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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Toward a real-time measurement of atmospheric mercury concentrations using cavity ring-down spectroscopy" *by* X. Faïn et al.

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We thank the anonymous referee for his/her attention and thoughtful comments that we addressed in our revised manuscript and which certainly improved our paper. The reviewer comments are answered in details below.

General comments

The paper is straightforward and I have only 1 serious comment. A comparison between results based on equation 4 and values from the Tekran show that the Tekran measures 21% higher than CRDS. This point needs more explanation. The Tekran instrument has been demonstrated to be a very reliable instrument but the calibration of

the instrument is based on the vapor pressure of Hg and thus the calibration might be wrong and CRDS should be an absolute method? Therefore this point needs further discussion.

Authors' Reply (AR): Similar comment was addressed in our answer to the first review. Our 2537B Tekran analyzer has been calibrated daily using its internal permeation source, and our laboratory has performed manual Tekran injections using an external calibration unit (Tekran model 2505), which has resulted in good agreement. In addition, we have performed simultaneous measurements of Hg0 levels using the Tekran 2537B with a second unit which has resulted in agreement of measurements within 4%. We hence have great confidence in the internal consistency of our measurements with the Tekran 2537B analyzer. The reasons for the 21% observed difference between theoretical and Tekran-based Hg0 absorption cross sections are presently unclear for us, but they may be based on problems with our modeling approach. Consequently, we decided to apply a calibration factor, which is based on comparing direct CRDS absorption measurements with Tekran 2537B analyzer (i.e., 6.03 , see Table 2). Based on this, we calculate an absorption cross section for Hg0 of 1.9 10-14 cm2/atom. Future work will attempt to reconcile theoretical and experimental approaches for calibration of our CRDS measurements. It is worth to note that little work has been conducted on determination of the Hg0 absorption cross section. Edner et al. (1989) report an experimental estimate, and more recently Spuler et al. (2000) published a theoretical value, similar to the Edner et al. estimation, but without detailing their calculations. We modified our manuscript, specifically section 5.1, addressing the reviewer's comment by extending the discussion about the observed difference between theoretical and Tekran-based Hg0 absorption cross sections.

Furthermore it would be interesting to see a comparison between CPDS and the Lumex the only alternative method which measures high time resolution Hg(0).

AR: Unfortunately, a Lumex analyzer was not available in our lab during this study. However, we agree with the reviewer that such comparison would be important, and

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we plan to include such comparisons in our future work.

Specific comments

P 22144 line 26. The range of Hg(0) lifetime is due to lack of knowledge of the removal reactions and not due to difference in lifetime in e.g. Northern and Southern Hemisphere. This has to be specified.

AR: We corrected the manuscript.

P 22145 line 2. an average conc. of 1.7 ng m-3 is valid for the Northern Hemisphere but not the Southern Hemisphere so add “in the Northern Hemisphere” after 1.7 ng m-3.

AR: We corrected the manuscript.

P 22160 Line 19-22. It would improve the paper significantly if measurements in ambient air were presented and at the same time give a direct indication of the reliability and robustness of the CRD instrument.

AR: We are actually working on improving our CRD setup (improvements discussed in section 6 of our manuscript), and we will run measurements of Hg0 in natural atmospheres soon. For ambient field measurements, the laboratory prototype needs to be stabilized in a specifically temperature-enclosed unit and this hence requires further development.

P 22161 Line 2. replace “that” with “than”.

AR: We corrected the manuscript.

P 22164 Line 6. After analyzers write: “Tekran 2537B and Lumex RA-915+.

AR: We corrected the manuscript.

Fig. 1 and 5. The figure texts are too small make them larger

AR: We provided figures 1,3, and 5 with increased font size.

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Additional references:

Edner H., Faris G. W., Sunesson A. and Svanberg S.; Atmospheric atomic mercury monitoring using differential absorption lidar techniques, Applied Optics, 28, 921, 1989.

Spuler S., Linne M., Sappey A. and Snyder S.; Development of a cavity ringdown laser absorption spectrometer for detection of trace levels of mercury, Applied Optics, 39, 2480-2486, 2000.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 22143, 2009.