

Title: Atmospheric Mercury in the Rocky Mountain Region

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Mercury (Hg) is a toxicant found ubiquitously throughout the environment with the potential to cause harm to ecosystems, wildlife, and human health. Emitted naturally and anthropogenically, Hg exists in the atmosphere at ultra-trace levels (picograms per cubic meter of air, or  $\text{pg}/\text{m}^3$ ) as either elemental Hg ( $\text{Hg}^0$ ) or oxidized Hg ( $\text{Hg}^{\text{II}}$ ) and can dynamically convert between the two forms. Oxidation of  $\text{Hg}^0$  to  $\text{Hg}^{\text{II}}$  is a critical step in determining how Hg impacts environments, since  $\text{Hg}^{\text{II}}$  readily deposits to the earth's surface. Uncertainty surrounds the mechanisms by which Hg is oxidized and reduced in the atmosphere, however. Many previous measurements of atmospheric  $\text{Hg}^{\text{II}}$  have been made with systems that utilize a KCl-coated denuder, and are biased low. We have developed a cation exchange membrane-based dual-channel system that avoids the low bias created by the denuder. We deployed this system from March through September 2021 at the mountain top Storm Peak Laboratory (3220 meters above sea level) in Steamboat Springs, Colorado. Measurements at this site are providing information about  $\text{Hg}^{\text{II}}$  sources, chemistry, and ecosystem impacts in the Rocky Mountain region.

Hourly averages ( $\pm 1\sigma$ ) for  $\text{Hg}^0$  and  $\text{Hg}^{\text{II}}$  were  $1.3 \pm 0.1 \text{ ng}/\text{m}^3$  and  $101 \pm 51 \text{ pg}/\text{m}^3$  respectively, with a maximum  $\text{Hg}^{\text{II}}$  measurement of  $520 \text{ pg}/\text{m}^3$ . During this deployment, four episodes of elevated levels of  $\text{Hg}^{\text{II}}$  were observed over multiple-day-long periods.  $\text{Hg}^0$  and  $\text{Hg}^{\text{II}}$  during these events were strongly anti-correlated ( $R^2 = 0.72$  to  $0.91$ ) suggesting in-situ oxidation of  $\text{Hg}^0$  to  $\text{Hg}^{\text{II}}$ . Relative humidity (RH) was low ( $<45\%$ ), and anti-correlated with  $\text{Hg}^{\text{II}}$  during these time periods ( $R^2 = 0.46$  to  $0.78$ ), suggesting the oxidation was occurring in the free troposphere. Furthermore,  $\text{Hg}^{\text{II}}$  exhibited temporal variability throughout the measurement campaign.  $\text{Hg}^{\text{II}}$  measurements from mid-March 2021 to early April showed a pronounced diurnal pattern with elevated  $\text{Hg}^{\text{II}}$  concentrations during the day. The pattern dissipated as measurements continued into the summer months. While the diurnal pattern was present,  $\text{Hg}^0$  and  $\text{Hg}^{\text{II}}$  showed little to no correlation ( $R^2 = 0.17$ ) suggesting that daytime increases in  $\text{Hg}^{\text{II}}$  during this time were from external sources, not in-situ oxidation of  $\text{Hg}^0$ . We will present in greater detail the oxidation events and temporal variability experienced during the 2021 field campaign, and report on new measurements as they continue into 2022.