Atmospheric Mercury in the Rocky Mountain Region

Tyler Elgiar[1], Seth Lyman[1], Lynne Gratz[2], Zoe Zwecker[2], Anna Gannet Hallar[3]

[1]Utah State University, [2]Colorado College, [3]University of Utah

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Oxidation events, temporal variability, and elevated levels of **atmospheric oxidized mercury** observed in an on-going study at Storm Peak Laboratory in the **Rocky Mountain region**

Introduction

- Mercury (**Hg**) is a toxicant emitted to the atmosphere via natural and anthropogenic sources.
- **Hg^0** = atmospheric elemental mercury (lifetime ~1 yr).
- **Hg^{II}** = atmospheric oxidized mercury (lifetime days to weeks).

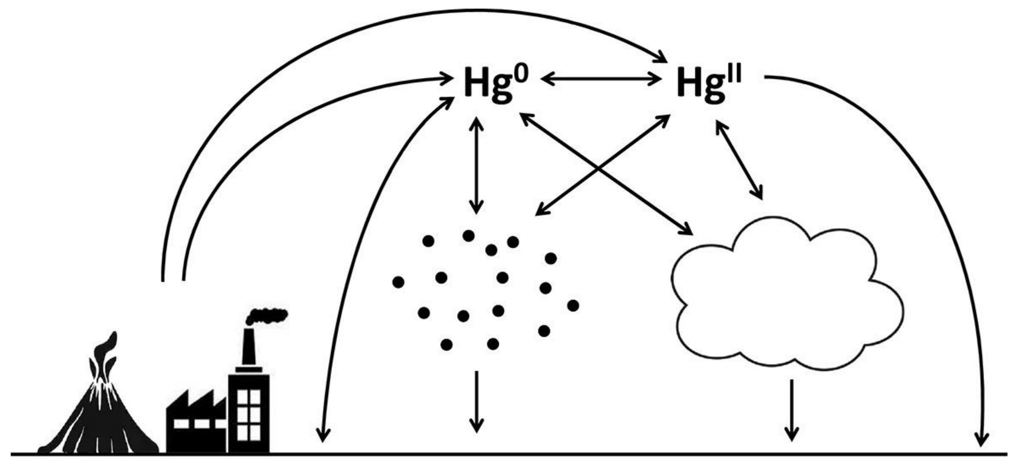

Figure 1. Diagram depicting the mercury cycle.

- Commercial Hg^{II} measurement systems utilize a KCl-coated denuder and are biased low.
- A **dual-channel system** was developed which avoids the low bias created by KCl-coated denuders.
- Our dual-channel system was deployed in an on-going study at **Storm Peak Laboratory (SPL)** in March 2021, a mountain top site where high levels of Hg^{II} have been previously observed (measurements were biased low).
- Other measurements at SPL include: meteorology, criteria gases (O3, NOx, SO2, CO), radon, and halogens.

Methods

- The **dual-channel system** (Figure 2.) samples air at ~1 L/min through two different channels.
- **Pyrolyzer** channel converts all Hg into Hg^0, **measures total Hg**.
- **Cation exchange membrane** channel collects Hg^{II} and allows Hg^0 to pass through, **measures only Hg^0**.

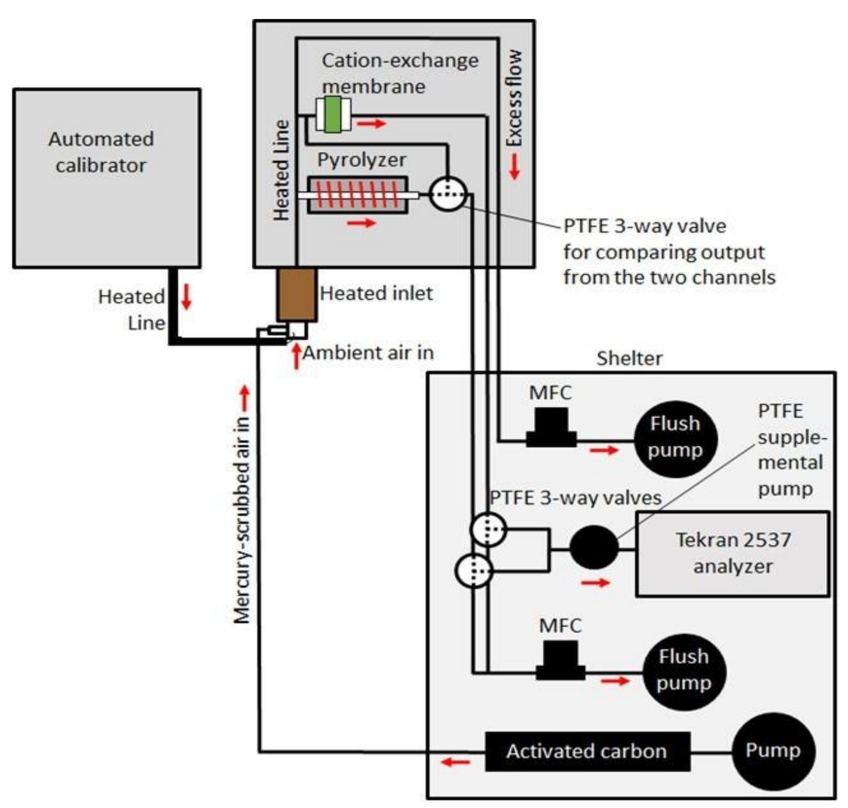

Figure 2. Diagram of USU's dual-channel system.

- All flow is routed into a Tekran 2537 X analyzer.
- **Total Hg – Hg^0 = Hg^{II}.**
- 1 hr detection limit of ~9 pg m^{-3}.
- Calibrated using an automated calibration system.

Data summary & Hg oxidation events

- Hourly averages (±1σ) from March 12th to September 15th for Hg^0 and Hg^{II} were 1.3 ± 0.1 ng m^{-3} and 101 ± 51 pg m^{-3} respectively, with a **maximum Hg^{II} measurement of 520 pg m^{-3}**.
- Four **Hg oxidation events** were Identified during 2021, as periods when hourly averaged Hg^{II} measurements increased 2σ above the seasonal mean, while Hg^0 simultaneously dropped 2σ below the seasonal mean.
- Concurrently identified by calculating the ratio of Hg^{II} to Hg^0 hourly averages. A high ratio (> 0.2) is indicative of in situ Hg oxidation. Although, this interpretation of this ratio can vary depending on site location and atmospheric conditions.

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Event #	Mean Hg^0 (±1σ)	Mean Hg^{II} (±1σ)	Mean Relative humidity (%)
1	1.2 ± 0.1 ng m^{-3}	104 ± 54 pg m^{-3}	43
2	1.0 ± 0.2 ng m^{-3}	171 ±49 pg m^{-3}	29
3	1.0 ± 0.0 ng m^{-3}	137 ± 31 pg m^{-3}	32
4	1.2 ± 1.0 ng m^{-3}	157 ± 35 pg m^{-3}	23

Table 1. Average Hg^0, Hg^{II}, and relative humidity measurements during the four observed Hg oxidation events.

- Low relative humidity (RH) (<45%) during all four events suggests influence from the upper atmosphere. RH during these events also shared strong anticorrelations with Hg^{II} (R^2 = 0.46 to 0.78).
- Figures 3, 4, 5, & 6 show event #2 in greater detail

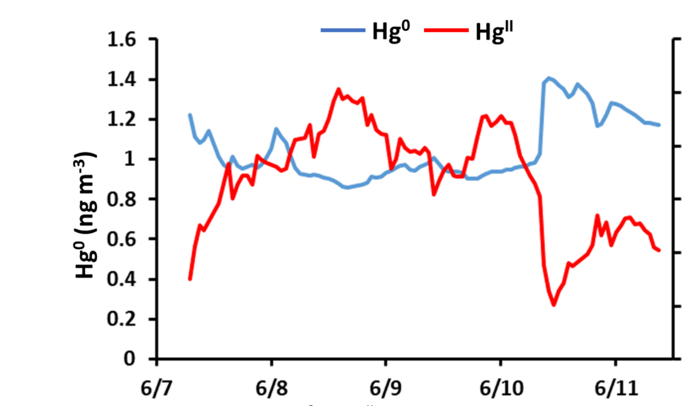

Figure 3. Time series of Hg^0 & Hg^{II} during Hg oxidation event #2

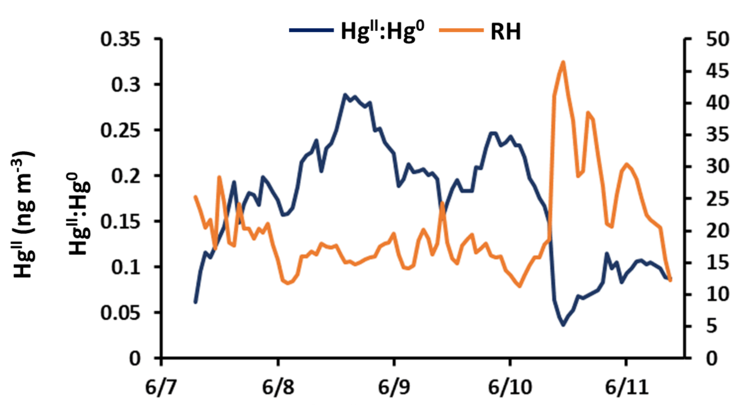

Figure 4. Time series of Hg^0:Hg^{II} ratio and RH during Hg oxidation event #2

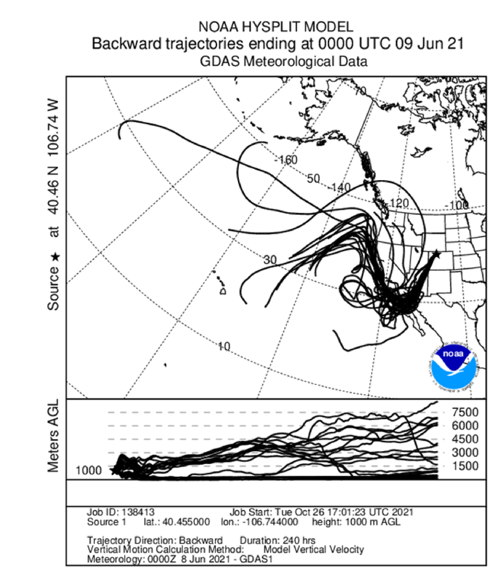

Figure 5. Backwards airmass trajectory, ran 240 hours prior to maximum Hg^{II}.

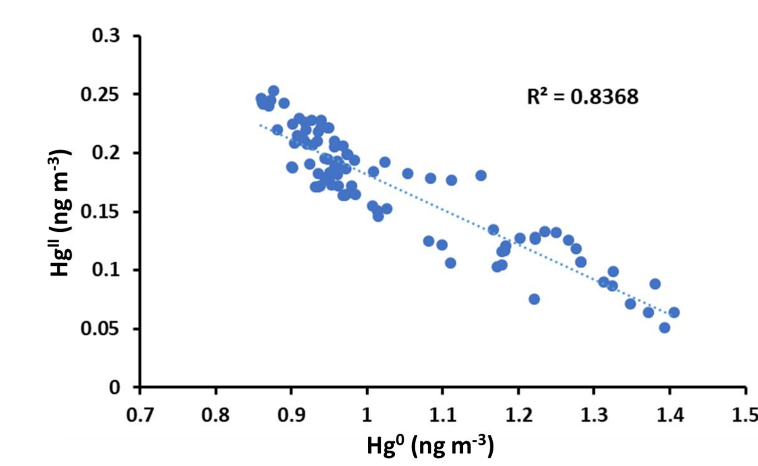

Figure 6. Regression showing Hg^0 & Hg^{II} anticorrelation during event #2

Temporal variability of Hg^{II}

- **Hg^{II}** measurements from mid-March 2021 to early April 2021 (while snowpack was present) show a strong diurnal pattern. The pattern dissipates as measurements continue into summer months. No meaningful relationship was observed between snow depth and Hg^{II}.

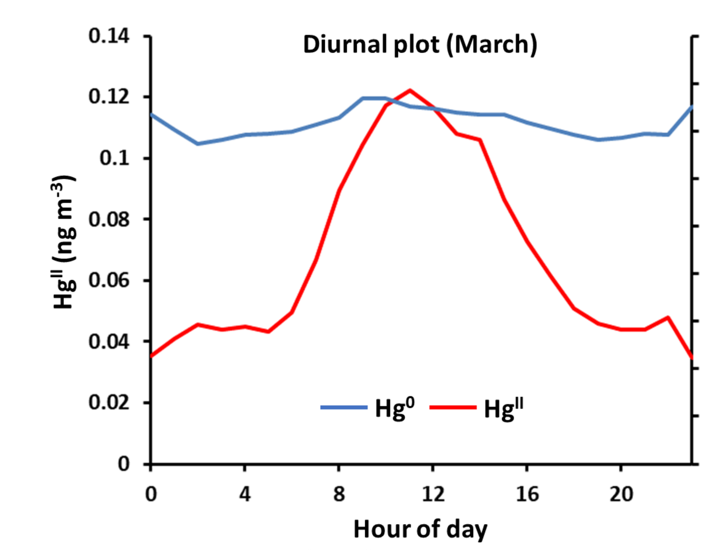

Figure 7. Diurnal plot or Hg^0 & Hg^{II} during March (snowpack present)

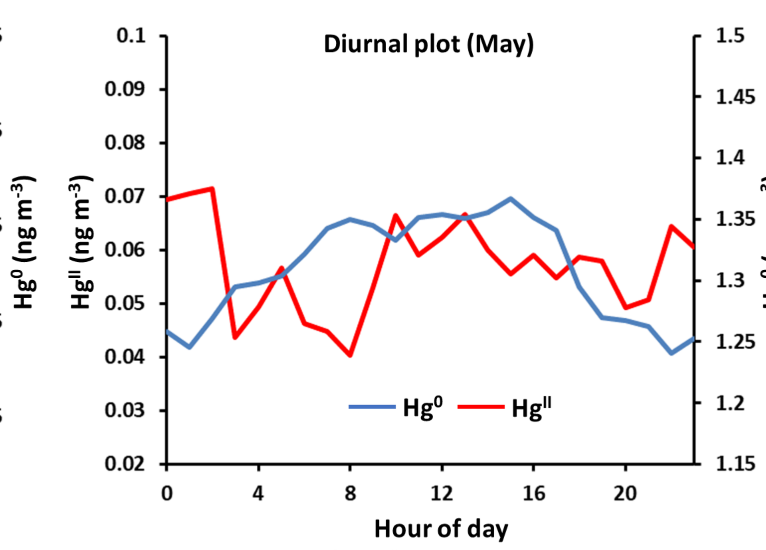

Figure 8. Diurnal plot or Hg^0 & Hg^{II} during May (snowpack absent)

- While the diurnal pattern is present, Hg^0 & Hg^{II} show little to no correlation (R^2 = 0.17). As the diurnal pattern dissipates, Hg^0 & Hg^{II} exhibit a stronger anticorrelation (R^2 = 0.40).
- These results suggest that daytime spikes in Hg^{II} (while diurnal pattern is present) are likely from external sources, not from in situ oxidation of Hg^0.

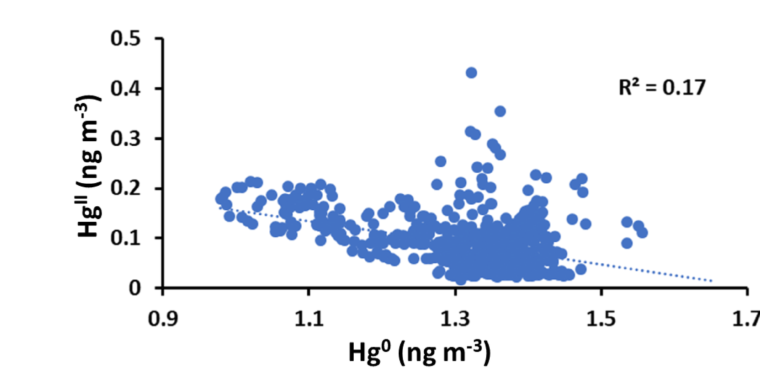

Figure 9. Hg^0 & Hg^{II} regression while diurnal pattern is present

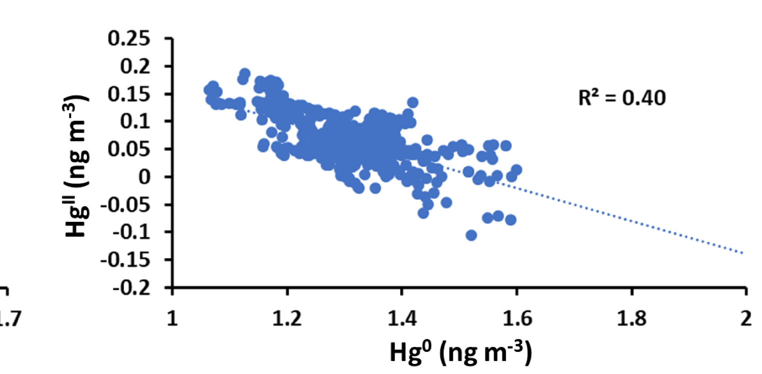

Figure 10. Hg^0 & Hg^{II} regression while diurnal pattern is absent