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# Gold sampling for atmospheric mercury analysis: insights and limitations

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# Origin of the idea

## Gold sorbent materials

- Used for atmospheric Hg sampling for decades
- Widely applied in commercial atmospheric Hg analyzers for Hg preconcentration

## But still some major unknowns:

- What atmospheric Hg forms are actually sampled on gold?  
TGM, GEM, a mix between TGM/GEM?
- To what extent does calibration influence atmospheric Hg monitoring results? Are the results comparable between different atmospheric Hg analyzers?

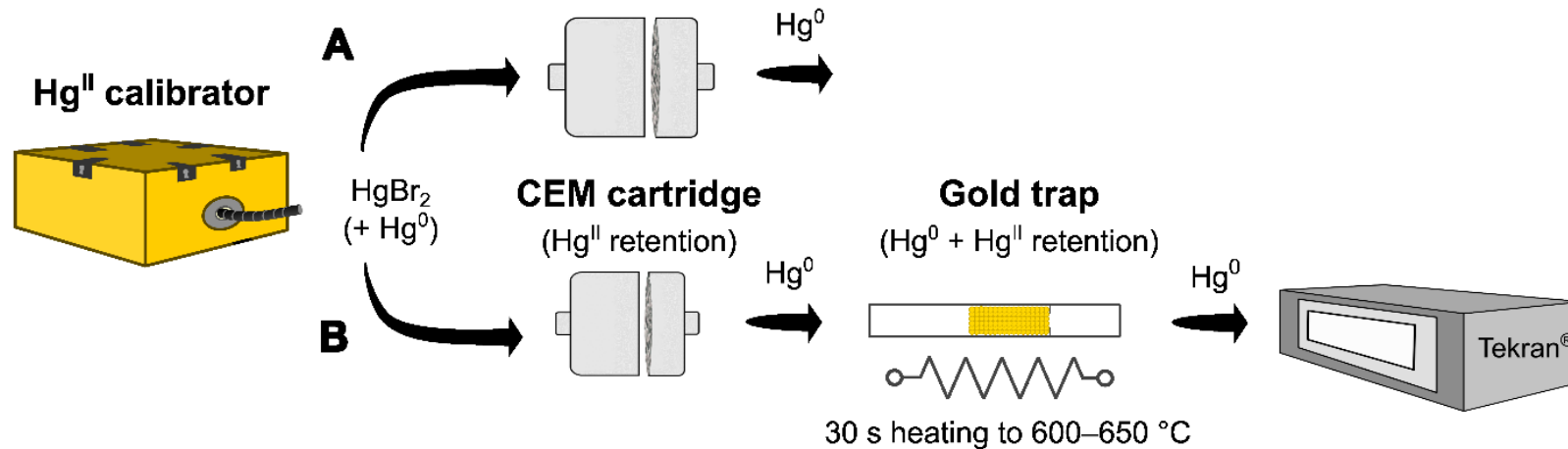
Recent improvements in gaseous Hg sources could provide answers to the questions above



# Experimental design

## Hg<sup>II</sup> permeation calibrator

### 1) Calibrator validation tests



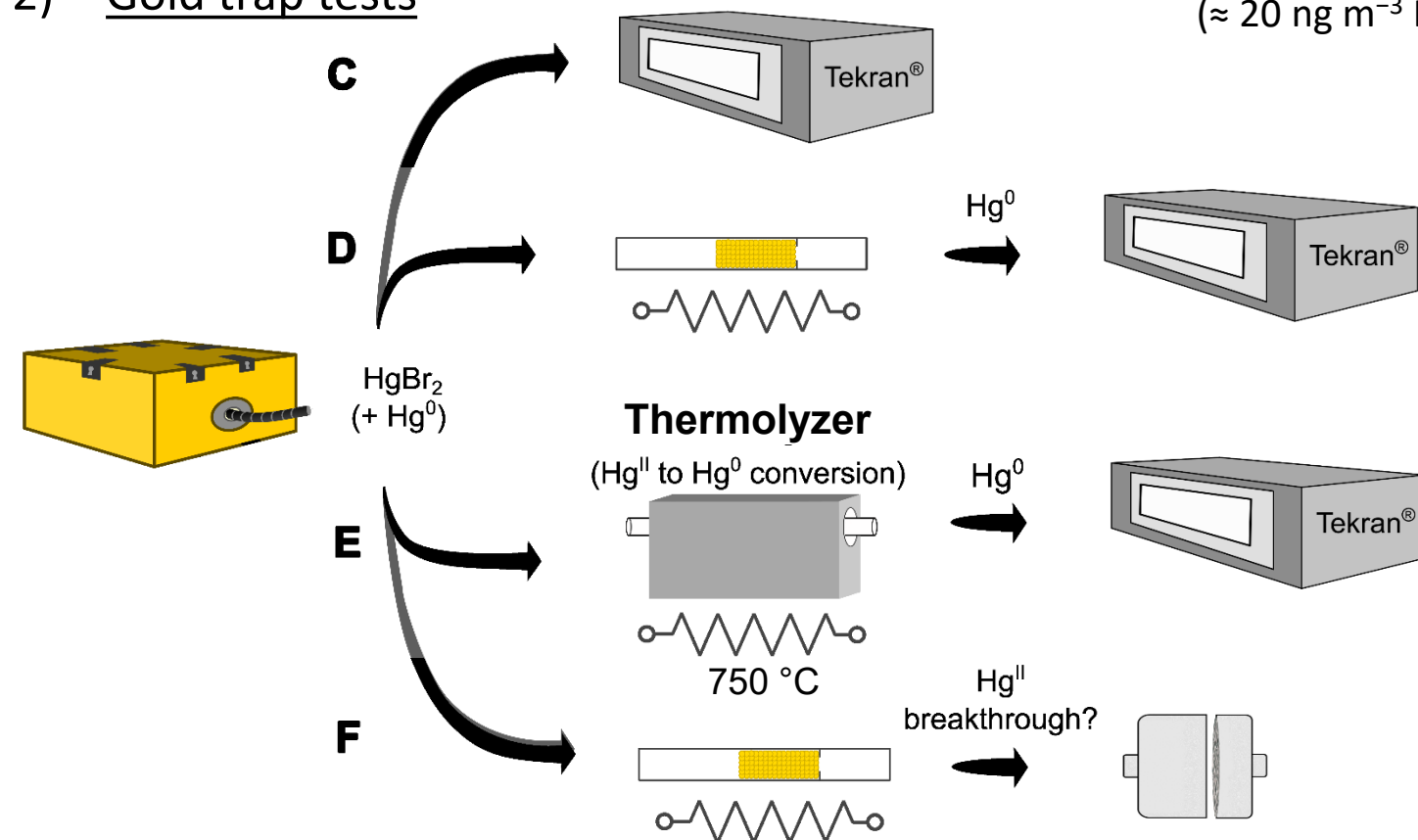
## Research questions

- A. Does the Hg<sup>II</sup> calibrator enable stable and reproducible HgBr<sub>2</sub> loading?
- B. Is there any Hg<sup>0</sup> in the calibrator output?

# Experimental design

## Hg<sup>II</sup> permeation calibrator

### 2) Gold trap tests



Tests were done with  $\approx 100$  pg of Hg  
( $\approx 20$  ng m<sup>-3</sup> Hg conc. on Tekran)

## Research questions

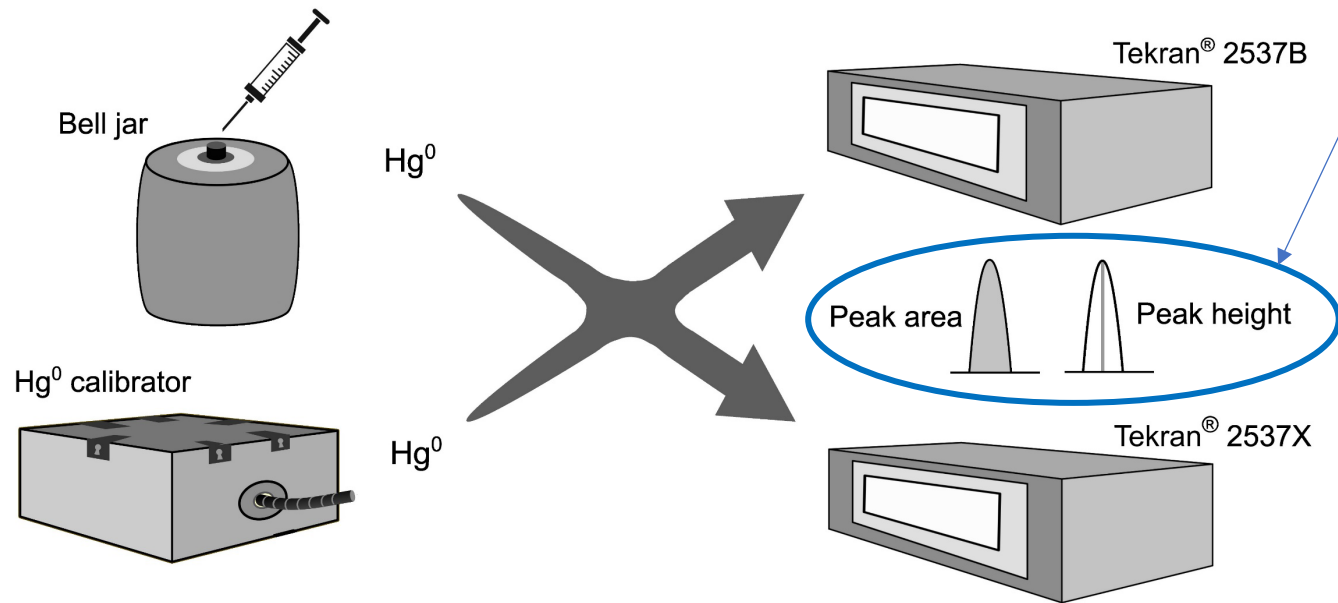
- C. What does Tekran 2537 measure when sampling Hg<sup>II</sup>?
- D. Does gold trap heating efficiently reduce Hg<sup>II</sup> to Hg<sup>0</sup> for analysis?
- E. Does an upstream thermolyzer change the results?
- F. Is there any breakthrough of Hg<sup>II</sup> during gold trap sampling?



# Experimental design

## Hg<sup>0</sup> permeation calibrator

- 1) Tekran 2537B vs Tekran 2537X
- 2) Bell jar vs permeation calibration
- 3) Peak area vs peak height



Signal processing algorithm, developed in-house.  
allows simultaneous peak area/height integration for 2  
different models of Tekran analyzers (2537B and 2537X)  
operating simultaneously.

## Research questions

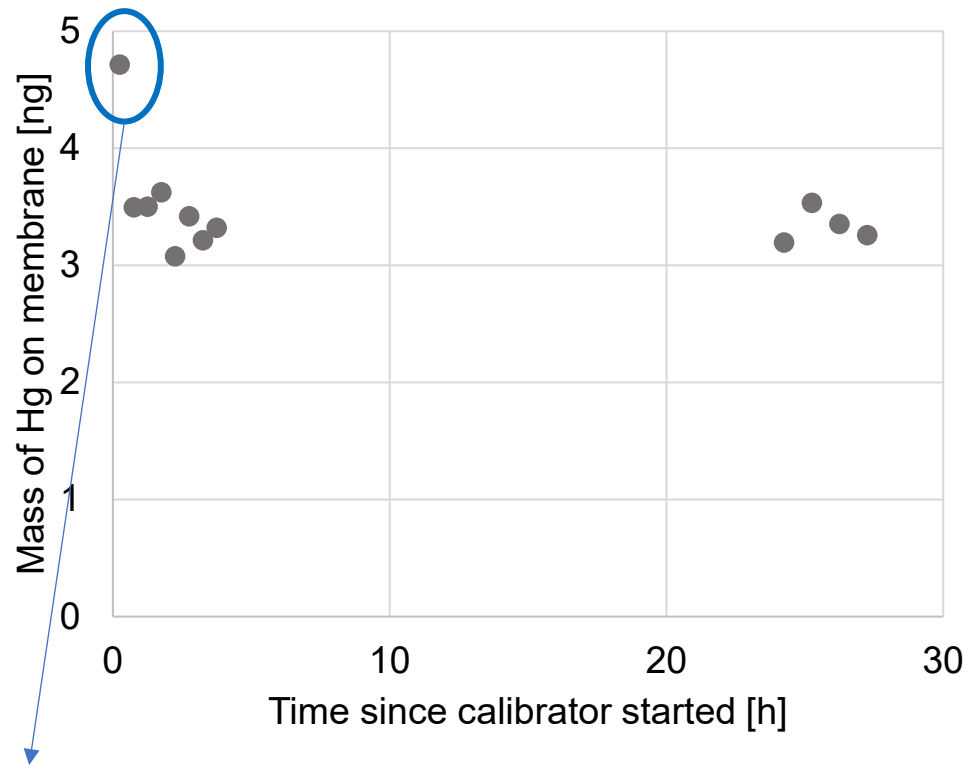
- Are different Tekran units and modules giving comparable results?
- Does the calibration type influence the results?
- Does the integration type influence the results?

Adapted from artwork by users Pixa and Ylivdesign (available at [www.pngtree.com](http://www.pngtree.com))

# Results

## Hg<sup>II</sup> permeation calibrator

### 1) Calibrator validation tests



Calibrator needs  $\approx 1$  h for equilibration

- A. Long-term Hg<sup>II</sup> permeation rate (over months of tests)  
 $2.2 \pm 0.1 \text{ pg s}^{-1}$
- B. Hg<sup>0</sup> permeation rate  
 $0.13 \pm 0.01 \text{ pg s}^{-1}$

Hg<sup>0</sup>/Hg<sup>II</sup> ratio: 6%



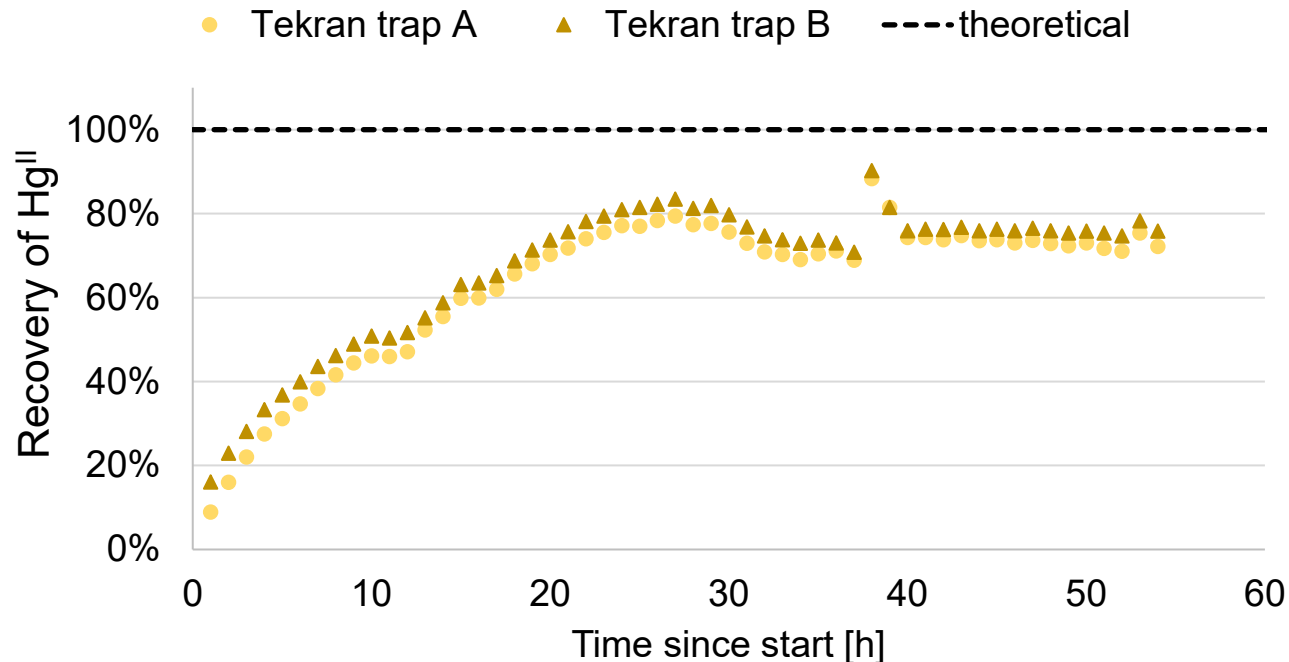
# Results

## Hg<sup>II</sup> permeation calibrator

### 2) Gold trap tests

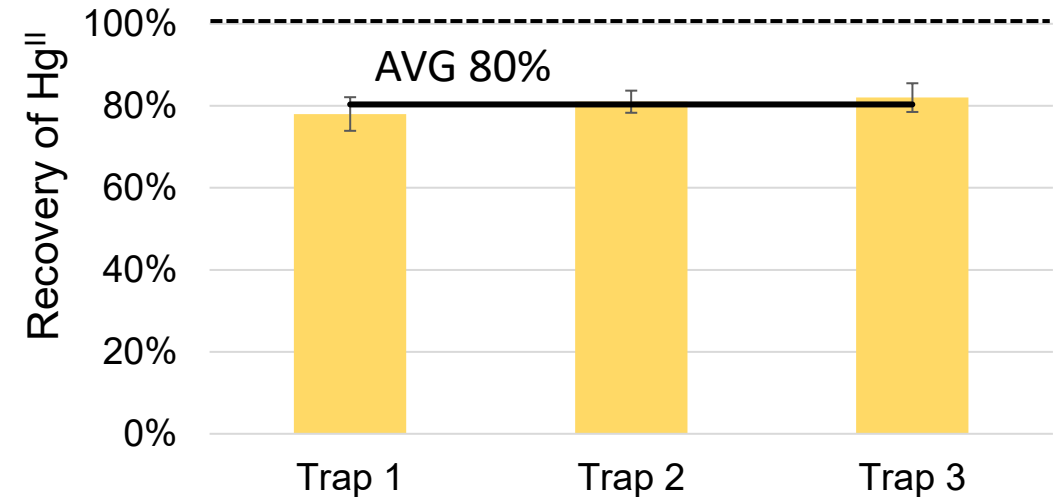
$$\text{Recovery of Hg}^{II} = \frac{\text{Measured Hg}^{II} \text{ conc.}}{\text{Theoretical Hg}^{II} \text{ conc. (based on known perm rate)}}$$

#### C. Continuous direct injection of Hg<sup>II</sup> into Tekran (1-h averages)



#### D.

#### Injection of Hg<sup>II</sup> into external gold trap with downstream Tekran

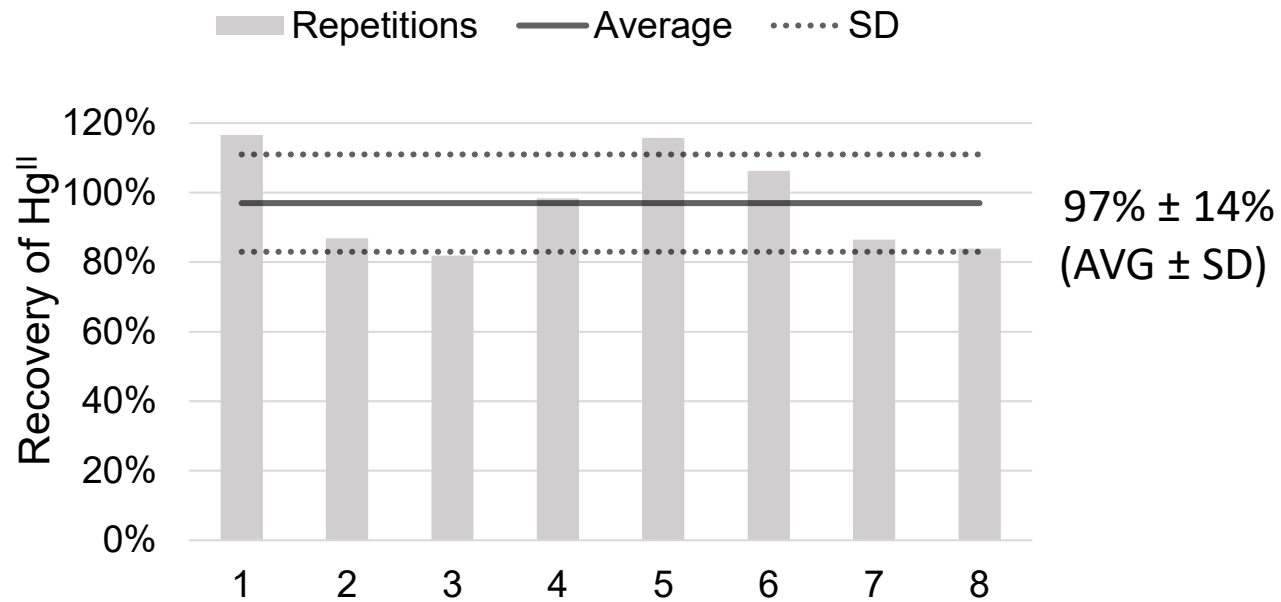


# Results

## Hg<sup>II</sup> permeation calibrator

### 2) Gold trap tests

E. Injections into Tekran with upstream thermolyzer

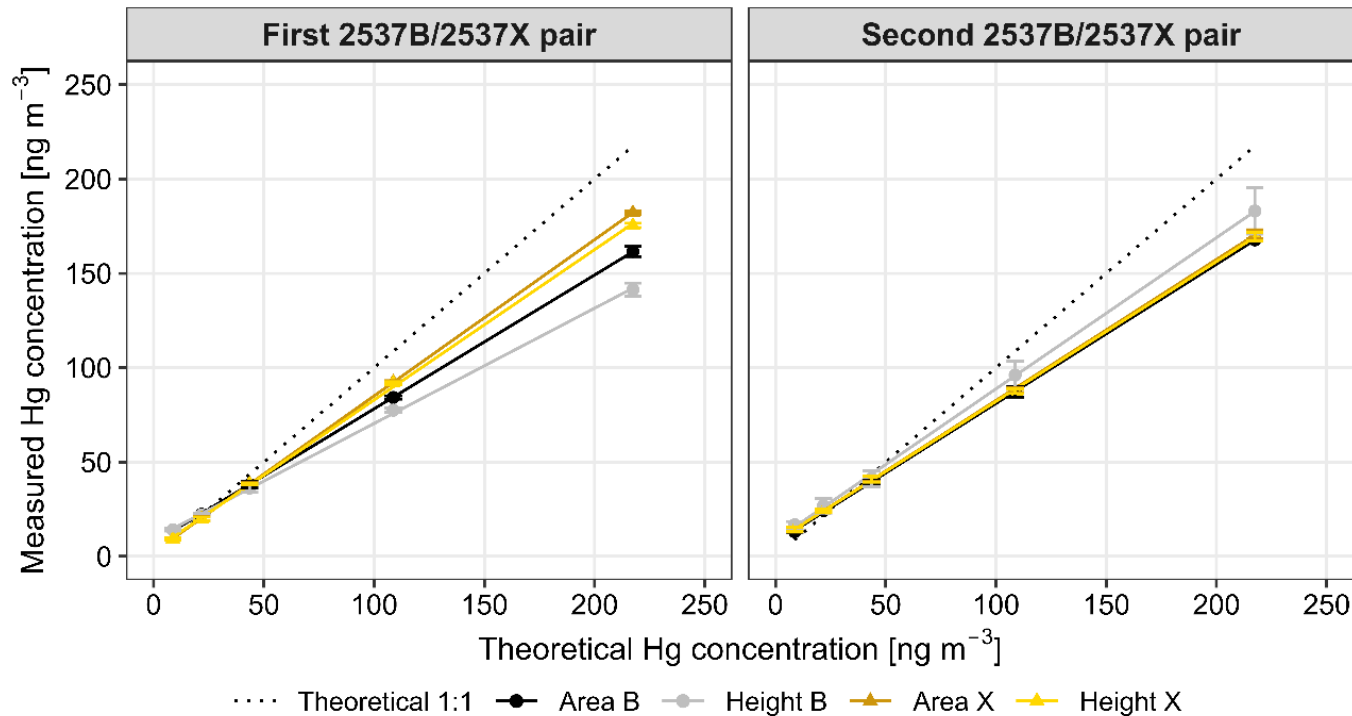


F. Breakthrough of Hg<sup>II</sup> when sampling with gold traps?  
<LOD (<1%)



# Results

## Hg<sup>0</sup> permeation calibrator



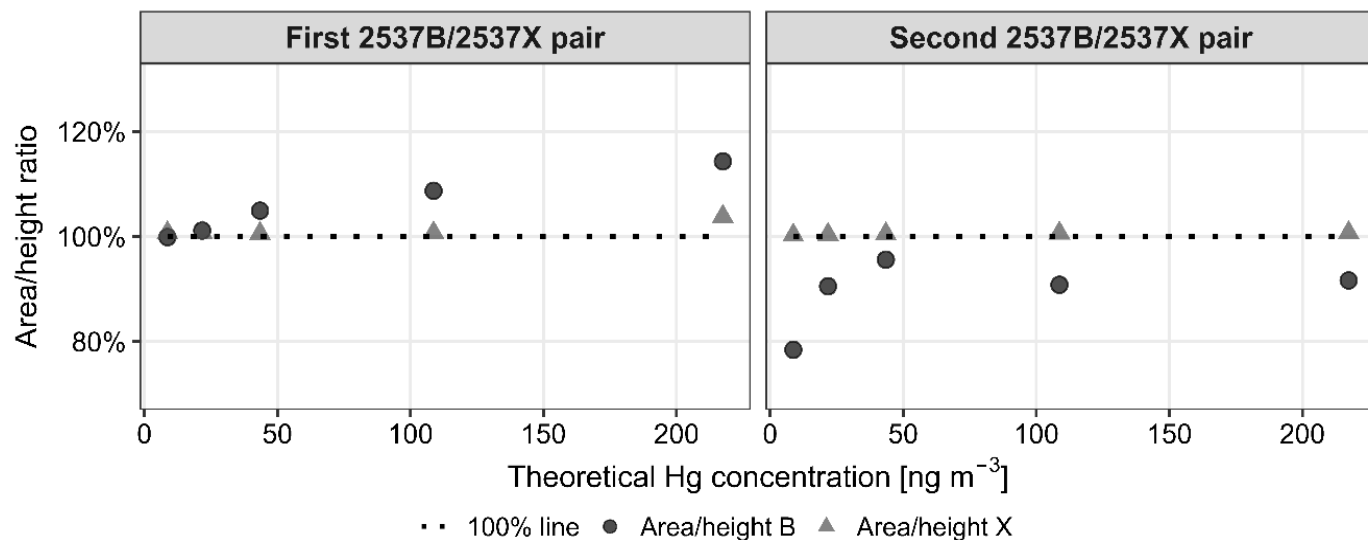
- Most consistent trend: Hg conc. measured with Tekrans B/X are lower than expected, why?
  - Bell jar vs permeation calibrator
  - 6% ± 7% (mean ± SD) underestimation from bell jar
- When using internal Tekran calibration – comparability is worse (regression slopes differ even more)



# Results

## Hg<sup>0</sup> permeation calibrator

Relative difference between peak area/height integration



- No considerable difference between peak area/height for 2537X modules,
- Inconsistent but significant difference between difference between peak area/height for 2537B modules
- Conclusion:  
**Multipoint calibrations traceable to the International System of Units (SI) are needed!**



# Implications & recommendations

- $\text{Hg}^{\text{II}}/\text{Hg}^0$  permeation calibrators → useful tool for testing atmospheric Hg methodology
- Tekran 2537 modules measure a Hg fraction somewhere between GEM and TGM, due to:
  - Adsorption of  $\text{Hg}^{\text{II}}$  on Tekran 2537 particulate matter filter and tubing
  - Inefficient conversion of  $\text{Hg}^{\text{II}}$  to  $\text{Hg}^0$  during gold trap heating

## Recommendations for future atmospheric Hg monitoring:

- 1) Use upstream double-stage CEM filter (RM retention) to measure GEM
- 2) Use upstream thermolyzer ( $\text{Hg}^{\text{II}} \rightarrow \text{Hg}^0$  conversion) to measure TGM
- 3) Use multipoint calibration and well-characterized mercury calibrators that are traceable to the International System of Units (SI) (when possible) to ensure the comparability of results



# Related ICMGP presentations

- Poster #65: Particulate-bound mercury sampling using membrane materials: biases due to adsorption of gaseous oxidized mercury
- Poster #155: Use of corrected reactive mercury measurements for model evaluation: Analysis and implications for global model estimates

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Users Pixa and Ylivdesign for copyright-free PNG artwork (available at [www.pngtree.com](http://www.pngtree.com)) that was used in part to make experimental design figures.



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