnace: 1000 °C

Acid type and concentration

2% KMnO_4 + 10% H_2SO_4 (v/v, 1:1)

CV-MC-ICP-MS

Cold-vapor Generation Multi-Collector Inductively Coupled Plasma Mass Spectrometry

Correction & Data Presentation

- Sample-Standard Bracketing: NIST SRM 3133)
- Mass Bias Correction (205TI/203TI) : NIST SRM 997

$$\delta^{xxx}\text{Hg} = \left\{ \left[\frac{\left(\frac{^{xxx}\text{Hg}/^{198}\text{Hg}}{\text{Sample}} \right)}{\left(\frac{^{xxx}\text{Hg}/^{198}\text{Hg}}{\text{NIST3133}} \right)} \right] - 1 \right\} \times 1000$$

xxx = 199, 200, 201, 202, 204

$$\Delta^{xxx}\text{Hg} \approx \delta^{xxx}\text{Hg} - (\delta^{202}\text{Hg} \times \beta_{xxx})$$

$\beta_{xxx} = 0.252, 0.502, 0.752, 1.492$

- Since the isotopic variation for some media is less than 1‰, it is important to ensure that isotopic fractionation does not occur during pretreatment and analysis.
- The optimal pretreatment method should be considered for each medium.
- It is important to find a reference material with a similar matrix to the sample and with a known Hg isotopic ratio.
- However, there are not many RMs with reported Hg isotopes, and some RMs having Hg isotopic ratios are no longer distributed.

The number of RMs with accurately measured Hg isotope ratios needs to be increased.

Today's Talk

1. Characteristics of Hg isotope
- 2. Contribution to accuracy control of Hg isotope analysis using NIES Reference Materials**



NIES Environment Reference Materials (since 1980)

CRM No. Name	Certified/Reference Values
No.3 Chlorella	Elements
No.10-d Rice Flour-Unpolished	Elements
No.12 Marine Sediment	Organo Sn
No. 13 Human Hair	MeHg, THg, Elements
No.15 Scallop	Organo Sn
No.18 Human Urine	Organo As
No.23 Tea Leaves II	Elements
No.24 Fly Ash II	PCDDs, PCDFs
No.26 Water Bloom	Microcystins, Elements
No.27 Typical Japanese Diet	Elements
No. 28 Urban Aerosols	Elements, THg (information)
No.29 Water Hyacinth	Elements
No.30 Gobi Kosa Dust	Elements
No.31 Lake Sediment	Elements
No.32 Bluegill	PFOS
No.33 Landfill Cover Soil	Elements, THg
No.34 Water Bloom (¹⁵ N-MC)	¹⁵ N-MC
RM No. Name	Reference Value
No. 1001 Pine Needles I	THg
No. 1002 Pine Needles II	THg



*A certified reference material (CRM) is a reference material, characterized by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability.

Procedures of developing NIES CRMs/RMs

■ Development



■ Evaluation (based on ISO Guide 35)

1. Optimal sample volume for the measurement (minimum volume)
2. Between-, within-bottle homogeneity
3. Long-term stability
4. Interlaboratory

Certified, reference, and information values are assigned.

(*Reliability level: certified > reference > information)

■ Registration to RM database

■ Start of distribution

Three to five year

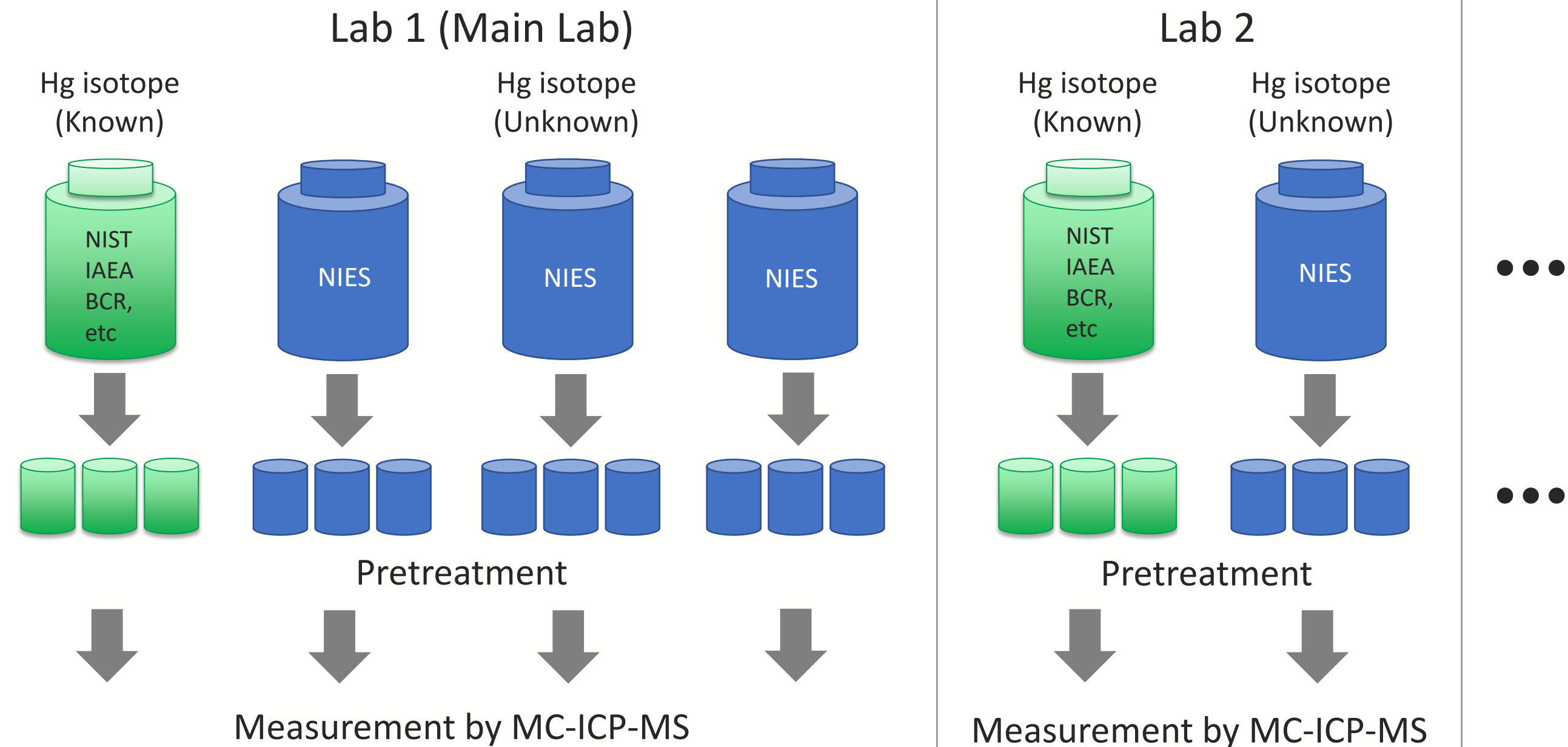
■ Evaluation of stability to extend the expiration date

For the developed RMs, Hg isotopes are determined using a method similar to the ISO guide to ensure accuracy of values.

Evaluations (homogeneity and stability, and handling skills, instrument stability, etc.)

Steps

1. Determination of pretreatment methods using reference materials
2. Randomly select 3 bottles from hundreds of bottles
3. Take 3 samples from the bottles
4. Pretreatment
5. Hg isotopic measurement
Day 1 Two measurements (intra-day variation)
Day 2 Two measurements (inter-day variation)
6. Long-term stability



NIES CRM No. 13 Human Hair

(Certified Reference Material)

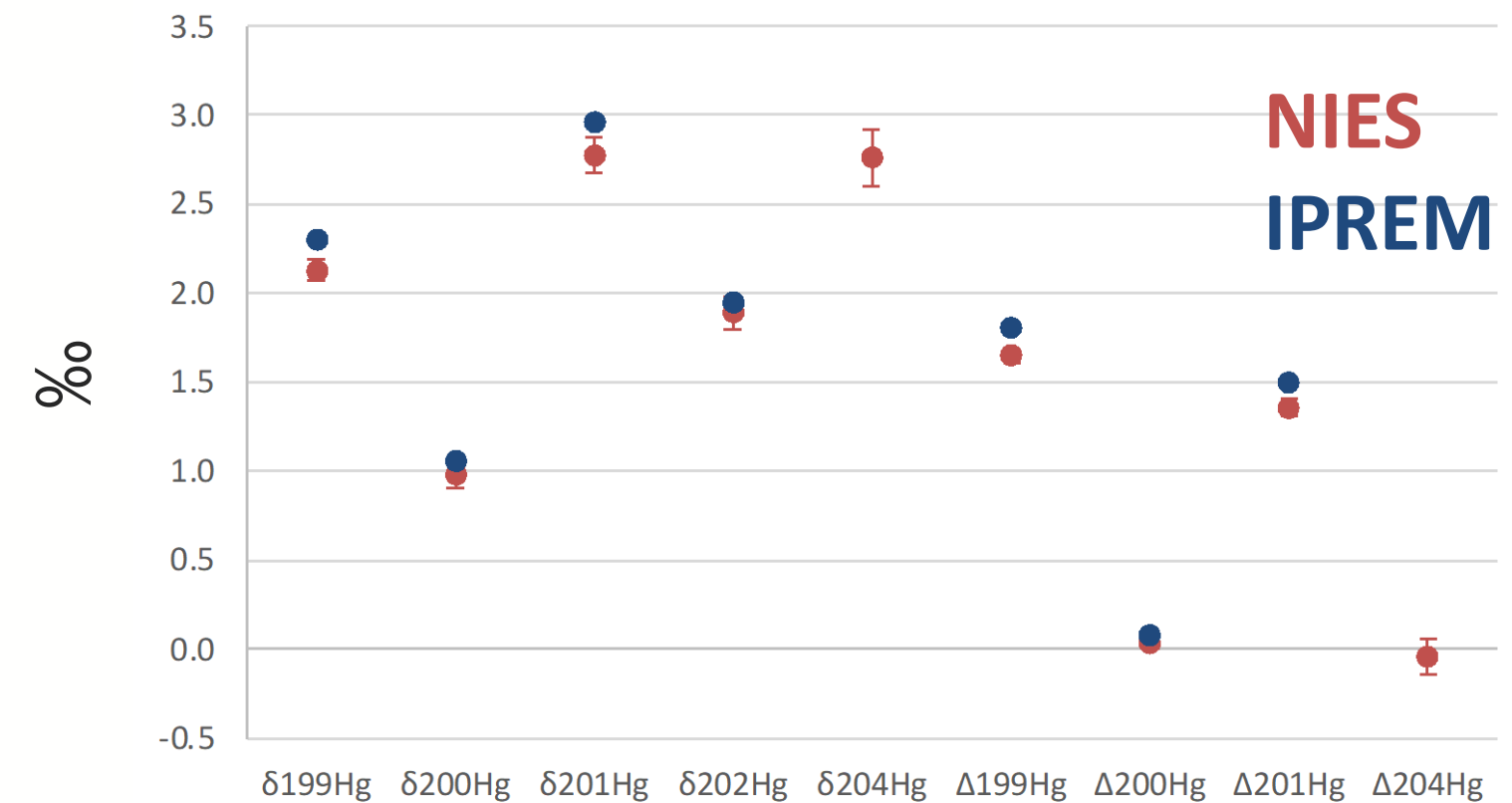
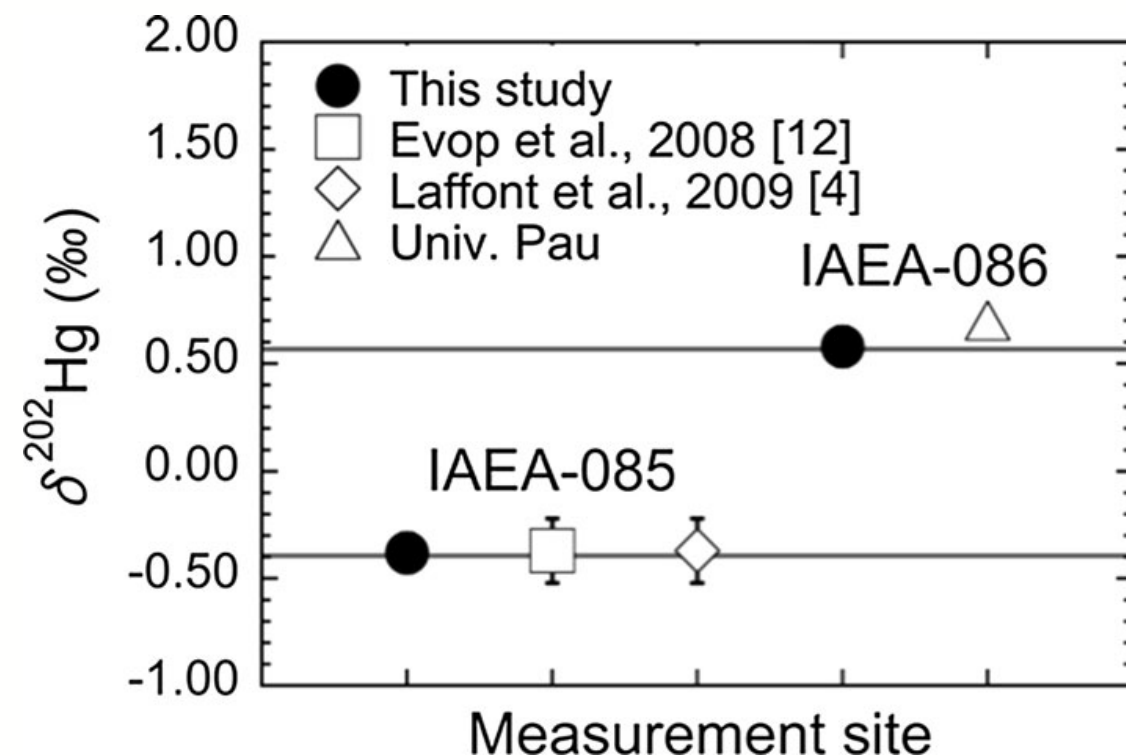
The male scalp hair of Japanese was collected in 3 barbershops in Tokyo and Tsukuba in 1980.

Inter-lab comparison (pretreatment method)

- NIES (microwave)
- IPREM (HotBlocks)

Reference materials (known Hg isotope)

- IAEA 085
- IAEA 086



Accred Qual Assur (2016) 21:197-202
DOI 10.1007/s00769-016-1196-x



PRACTITIONER'S REPORT

Determination of Hg isotopic compositions in certified reference material NIES No. 13 Human Hair by cold vapor generation multi-collector inductively coupled plasma mass spectrometry

Akane Yamakawa¹ · Akinori Takeuchi¹ · Yasuyuki Shibata¹ · Sylvain Berail² · Olivier François Xavier Donard²

NIES CRM No. 28 Urban Aerosols

(Certified Reference Material)

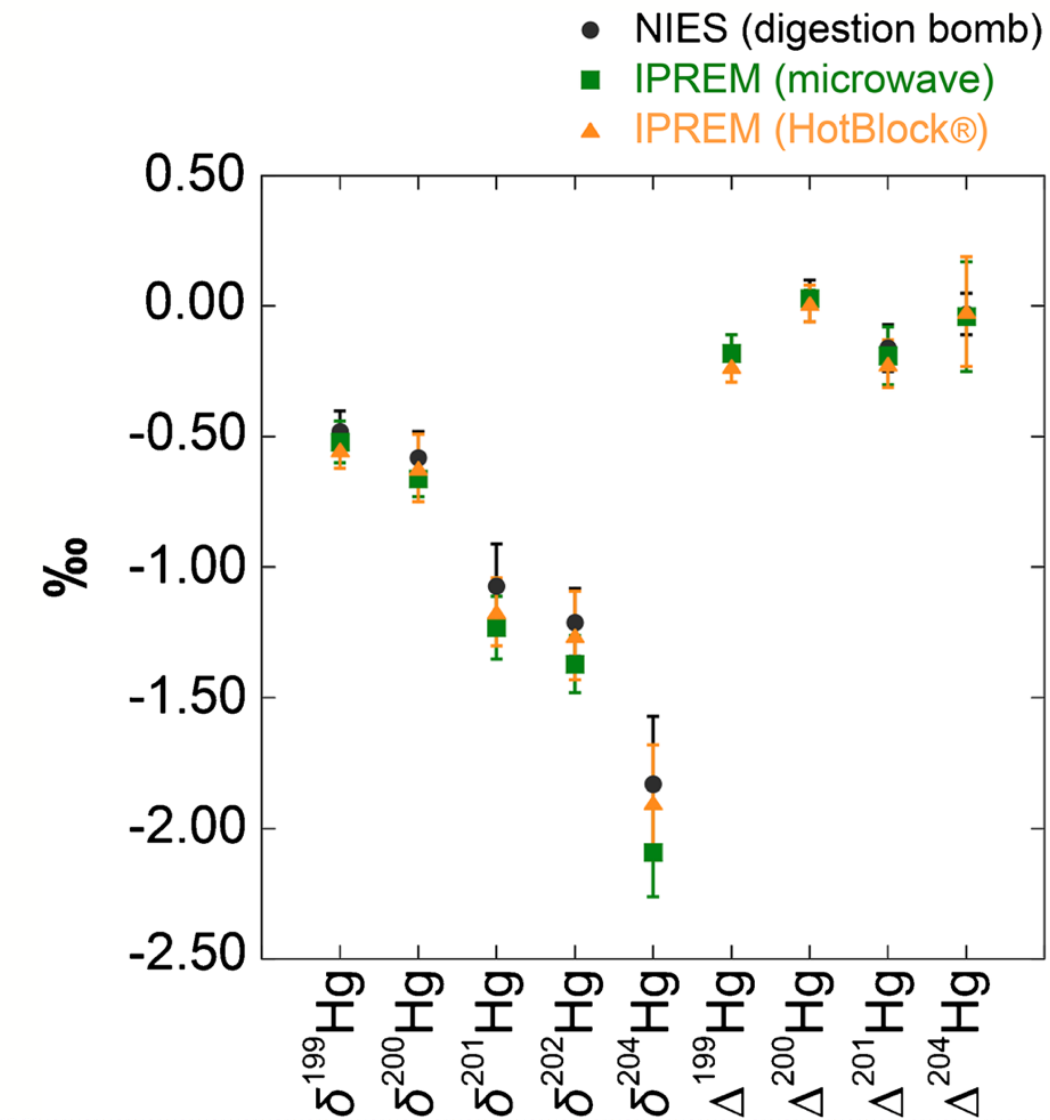
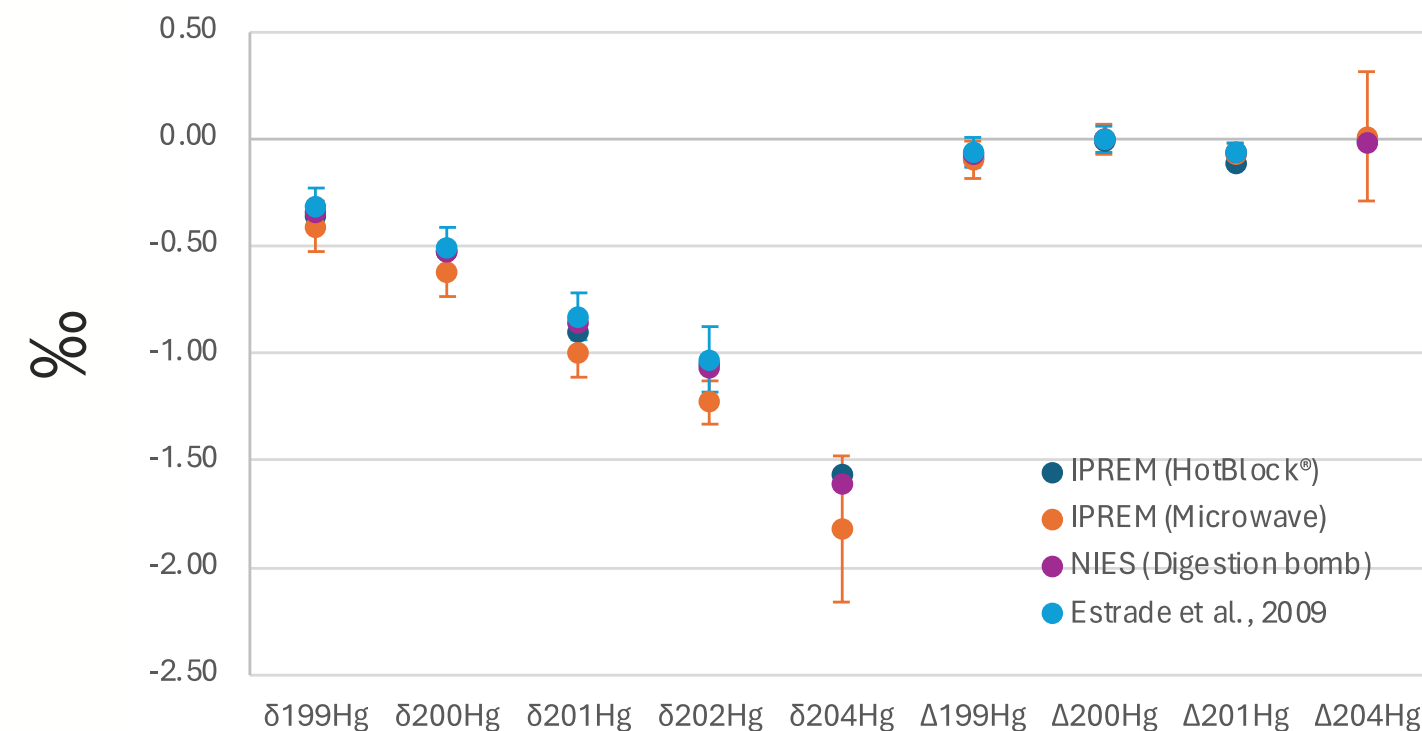
The raw material is atmospheric dust collected in building ventilation filters in central Beijing from 1996 to 2005.

Inter-lab comparison (method)

- NIES (digestion bomb)
- IPREM (microwave)
- IPREM (HotBlocks)

Reference standard (known Hg isotope)

- BCR-176R



Analytical and Bioanalytical Chemistry
<https://doi.org/10.1007/s00216-020-02691-9>

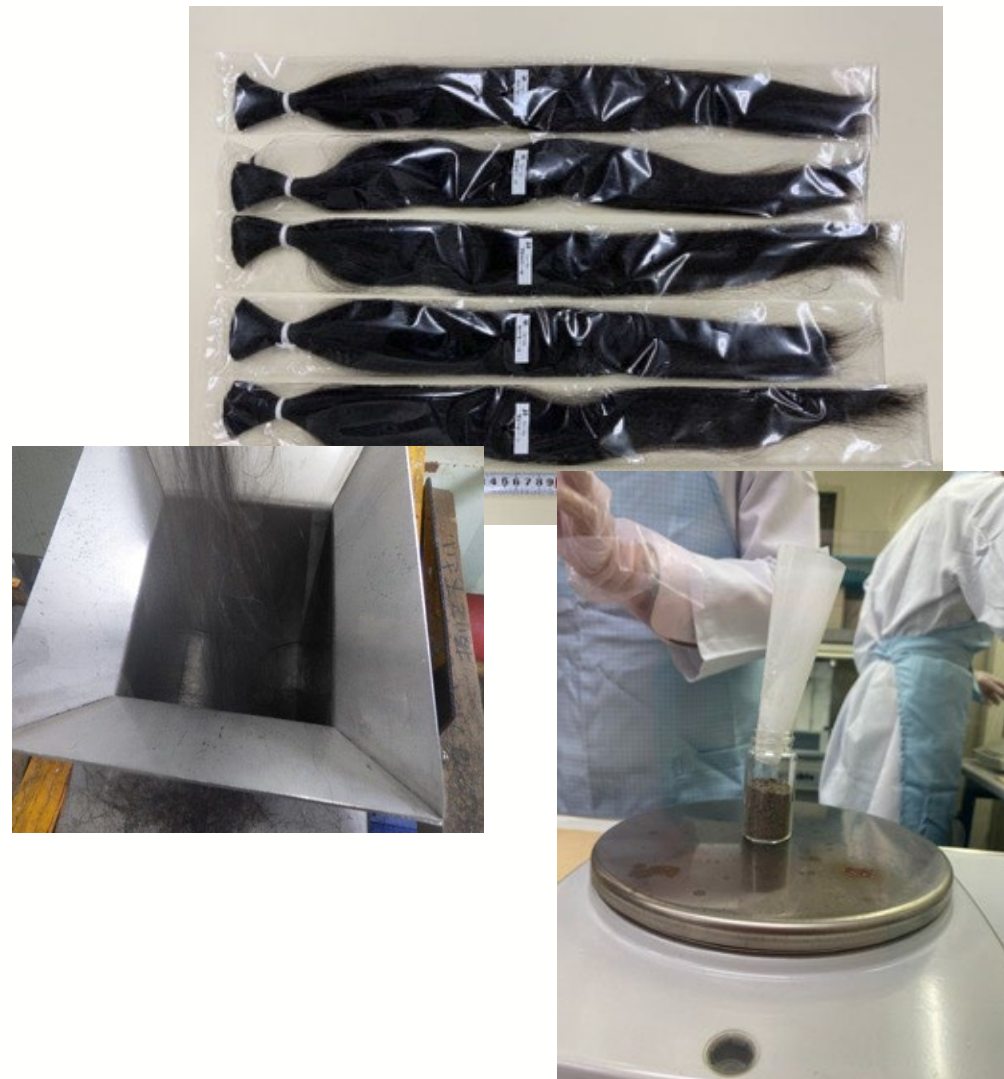
PAPER IN FOREFRONT

Hg isotopic composition and total Hg mass fraction in NIES Certified Reference Material No. 28 Urban Aerosols

Akane Yamakawa¹ · Sylvain Bérail² · David Amouroux² · Emmanuel Tessier² · Julien Barre³ · Tomoharu Sano¹ ·
Kimiyo Nagano¹ · Sadia Kanwal⁴ · Jun Yoshinaga^{5,1} · Olivier F. X. Donard²



Human Hair CRM (Successor to No. 13)



Certified: MeHg, THg, elements
Information: Hg isotope

Sales start on Aug. 1

Urban Dust CRM (Successor to No. 28)



Certified: MeHg, THg, elements
Information: Hg isotope, particle size, etc

Pine Needles RM



Reference: THg, elements
Information: Hg isotope, elements

Sales start on Aug. 1

Summary

- Hg isotopic analysis is a promising tracer for environmental samples to reveal the chemical behavior of mercury.
- The Hg isotopic composition in environmental samples often varies by less than ‰, so extreme care must be taken in experiments.
- For the quality control, it is important to use reference materials with known Hg isotopes.
- Due to the complexity of the matrix of environmental samples, it is useful to have a large number of options by assigning Hg isotope ratios to reference materials.
- For this reason, NIES is working on determining the Hg isotopes to NIES RMs.



NIES Certified Reference Materials

CRM No. Name	Certified/Reference Values	Information Value
No.3 Chlorella	Elements	
No.10-d Rice Flour-Unpolished	Elements	
No.12 Marine Sediment	Organo Sn	
No. 13-a Human Hair	MeHg, THg, Elements	Hg isotope
No.15 Scallop	Organo Sn	
No.18 Human Urine	Organo As	
No.23 Tea Leaves II	Elements	
No.24 Fly Ash II	PCDDs, PCDFs	
No.26 Water Bloom	Microcystins, Elements	
No.27 Typical Japanese Diet	Elements	
No.29 Water Hyacinth	Elements	
No.30 Gobi Kosa Dust	Elements	
No.31 Lake Sediment	Elements	
No.32 Bluegill	PFOS	
No.33 Landfill Cover Soil	Elements, THg	
No.34 Water Bloom (¹⁵ N-MC)	¹⁵ N-MC	
No.35 Water Bloom (¹⁵ N-CYN)	¹⁵ N-CYN	
<i>No.36 Urban Dust</i>	<i>THg, Elements</i>	<i>Hg isotopes</i>
RM No. Name	Reference Value	Information Value
No. 1001 Pine Needles I	THg	Elements, Hg isotopes
No. 1002 Pine Needles II	THg	Elements, Hg isotopes

- 17 CRMs and 2 RMs are available.
- Any ideas or request to assign THg/MeHg concentrations, and Hg isotopes? Please let me know!
- We need collaborators to measure THg/MeHg and Hg isotopes!

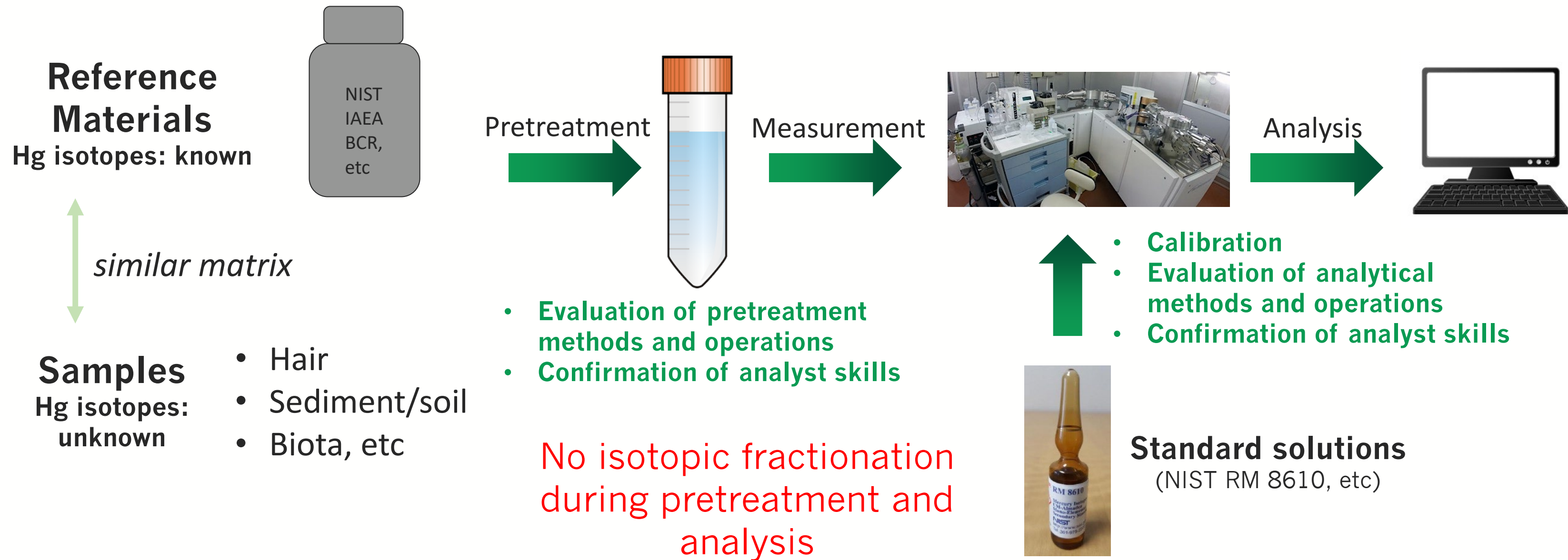
NIES CRM website



	Between-, within-bottle homogeneities	Long-term stability (typically 1 year)	Intercomparison
Reliable level ↑ Certified value	✓	✓	>8 lab.
Reference value	✓	✓	<8 lab.
Information value	?	?	?

- Reference materials with high reliable grade is called Certified Reference Materials (CRMs).
- A certified value has a certain value with uncertainty, which was determined from homogeneity, stability and intercomparison. Reference materials with certified values are called CRMs.
- If the results of joint analysis, homogeneity, and long-term stability are insufficient, the value will be a reference value, and the reference material to which only a reference value is assigned is called a RM.
- There is no definition for information value.

General procedure for Hg isotopic measurement



Proper use of appropriate reference materials is important to obtain reliable values.

**As a contribution to the accuracy control of the analysis,
the Hg isotope ratios is assigned to the NIES RMs.**