Atmospheric Mercury Instrument Intercomparison

Mark L. Olson [1], David P. Krabbenhoft [2], and Philip Kilner [3] [1] National Atmospheric Deposition Program, U.S. Geological Survey, [2] U.S. Geological Survey, [3] Frontier Geosciences (currently with Tekran Research and Development)

Introduction

As part of an interagency effort between the USGS and USEPA-CAMD, we conducted a multi-instrument atmospheric mercury comparison to provide an unbiased assessment of performance and intercomparability. Four speciation systems were compared which continuously measure gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and fine-fraction particulate-bound mercury ($PBM_{2.5}$), respectively. The study was conducted at a warehouse facility the USGS uses for instrument set-up and testing. Instrument intakes were connected to a common high-flow unheated manifold, and inlet concentrations were varied to create dynamic conditions simulating variability observed in the field. Accuracy of the GOM thermal desorption, line transfer, and quantification was evaluated both in the warehouse and the field using pre-spiked denuders with a known loading of $HgCl_2$.

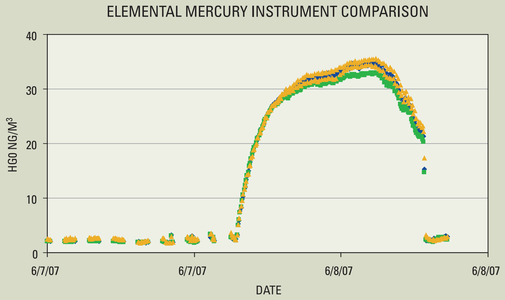


Figure 1. Elemental mercury concentrations from June 7th and 8th. Study period of June 4th through 8th, 580 observations with an average concentration of 10.9 ng/m3 and RSD of 5.9%.

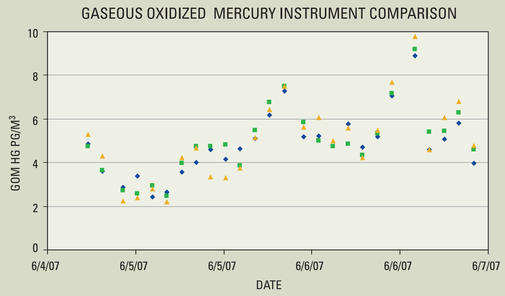


Figure 2. Gaseous oxidized mercury concentrations from June 4th through 7th. Target values are lower than desirable with an average concentration of 2.6 pg/m3, RSD of 34.2% in 34 observations.

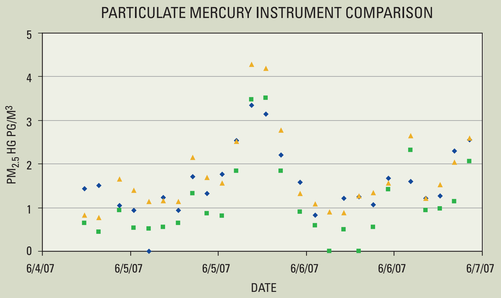


Figure 3. Particulate-bound mercury ($PBM_{2.5}$) concentrations from June 4th through 7th. Target values are lower than desirable with an average concentration of 5.8 pg/m3, RSD of 8.3% in 34 observations.

The instruments

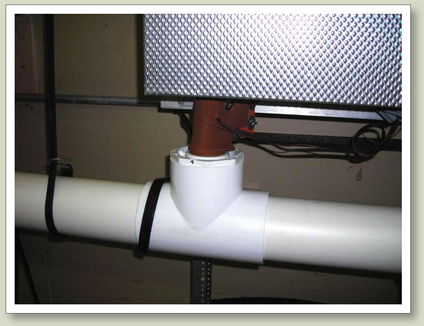
Three instruments (Cartman, Stan, and Kyle) were provided by the USGS and Kenny was on loan from the UW–Madison. Each instrument's sample flow and internal permeation source was checked and adjusted prior to the experiment. Manual injections were performed throughout the experiment. Due to contamination problems during the specified study period, Cartman's data were omitted from these calculations.

The manifold

The manifold was constructed of 10 cm (id) Schedule 40 PVC with a high volume fan on the outlet. The fan supplied air at a rate of 2.8 m^3/min. A 7.5-m flexible insulated duct was attached to sample outside air or disconnected to sample air inside the storage facility. Each instrument was set side-by-side with the inlets approximately 1 cm below the inside surface of the pipe. The sides of each instrument inlet were sealed to the manifold.

Events and data

The experiment was set up in late April and ran through the middle of June, 2007. The design was to increase the atmospheric elemental mercury concentrations using liquid mercury, then release an oxidant into the atmosphere to create a GOM event. Early in the experiment there was a liquid mercury spill within the facility. This spill increased the elemental concentrations above targeted values, making them difficult to control. Due to the high elemental values, interior air needed to be diluted, making target values for GOM and $PBM_{2.5}$ difficult to achieve. Data from June 4th through June 8th are evaluated in this poster.



Denuder spiking

Two separate spiked denuder experiments were performed, one in the warehouse on May 31, 2007, and the second *in-situ* on September 20th and 21st. For each experiment, denuders were freshly coated with 2.4M KCl, baked in a tube furnace and shipped overnight to Frontier Geosciences, Inc. Upon arrival, the denuders were blanked using a tube furnace and Tekran 2537. Once blanked, 48.4 pg of GOM surrogate was added to each denuder. Denuders were then shipped overnight for analysis the following day. The warehouse experiment consisted of 12, while the *in-situ* experiment consisted of 16 spiked denuders. Each experiment had one blank for each instrument. Both sets of data are shown to the right (fig. 4). All four instruments were used in both experiments.

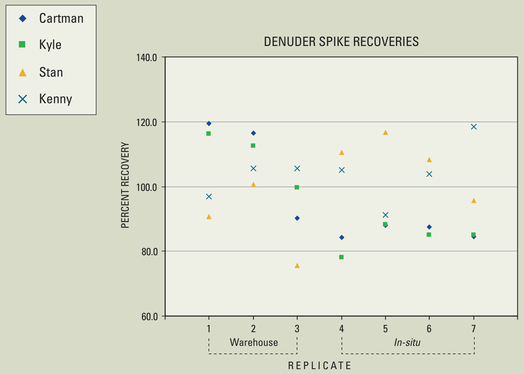


Figure 4. Spike recoveries from denuder spiking experiment. The first 3 replicates were analyzed in the USGS warehouse, replicates 4–7 were analyzed *in-situ*. The overall average spike recovery was 98.6% with a standard deviation of 13.1. Elemental spikes were performed immediately following each experiment, all were between 97–105% with an average of 102 and standard deviation of less than 1.

Summary

Accuracy assessments for GEM, GOM, and $PBM_{2.5}$ were performed using a common manifold and three Terkan speciation instruments. Concentrations were varied to simulate environmental episodes. Target concentrations were achieved for GEM, producing a RSD of 5.6%. Concentrations for GOM and $PBM_{2.5}$ were lower than desirable, making it difficult to achieve an accurate assessment. Spiked denuders were used to assess precision, and showed promising results with average spike recoveries of 102%. More work needs to be done in an environment with higher concentrations of GOM and $PBM_{2.5}$ to achieve accuracy assessments.