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Cavity ring-down spectroscopy (CRDS) system for measuring atmospheric mercury using differential absorption

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Atmospheric elemental mercury (Hg0) is a globally pervasive element that can be transported and deposited to remote ecosystems where it poses — particularly in its methylated form — harm to many organisms including humans. Current techniques for measurement of atmospheric Hg0 require several liters of sample air and several minutes for each analysis. Fast-response (i.e. 1 second or faster) measurements would improve our ability to understand and track chemical cycling of mercury in the atmosphere, including high frequency Hg0 fluctuations, sources and sinks, and chemical transformation processes.

We present theory, design, challenges, and current results of our new prototype sensor based on cavity ring-down spectroscopy (CRDS) for fast-response measurement of Hg0 mass concentrations. CRDS is a direct absorption technique that implements path-lengths of multiple kilometers in a compact absorption cell using high-reflectivity mirrors, thereby improving sensitivity and reducing sample volume compared to conventional absorption spectroscopy. Our sensor includes a frequency-doubled, dye-laser emitting laser pulses tunable from 215 to 280 nm, pumped by a Q-switched, frequency tripled Nd:YAG laser with a pulse repetition rate of 50 Hz. We present how we successfully perform automated wavelength locking and stabilization of the laser to the peak Hg0 absorption line at 253.65 nm using an external isotopically-enriched mercury (202Hg0) cell.

An emphasis of this presentation will be on the implementation of differential absorption measurement whereby measurements are alternated between the peak Hg0 absorption wavelength and a nearby wavelength “off” the absorption line. This can be achieved using a piezo electric tuning element that allows for pulse-by-pulse tuning and detuning of the laser “online” and “offline” of the Hg absorption line, and thereby allows for continuous correction of baseline extinction losses. Unexpected challenges with this approach included different efficiencies of laser performance (e.g., frequency doubling) at the two wavelengths and temperature dependence. We will discuss improvements on the control of our system to eliminate drift due to conversion efficiency and temperature dependence. We will detail complications with operating this instrument from a mobile platform for in situ measurements in the field. Finally, we will present data acquisition and processing approaches along with results of calibration curves, and comparisons to conventional mercury analyzers (i.e. a Tekran 2537 mercury vapor analyzer) during ambient air measurements.