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Stability of Common Preconcentration Methods for Gaseous Oxidized Mercury in Air

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INTRODUCTION

Atmospheric mercury (Hg): Elemental form (**GEM**)

Oxidized forms (Particle bound, **PBM** & Gaseous oxidized, **GOM**)

Ultra-trace level concentration and high reactivity

GOM measurements: requires a pre-concentration step

Biased low and lack of comparable measurements results

- Biases from improper calibration (traceability)
- Biases from sampling methods

Accurate measurements – critical for Minamata Convention effectiveness evaluation!!!

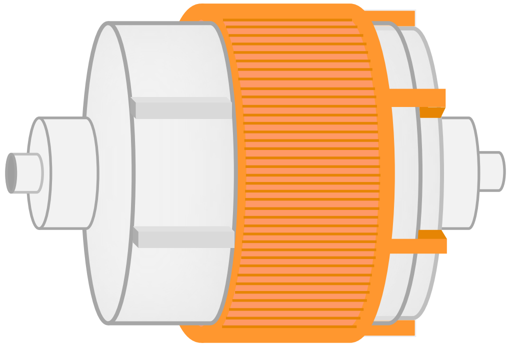
Common methods

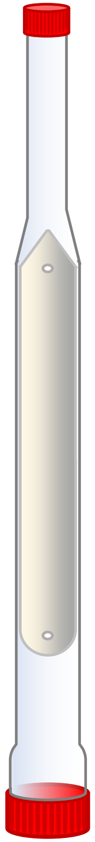
Denuders (1 – 2 hours)

&

CEMs

(days to weeks)





under-estimation of Hg^{II} in air

- used for sampling GOM (Hg^{II})
- sampling losses → **biases**

Denuders: analysis by thermal decomposition of Hg^{II} to Hg^{0} and detection by CVAFS

CEMs: Overnight digestion in BrCl solution, followed by analysis using CVAFS

OBJECTIVES

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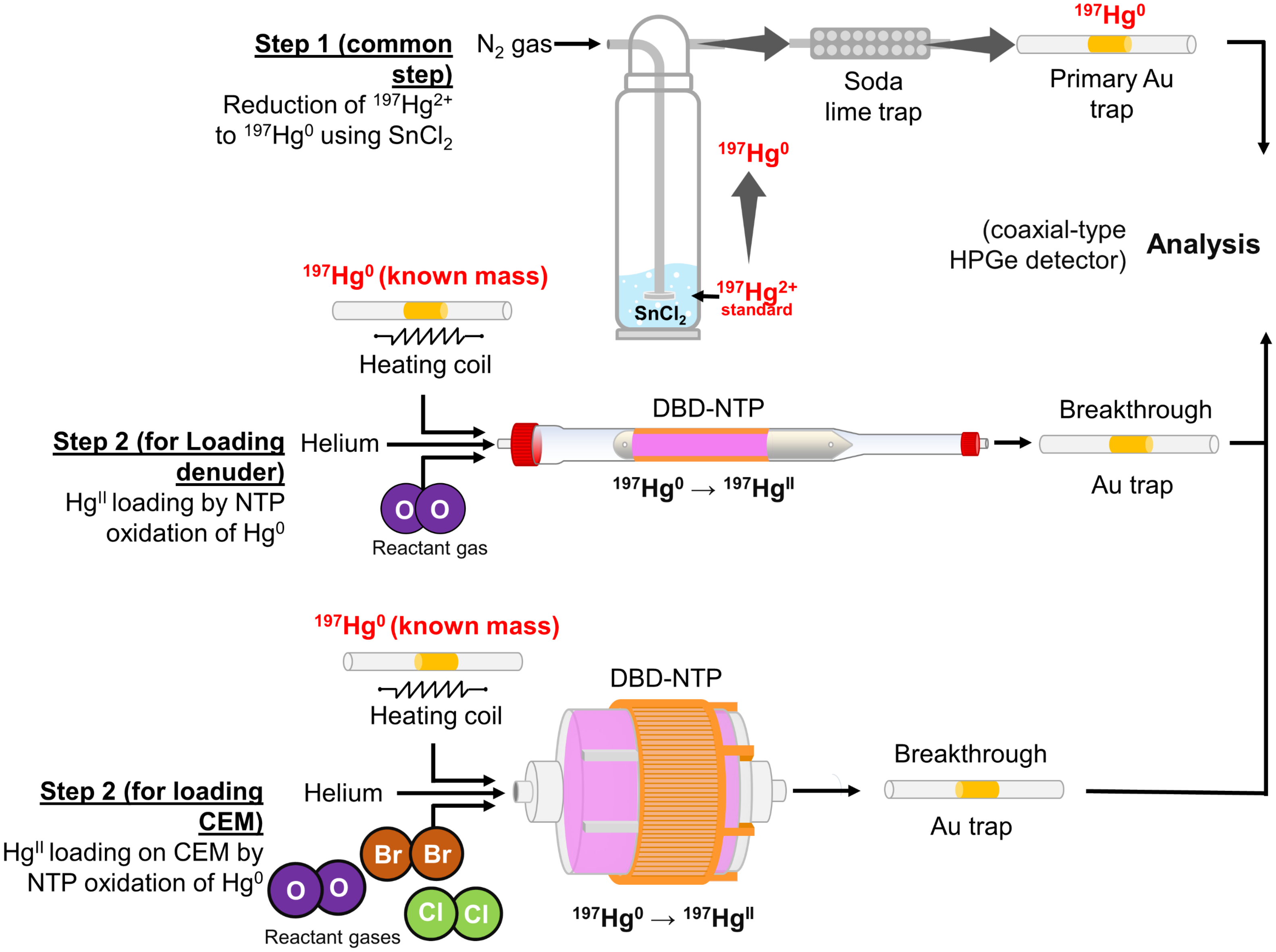
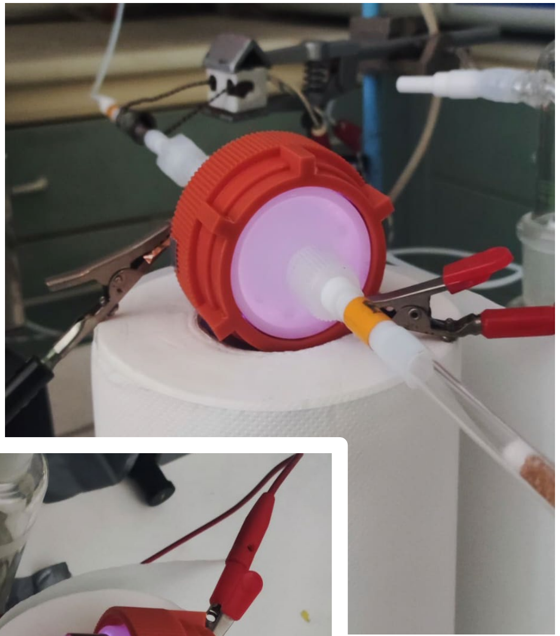
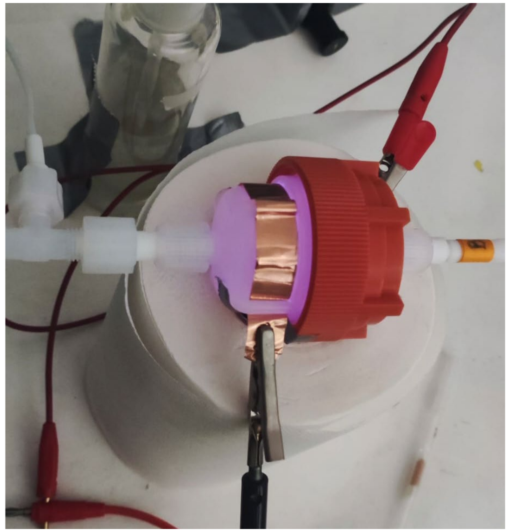
- Laboratory experiments were performed using ^{197}Hg radiotracer
  Advantages:
  - Enhanced experimental precision
  - No blank or contamination issues
  - High specificity and ease of detection
  - Experiments at environmentally relevant concentration
- Quantification of biases: based on precise mass balance budget

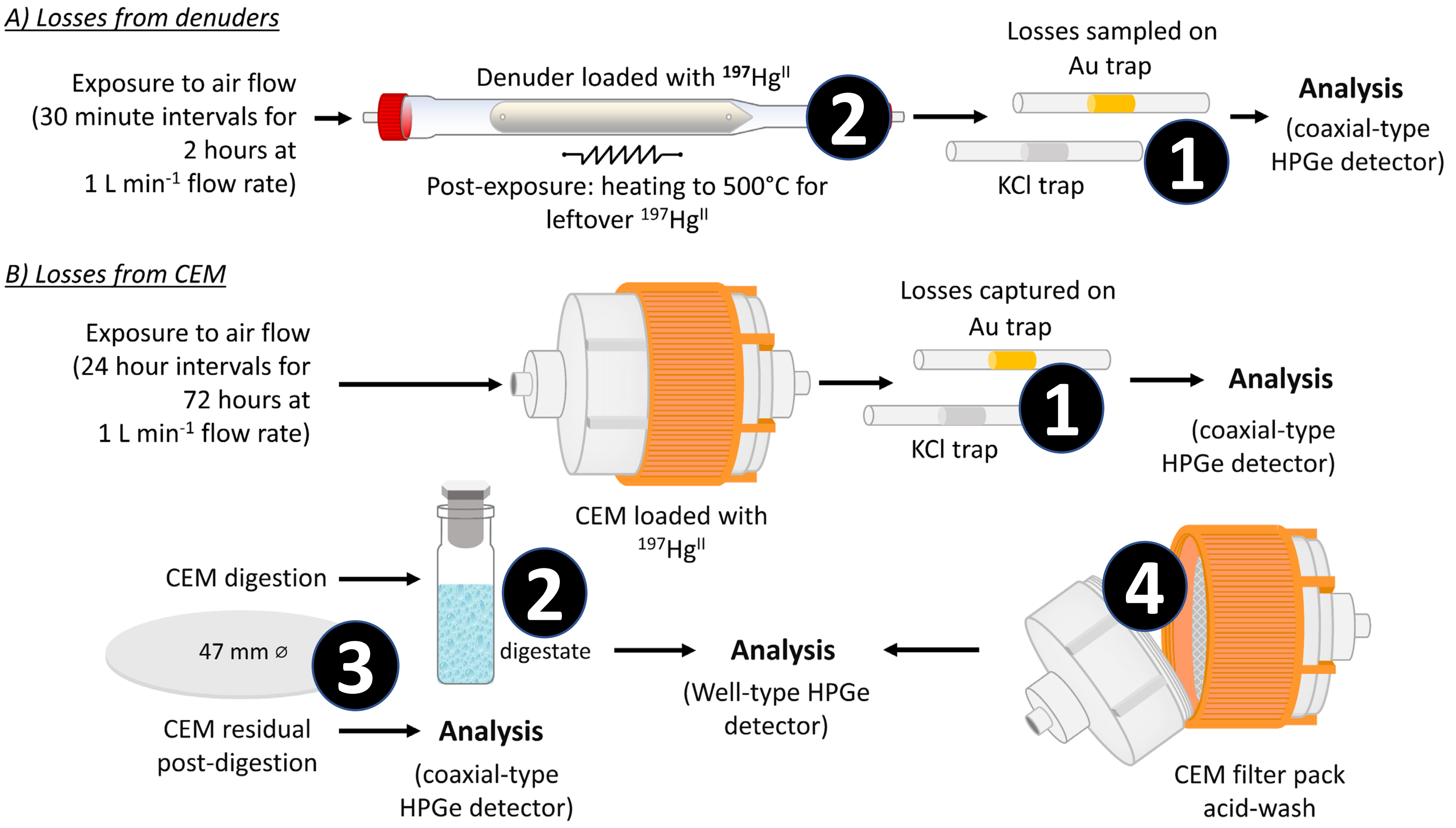
- Evaluate the performance of denuders & CEMs in retaining different GOM species
- Assess the recovery efficiency of GOM from denuders and CEMs

METHODOLOGY









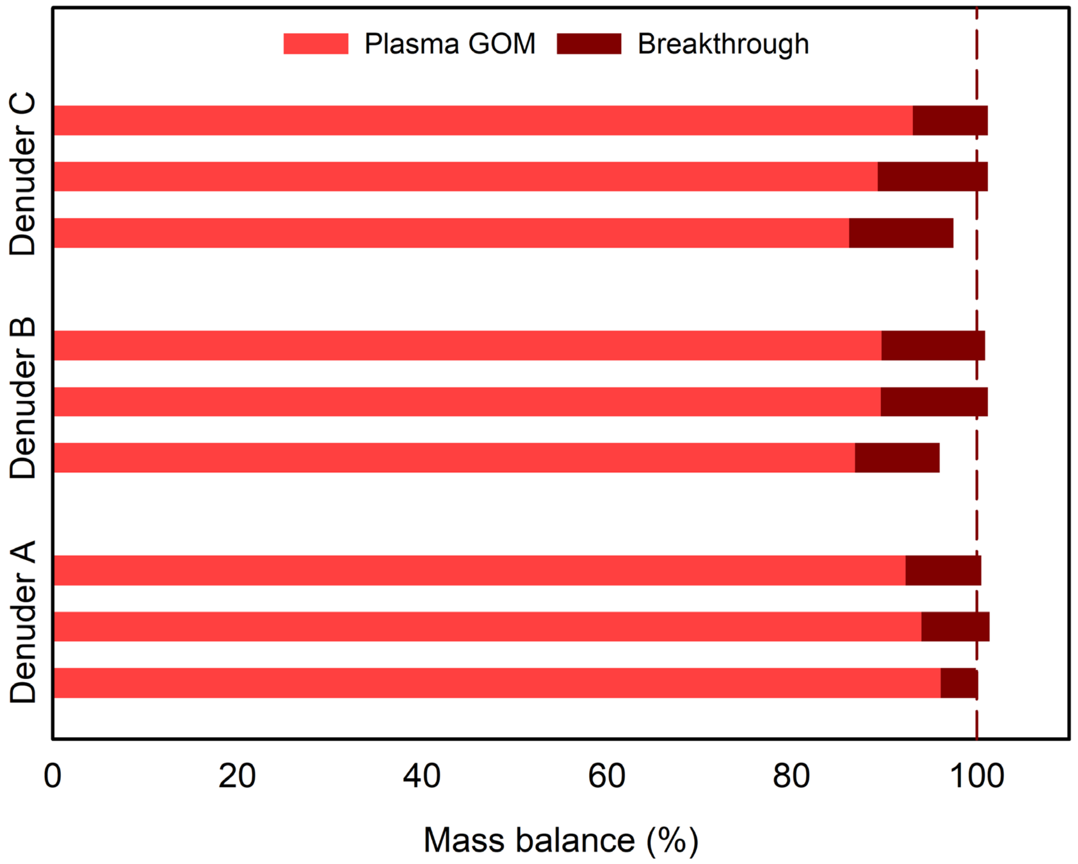
CEMs

1. Hg^{II} losses captured on Au & KCl traps (during exposure)
2. Hg^{II} recovered by digestion (post-exposure)
3. Residual Hg^{II} recovered from CEM (post-digestion)
4. Hg^{II} recovered from inner Teflon parts (acid-wash)

Denuders

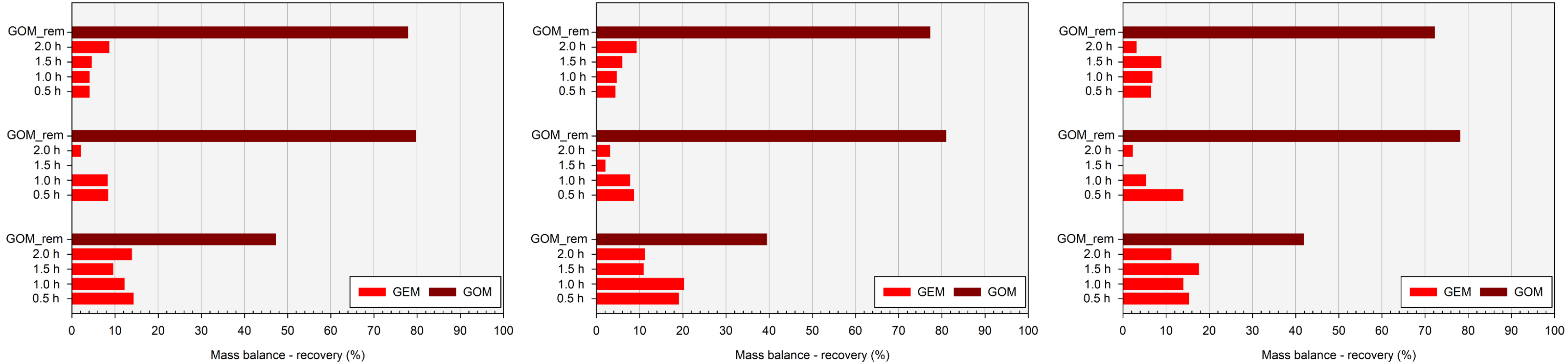
1. Hg^{II} losses captured on Au & KCl traps (during exposure)
2. Hg^{II} recovered from denuders (post-exposure)

Plasma loading efficiency - denuders



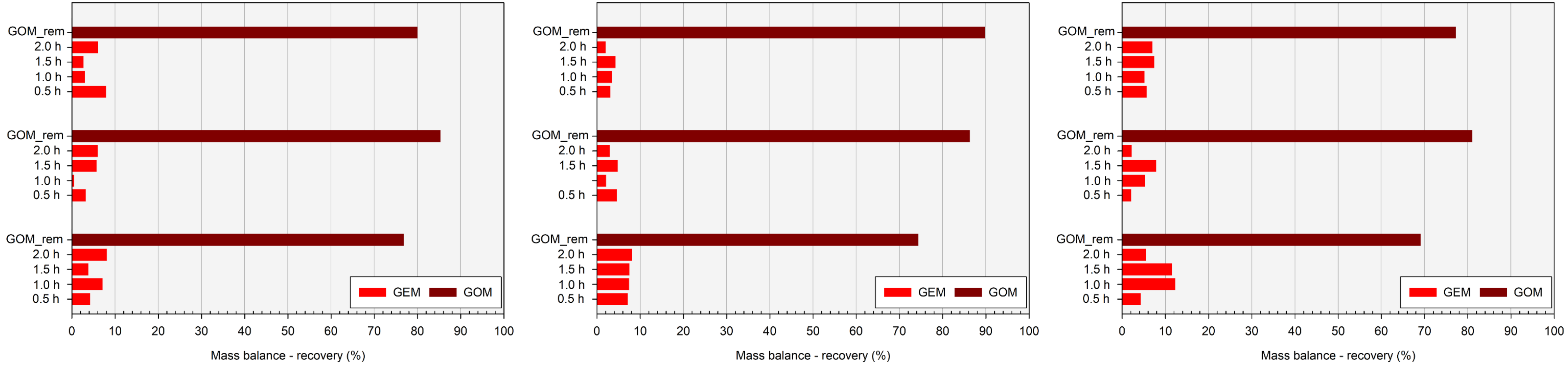
- NTP loading efficiency ranged between 86.2–96.1%.
  Avg. efficiency:
  DEN A – 94.2%
  DEN B – 89.0%
  DEN C – 90.0%
- Avg. breakthrough:
  DEN A – 6.5%
  DEN B – 10.6%
  DEN C – 10.4%
- GOM recovery by thermal decomposition (500 ^{0}C ~ 15 min)

  DEN A – 101%
  DEN B – 100%
  DEN C – 99.9%



- Avg. losses 30.1%, 35.9%, and 35.1% for denuder A, B, and C respectively

Condition: Ambient air (dark)



- Avg. losses 19.5%, 19.1%, and 25.5% for denuder A, B, and C respectively

Condition: Ambient air (light exposure)

Summary (denuders)

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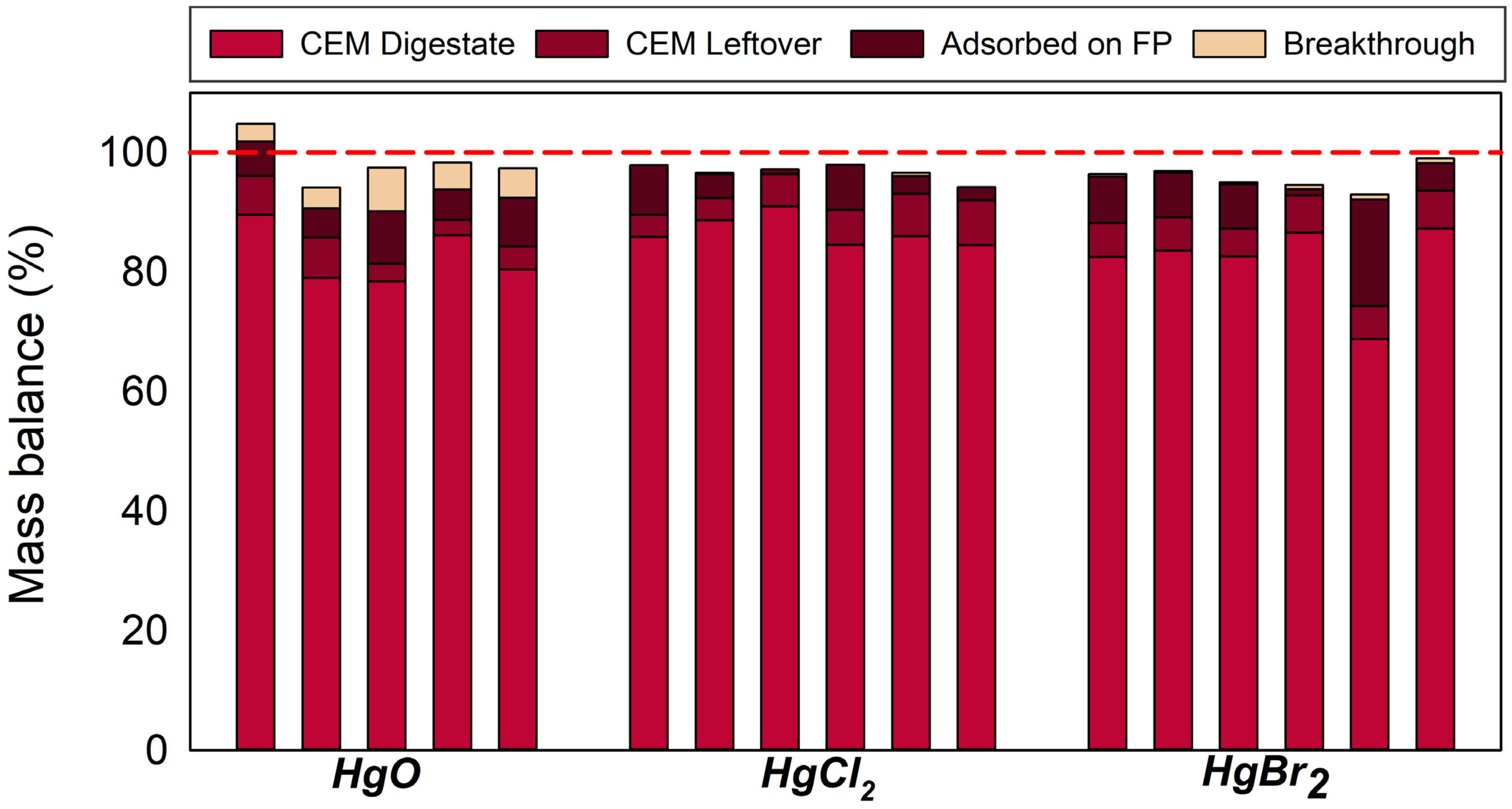
- Freshly prepared denuders lost upto **36% GOM (Hg^{II} reduced to Hg^0)** ‹‹‹ when exposed to ambient air (exposure period – 2 hours)
  - ➢ No losses were observed in the form of Hg^{II} (no Hg^{II} captured on KCl traps)
  - ➢ More humidity in air, more losses
  - ➢ Minimum **64%** of Hg^{II} loaded in denuders were left for measurement after the exposure period
- Re-used denuders lost upto **79.7% GOM**; Avg. loss was 51%

Plasma loading efficiency - CEMs



NTP oxidation efficiency

- 90.2–102% for HgO
- 94.2–98.0% for $HgCl_2$
- 92.2–98.2% for $HgBr_2$

CEM digestion (Avg. recoveries)

- 94.8% for HgO
- 94.0% for $HgCl_2$
- 93.7% for $HgBr_2$

Teflon walls (Avg. recoveries)

- 6.5% for HgO
- 4.3% for $HgCl_2$
- 7.7% for $HgBr_2$

Postdigestion residuals on CEM (Avg.)

- 5.5% for HgO
- 6.4% for $HgCl_2$
- 6.7% for $HgBr_2$

i) Hg^{II} losses from CEM (72 hours): HgO loaded on CEM

Amount (ng)	Losses (%)	CEM Digestate (%)	CEM Leftover (%)	FP wash (%)	Mass balance (%)
2.5/60	17.6	64.8	7.5	5.0	94.8
10	18.3	74.4	5.7	1.4	99.9
30	14.4	71.8	6.4	6.2	98.8
Average	**16.7**	**70.3**	**6.5**	**4.2**	**97.8**

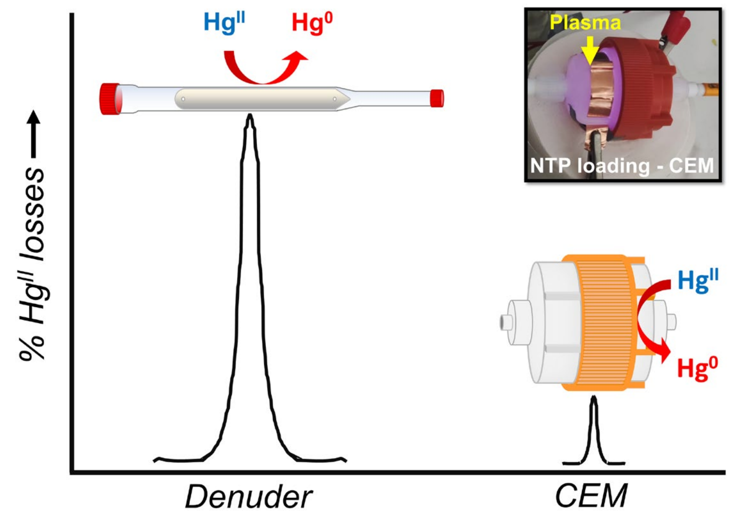
ii) Hg^{II} losses from CEM (72 hours): $HgCl_2$ loaded on CEM

Amount (ng)	Losses (%)	CEM Digestate (%)	CEM Leftover (%)	FP wash (%)	Mass balance (%)
2.5	3.1	86.1	5.6	3.0	97.7
10.0	3.0	87.2	4.0	2.5	96.7
30.0	2.1	90.6	5.0	1.2	99.0
Average	**2.7**	**88.0**	**4.9**	**2.2**	**97.8**

iii) Hg^{II} losses from CEM (72 hours): $HgBr_2$ loaded on CEM

Amount (ng)	Losses (%)	CEM Digestate (%)	CEM Leftover (%)	FP wash (%)	Mass balance (%)
2.5	3.1	92.4	4.7	1.0	101.2
10.0	5.2	86.2	4.0	3.6	99.0
30.0	3.1	92.4	4.7	1.0	101.2
Average	**3.8**	**90.4**	**4.5**	**1.9**	**100.5**

Summary (CEMs)



- CEM-based measurements demonstrate greater reliability over denuders (lower losses of Hg^{II} compounds)
  - HgO – 16.7% (average loss)
  - $HgCl_2$ and $HgBr_2$ – 2.7% and 3.8%, respectively (average loss)

- CEMs may not uniformly collect all types of GOM species with equal efficiencies
  - better performance in retaining cationic species of GOM (chlorides and bromides)
  - not optimal for neutral species such as HgO

- Hg^{II} recovery from CEMs may not be adequate (few % lost to Teflon walls and CEMs as residuals; post-digestion)
  - Alternative methods:

    1) Leaching using tetrabutylammonium (commonly used for aqueous biphasic extraction of metal ions) – recovery improved by 3.5%, but not complete.
    2) ultra-wave digestion method recovered upto 100.4% residuals from CEMs

  - future studies to assess its robustness and potential as a viable alternative to BrCl digestion

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