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Atmospheric Chemistry and Physics Discussions

Interactive comment on "In-situ and Denuder Based Measurements of Elemental and Reactive Gaseous Mercury with Analysis by Laser-Induced Fluorescence. Results from the Reno Atmospheric Mercury Intercomparison Experiment" *by* Anthony J. Hynes et al.

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Reply to Referee #1.

We appreciate the comments of the referee and we include our responses below the comments.

P. 4, line 124 – Your inlet was 25 feet long and made of Teflon (type unknown). Teflon is OK for passing elemental mercury, but it has memory problems when going from

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high to low mixing ratios. Did you determine the passing efficiency of the tubing that was used and check for memory (passing zero air through it after sampling air)? This memory problem is not obvious unless it is carefully checked. It may have influenced some of your results. RGM will also stick to that length of Teflon tubing. This may also have influenced your results (TGM).

Reply: We believe that the data from Fig. 2 (September 5th) best address the issue of passing efficiency and memory effect. The three independently operated Tekrans and the LIF system show excellent agreement switching from ∼23 ng m3 to ambient, and then from ∼ 10 ng m-3 to ambient. All three instruments had very different sampling lines, with the lines to the UW DOAGHS and the UNR Tekran being much shorter than the ∼25 Ft sampling line to our instrument. We noted, and Fig 2 shows clearly, that at the completion of the second spike all the instruments drop to ambient but the UNR instrument sees two Hg(0) "pulses" that show up with greatly reduced amplitudes in the UW and UM Tekran signals and also in the 2P-LIF signal. These occur ∼49 and 88 minutes after the spike and we do not think that these are associated with memory effects.

It is certainly possible that reduction of RGM on the walls could influence the results. We noted in section 3.3.1 "It is not clear if the deviations that are observed, particularly the large deviations seen by the UNR Tekran after the second spike are related to presence of elevated levels of HgBr2, or other issues related to manifold operation." We also noted in section 3.4 that "As we have noted previously (Bauer et al., 2014), condensation in our sampling lines can produce artifacts in Hg(0) concentration measurements. Because of the low humidity in Reno it was not necessary to use any type of cold trap during ambient measurements but we did use a trap during manifold spikes of H2O so our measurements do not address this as a potential interference." When condensation occurs in the sampling lines we see increases in Hg(0) that are presumably related to reduction of RGM deposited on the walls of the sampling lines. We have only seen these effects when we have condensation but these humidity effects merit

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further investigation.

P. 4, Section 2.3 – Measuring TOM by difference is tricky to accomplish accurately, especially in ambient air. What was your estimated LOD for TOM using this method? How was the uncertainty determined?

Reply: We would certainly agree that this approach is tricky! As we noted in section 3.5 “TOM was calculated from the difference in the TGM and Hg(0) concentrations and in this sampling configuration the limit of detection for TOM depends on the short term variability in ambient Hg(0) which is significant and shows a diurnal variation.” and “We calculated the means of the pyrolysis and ambient channel concentrations, and the difference which gives the TOM concentration. We also calculated the standard deviations and standard errors (SE) and used these errors to calculate in quadrature the 2SE uncertainty in the derived TOM concentration. However, as discussed below, the errors in the means do not appear to capture the full variability in Hg(0), particularly at shorter sampling times.” The 2SE uncertainties were typically on the order of 50-100 pg m-3 but we again emphasize that these seem to underestimate the real uncertainty associated with Hg(0) variability. We concluded in section 3.6 “Our results suggest that the use of single detection channel with switching between ambient and pyrolyzed samples is not adequate to resolve the small concentration differences that are necessary to be able to monitor ambient TOM. It is necessary to set up two detection systems, one continuously monitoring ambient Hg(0) and the other continuously monitoring a pyrolyzed sample stream giving TGM, to get the precision necessary to monitor ambient TOM.”

P. 6, lines 184 ... - These syringe injections can be difficult to duplicate with high precision. Did this add additional uncertainty to your data?

Reply: Figure 10 shows an example of data including two syringe injections. The difference in the area of these calibration injections is $\sim$1.5%. The differences in duplicate samples from denuders that are not affected by particulate sampling (i.e. 3 of the

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September 16th samples in Table 1) are significantly larger than this so we do not believe the calibration method adds significant uncertainty to this data.

We concur with the remaining comments:

P. 7, lines 230-233 – I agree that these changes are highly unlikely to be caused by chemical reactions in the manifold. This was a dark environment presumably without photochemical processes occurring. P. 8, line 258 – I agree that the calibration of the elemental mercury spikes in the manifold must of have much higher uncertainty than stated by the operators. P. 8, lines 273-274 – This is hard to rationalize and it points to the need for a new blind inter-comparison done with third party observers as suggested in this manuscript. The NSF and NASA inter-comparisons are an excellent example of how these should be conducted. P. 16, lines 563 . . . - This all points to the need for better calibration of all instruments and a more carefully conducted inter-comparison. The LIF system is capable of finding problems not apparent with the two Tekrans. In summary, this manuscript emphasizes the need for a more carefully conducted inter-comparison for atmospheric mercury.

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