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Advancements in Mercury Measurement and Global Comparability: Insights from Inter-Laboratory Exercises and Proficiency Testing Programs

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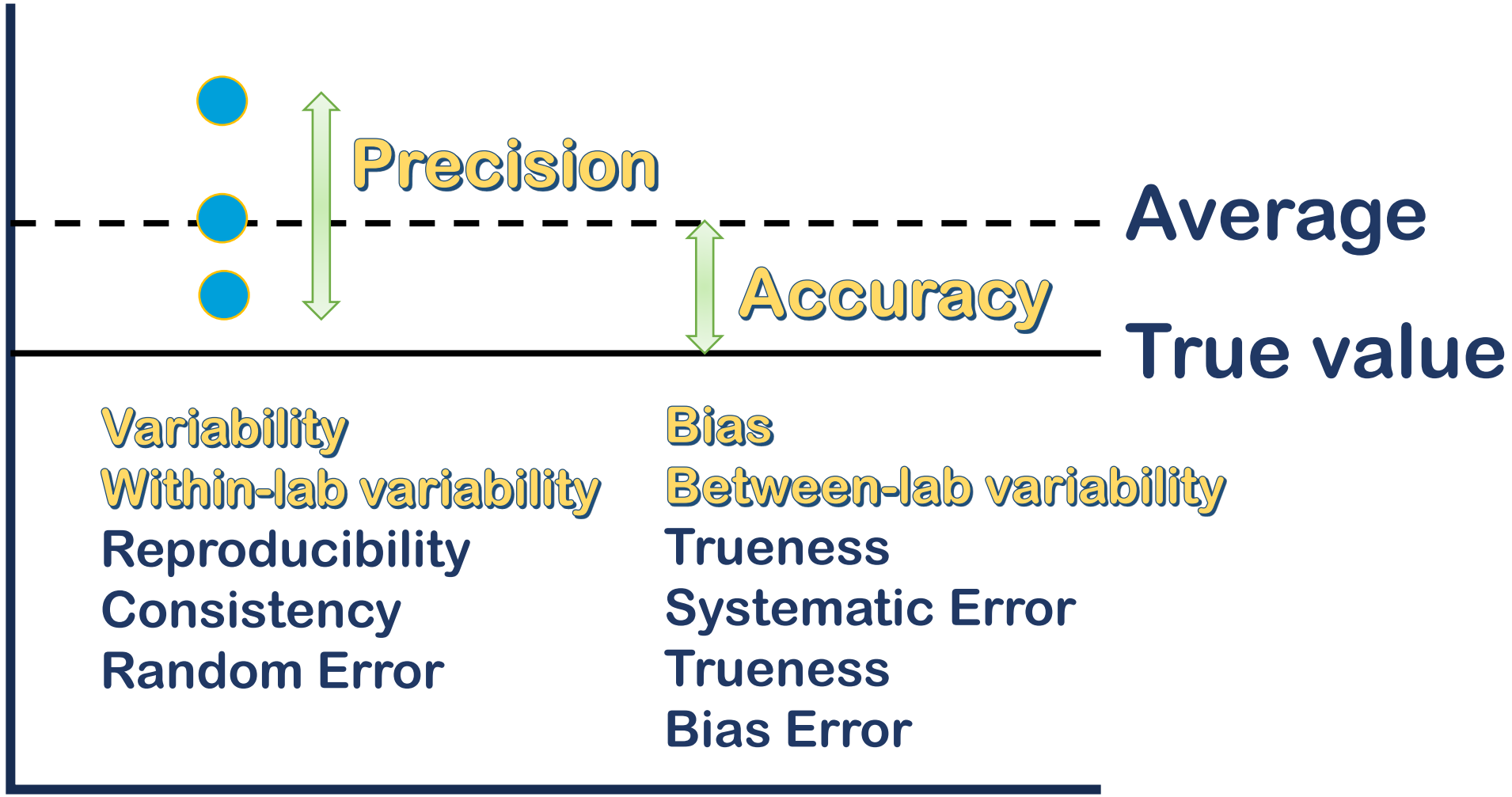
Session 25: Advancing Metrological Practices

Thursday 25 July 2024, 09:15 - 09:30

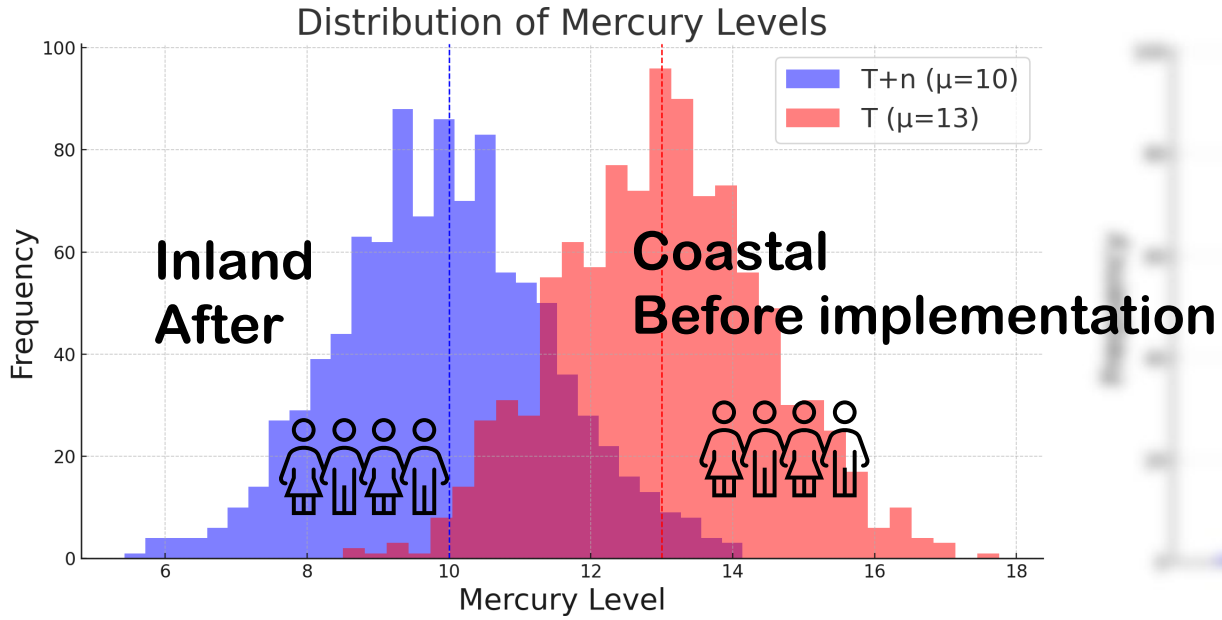
Variability and Bias in Measurements

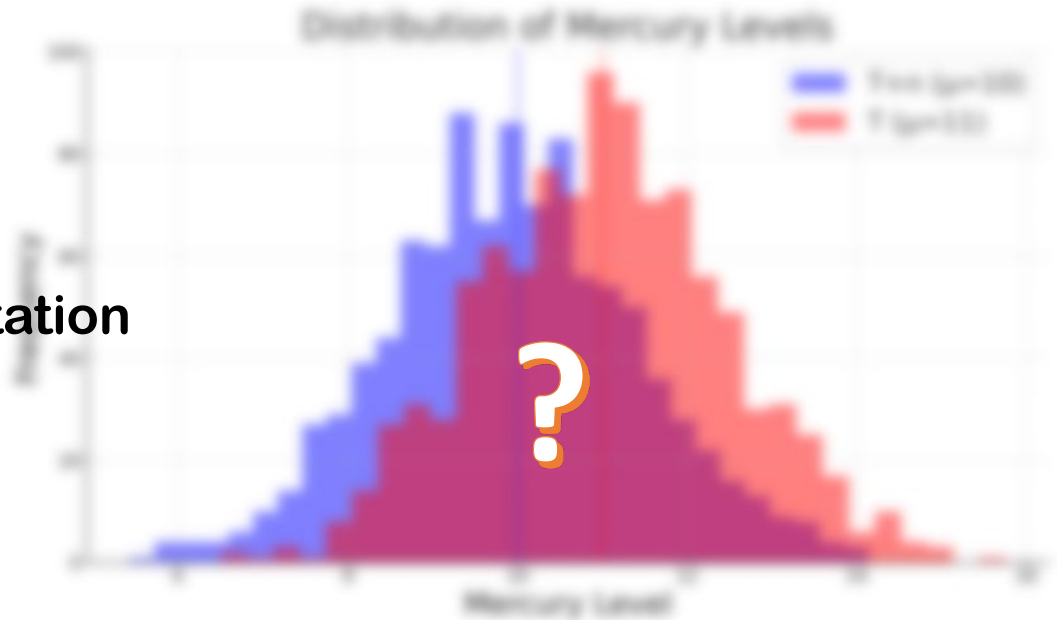


Variability
Within-lab variability
Reproducibility
Consistency
Random Error

Bias
Between-lab variability
Trueness
Systematic Error
Trueness
Bias Error

The Impact of Analytical Quality on Detecting Differences between Two Groups in Multi-laboratory Analyses





Introduction

- Maintaining consistent accuracy across multiple laboratories is challenging due to variations in proficiency (Trantnik 2019).
- Large-scale HBM requires the collaboration of multiple laboratories.
- Harmonizing different labs requires external quality control, including regular PT and CRMs (Vorkamp 2023).

Acceptable Ranges for Analytical Accuracy

Measurement Aspect	Acceptable Range/Value	Brief Note	Reference
Precision (RSD)	≤15%	MeHg in Water	U.S. EPA Method 1630 (1998)
	≤10%	THg in solids/solutions	U.S. EPA Method 7473 (2007)
Accuracy (Bias Error)	± 25%	THg in Water	U.S. EPA Method 1631 (2002)
	± 10%	ICP-MS	U.S. EPA Method 6020B (2014)
	± 5%	Typical in ref. labs	NIST Spec. Pub. 260-136 (2020)

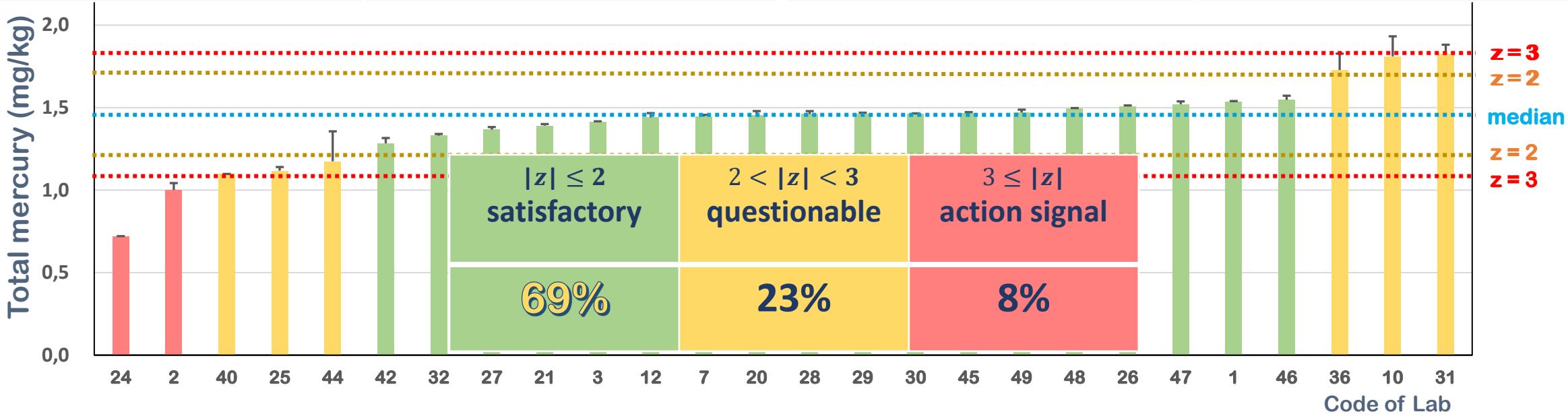
Evaluating data from recent PT and CRM studies reveals the current standards and practices in mercury biomonitoring accuracy.

A Multi-Laboratory Study for Mercury in Hair: PT and CRM Development

	PT round 1		CRM NIMD-01	
Participating Labs	24 Labs (Asia)		11 Labs (Reference)	
Number of Measurements	3 × 1 day		4 × 2 days	
Assigned/Certified Value	Median 1.46 mg/kg		Mean 0.794 mg/kg	
Methods	TD AAS (15) CV AFS (2)	CV AAS (7) ICP-MS (2)	TD AAS (8) CV AFS(1)	CV AAS (2) ICP-MS (0)

Proficiency Testing Results - Z-Score

	mg/kg		mg/kg
Mean	1.41	25 percentile	1.34
Median	1.46	75 percentile	1.50
Standard deviation	0.24	Interquartile range (IQR)	0.17
Minimum	0.72	Normalized IQR (NIQR)	0.12
Maximum	1.82		



Compared to the 80% satisfactory rate in the 2018 Euro UNEP PT for THg in hair, the 69% rate in our Asian PT results highlights a need for improvement and harmonization.

Assessing Multi-Lab Measurement Variability

NIMD

1. Within-Laboratory Variability (Intralaboratory Variability) (RSD): $\sigma_w = \frac{\text{tandard Deviation of the three measurements}}{\text{Mean of the three measurementsS}}$

2. Between-Laboratory Variability (Interlaboratory Variability) (Bias): $\sigma_b = \frac{\text{Mean Reported Value} - \text{Assigned Value}}{\text{Assigned Value}}$

3. Combined Standard Deviation for Each Lab: $\sigma_{Lab} = \sqrt{\sigma_w^2 + \sigma_b^2}$

4. Overall Combined Standard Deviation: $\sigma_{combined} = \sqrt{\frac{1}{N}\sum_{i=1}^{n}(\sigma_{Lab})^2}$

5. Least Significant Difference (LSD): $LSD = t_{\alpha/2,\text{df}} \times \sqrt{2} \times \sigma_{combined}$

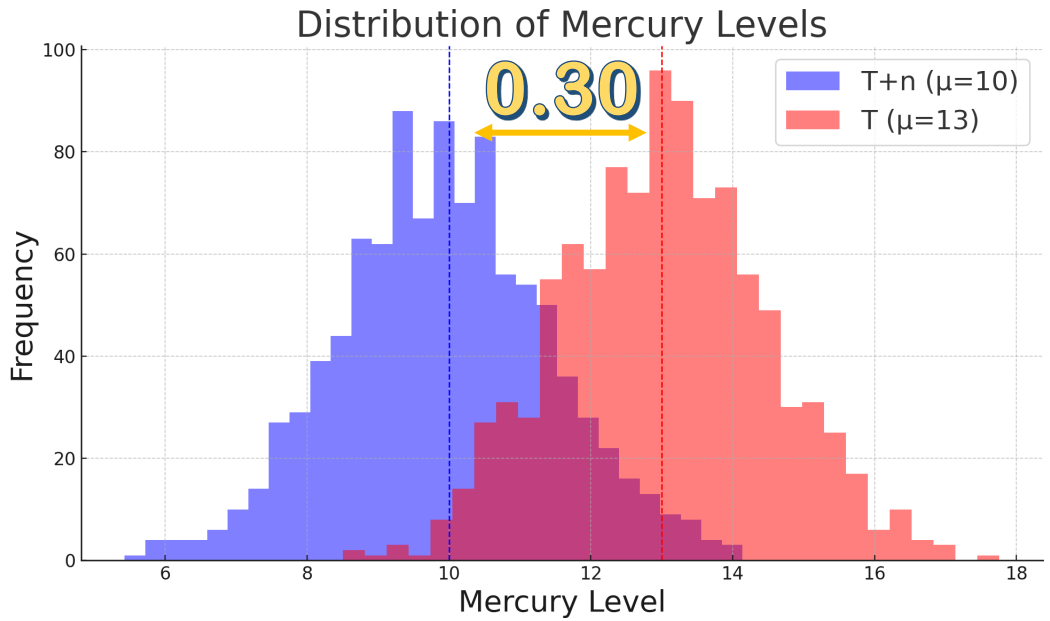
- $t_{\alpha/2,df}$ adjusts for confidence (about 1.96 for 95% confidence).
- $\sqrt{2}$ is a constant used when comparing two measurements.

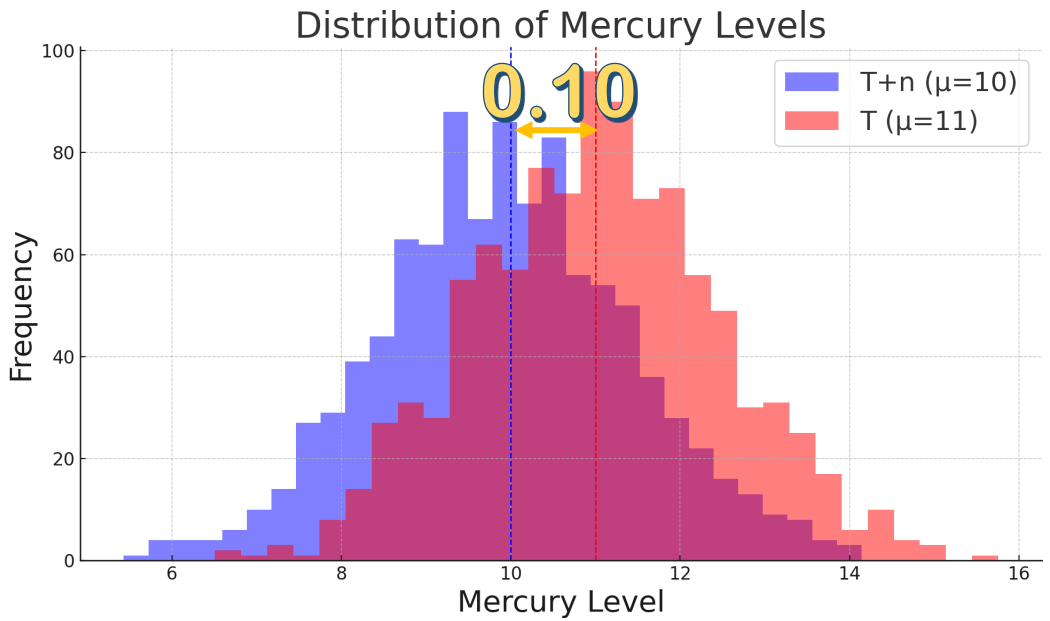
6. Time to Detect Significant Change: $n = \left(\frac{t \times \sigma_{combined}}{\delta}\right)^2 t = \frac{\delta}{\text{Standard Error}} \leftarrow \text{Standard Error} = \frac{\sigma_{\text{combined}}}{\sqrt{n}}$

- t-value for the significance level and power (typically 2.80 for 95% confidence and 80% power).
- δ is the annual decreasing rate.

Influence of Multi-Laboratory Proficiency on LSD (Least Significant Difference)

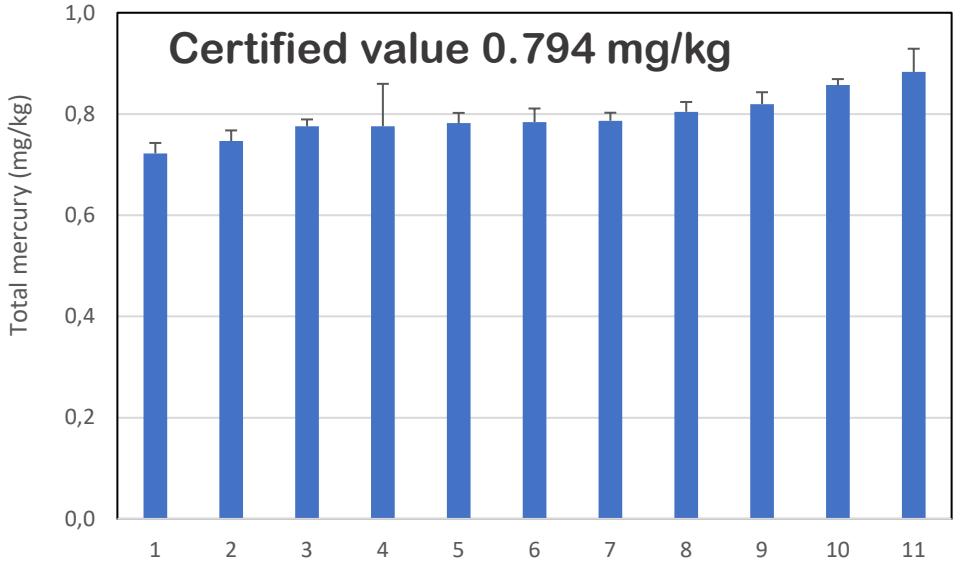
	n	Within-Laboratory Variability (σw)	Between-Laboratory Variability (σb)	Combined Measurement Variability (σc)	LSD
All Labs	24	0.02	0.11	0.11	0.30
Proficient Labs(|z| ≤ 2)	18	0.01	0.03	0.03	0.10

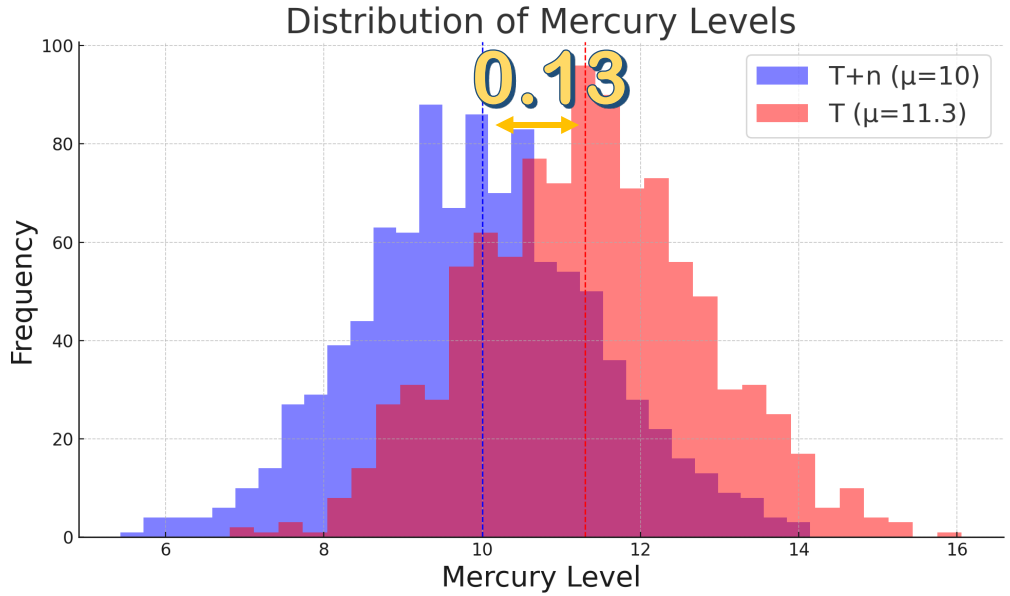




Comparison of PT Results with CRM Reference Labs Performance

	n	Within-Laboratory Variability (σw)	Between-Laboratory Variability (σb)	Combined Measurement Variability (σc)	LSD
All Labs	24	0.02	0.11	0.11	0.30
Proficient Labs(|z| ≤ 2)	18	0.01	0.03	0.03	0.10
Reference Labs	11	0.02	0.04	0.05	0.13

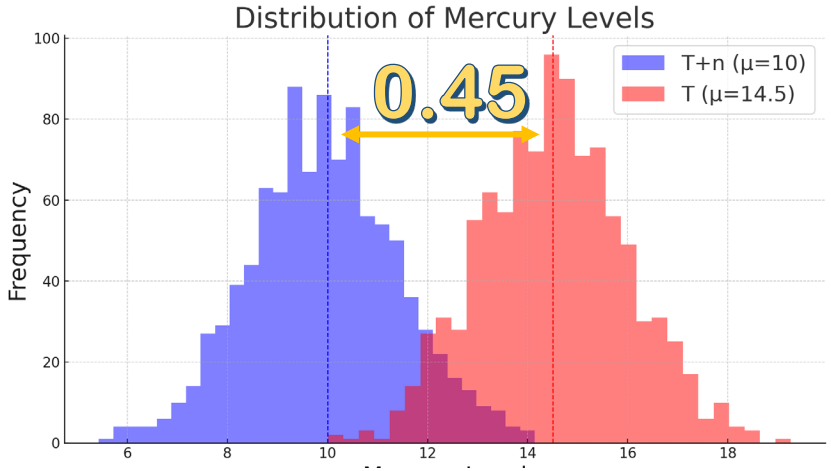




Method Differences in Total Mercury Analysis

	n	Within-Laboratory Variability (σw)	Between-Laboratory Variability (σb)	Combined Measurement Variability (σc)	LSD
All Labs	24	0.02	0.11	0.11	0.30
Proficient Labs($\|z\| \leq 2$)	18	0.01	0.03	0.03	0.10
Reference Labs	11	0.02	0.04	0.05	0.13
TD AAS Method	15	0.01	0.07	0.07	0.19
CV AAS Method	6	0.04	0.16	0.16	0.45

Sample pretreatment	Methods	n	$\|z\| \leq 2$	$2 < \|z\| < 3$	$3 \leq \|z\|$
no	TD AAS	15	13 (87%)	1	1
yes	CV AAS	7	3 (42%)	3	1
	CV AFS	2	1 (50%)	1	0
	ICP-MS	2	1 (50%)	1	0



TD AAS: Achieved 87% satisfactory results with a low LSD of 0.19. Suitable for labs with varying experience levels (Esteban 2015; Hwijin 2019).

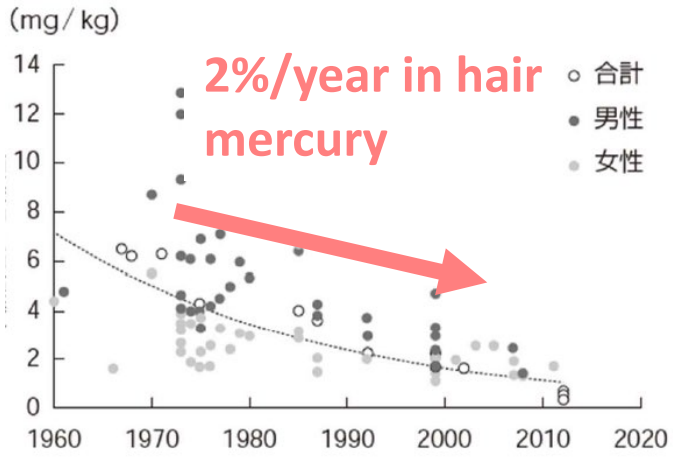
CV AAS: Requires sample digestion, higher variability, and a high LSD of 0.45.

Accuracy Issues: Incomplete digestion, contamination, and insufficient stannous chloride.

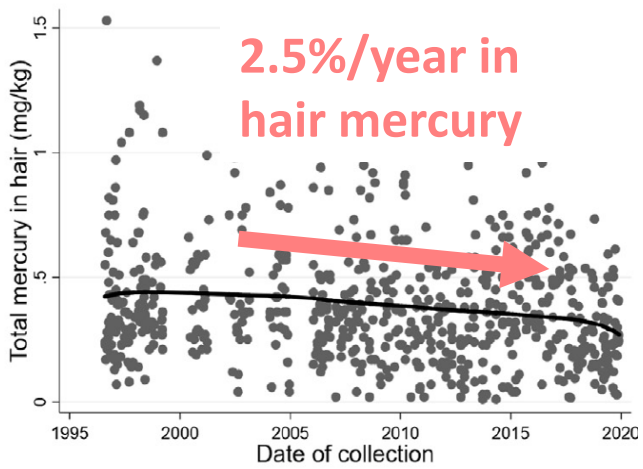
The Role of Measurement Reliability in Monitoring Periods

	n	LSD	2%/year (year)	2.5%/year (year)	6.3%/year (year)
All labs	24	0.30	245	149	24
Proficient Labs(|z| ≤ 2)	18	0.10	25	15	2
Reference Labs	11	0.13	27	16	4
TD AAS Method	15	0.19	101	61	10
CV AAS Method	6	0.45	532	323	51
All Asian Labs	21	0.30	242	148	23
Proficient Asian Labs (|z| ≤ 2)	14	0.06	11	6.8	1

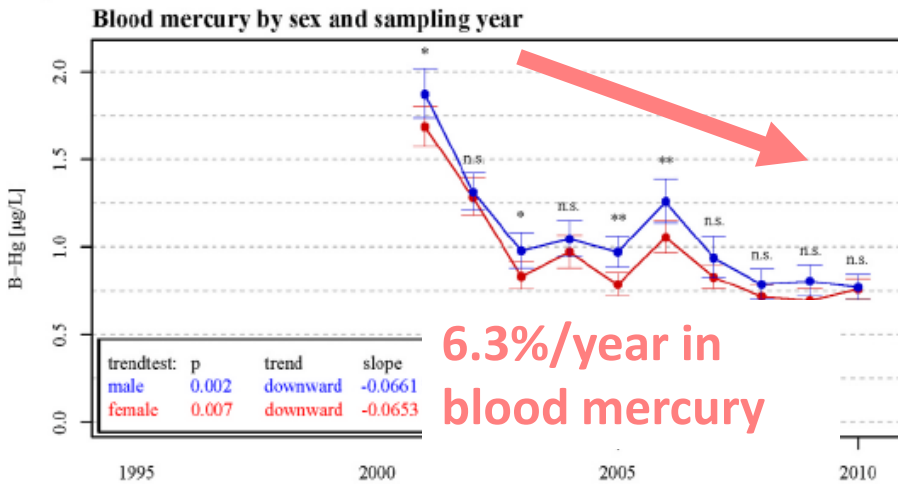
32 studies, ~20,000 Japanese (1960s-2010s) (Haraguchi 2023)



655 Swedish women over 23 years (Kippler 2021)



Young Germans (2001-2010) (Bartel-Steinbach 2022)



Key Findings

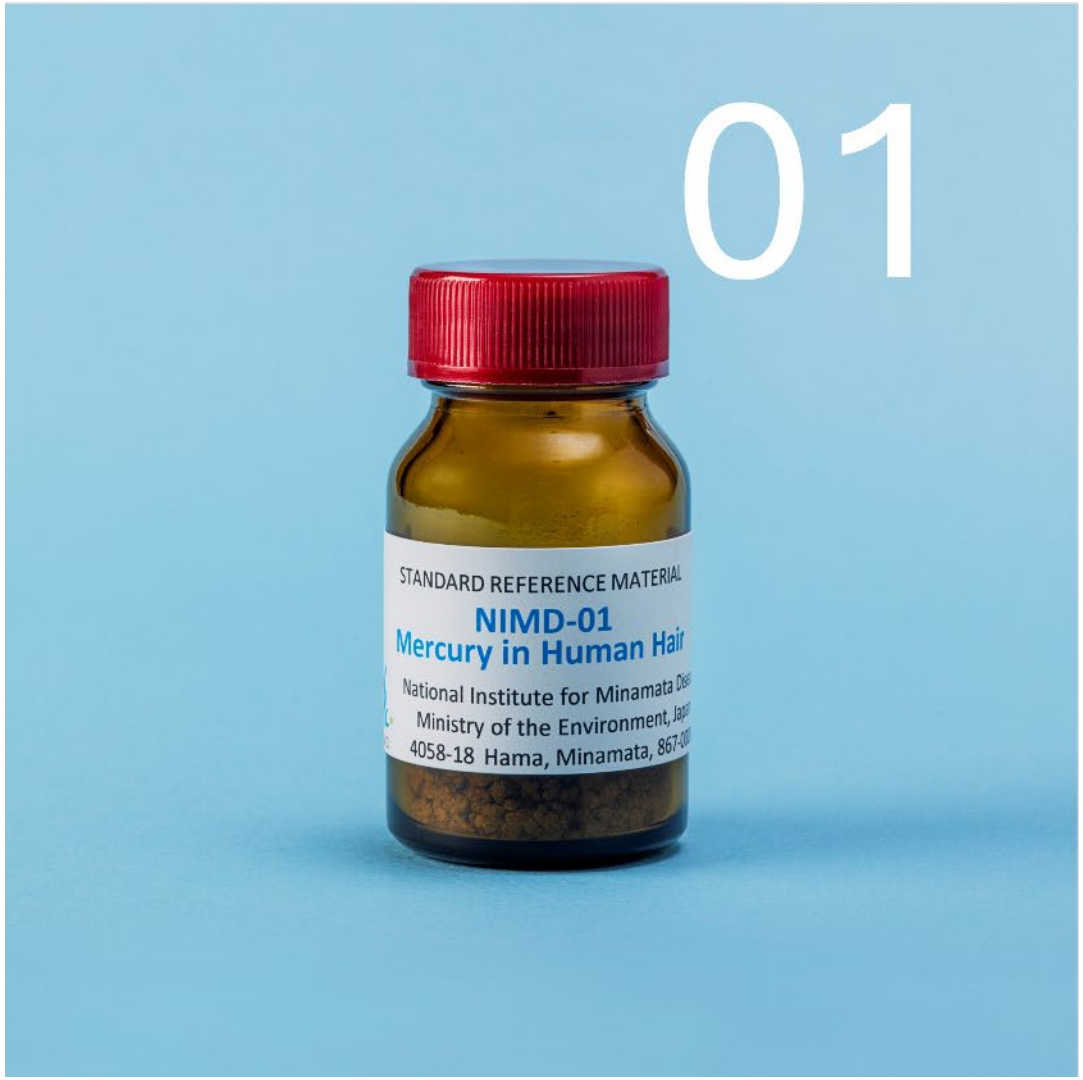
- 30% difference needed to detect changes across all labs, reduced to 10% for proficient labs.
- Asian labs with $|z| \leq 2$ can detect 6% differences in 1 to 11 years.
- TD AAS achieved 87% satisfactory results with an LSD of 0.19.

Next Step and Recommendation

- Incorporate group size and variability in future LSD.
- Consider adopting the TD AAS if acquiring new equipment.

Improvements needed

- Train staff, Use CRMs and participate in PT.



NIMD-01
Human Hair

Analyte	Certified value (mg/kg)
Methylmercury	0.634 ± 0.071
Total mercury	0.794 ± 0.050
Copper	12.8 ± 1.4
Zinc	234 ± 29
Selenium	1.52 ± 0.29
Arsenic	0.17 ± 0.03※

※Indicative value