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Atmospheric Measurement Techniques Discussions

Interactive comment on "Deployment of a sequential two-photon laser induced fluorescence sensor for the detection of gaseous elemental mercury at ambient levels: fast, specific, ultrasensitive detection with parts-per-quadrillion sensitivity" *by* D. Bauer et al.

Anonymous Referee #1

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This paper describes a new two-photon laser-induced fluorescence (2P-LIF) instrument for the detection of gas-phase elemental mercury in the atmosphere. The detection of atmospheric mercury concentrations is important in order to improve our understanding of the sources and fate of mercury emissions to the atmosphere. As discussed in the paper, current techniques to measure atmospheric mercury concentrations suffer from issues of specificity relative to the detection of gaseous elemental

mercury (Hg(0)) vs. reactive gaseous mercury (RGM) as well as being limited in sampling time. The new instrument described in this paper provides a fast, sensitive, and specific technique for measuring Hg(0) in the atmosphere.

The paper presents some preliminary measurements using this technique during the RAMIX (Reno Atmospheric Mercury Intercomparison Experiment), and the measurements are compared to that obtained using commercial Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS) instruments. The fluorescence signals obtained using the 2p-LIF instrument are shown to strongly correlate with the CVAFS measurements, and data is also shown that suggests that the instrument is capable of measuring rapid changes in concentration. The measurement also appears to be free from significant interferences. However, the stability of the laser system appears to be an issue that is currently limiting the overall precision and accuracy of the measurements.

The paper is generally well written and appropriate for publication in AMT after the authors have addressed the following comments. In addition, there are details regarding specific aspects of the instrument that should be included (outlined below):

1) As mentioned in the paper, the LIF signal must be calibrated to convert the fluorescence signal to an absolute concentration. The data in this paper appear to have been calibrated by reference to a commercial CVAFS instrument rather than using a calibration standard. In addition, the signal is shown to be sensitive to the concentration of water vapor. Unfortunately there is little discussion regarding the absolute calibration of the instrument, although it appears that an expanded discussion will appear elsewhere (pages 5661 and 5668). Given the importance of accurate calibrations, the authors should include an expanded discussion on how they plan to calibrate the instrument in the laboratory and in the field.

2) Much of the variability in the measurements appears to be the result of instabilities associated with the laser wavelength and power (page 5660). To account for these changes, the authors normalize the measurements to changes in the reference cell

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signal. However, this normalization depends on the stability of the concentration of Hg(0) in the reference cell. It also assumes that any saturation of the fluorescence signal is similar in the reference cell compared to the sampling cell. Did the authors measure the Hg(0) from the reference cell using one of the Tekran instruments to test its stability? Have the authors demonstrated that changes in the reference cell signal with respect to laser power and wavelength were similar to changes in the sampling cell? What impact would multiple pulses on the same airmass in the reference and sampling cell have on the fluorescence signal in terms of saturation of the transition? Would this impact the ambient (roof) measurements (where the flow of air is variable)?

Minor comments:

1) Given the complexity of the instrument, the paper would benefit from a schematic figure illustrating the various components of both the “first generation” system and the “second generation” system.

2) It would be useful to provide more details regarding the lasers, PMTs, etc. used in the instrument (manufacturer, model numbers, etc).

3) What laser powers were used for each wavelength, and how did they vary? Was there a significant drop in laser power between the reference cell, the detection cell, and the roof measurements? Information regarding the dye concentration and solvent used should be provided.

4) More details regarding the geometry of the sampling cell and reference cell should be provided, perhaps with a figure. What was the flow rate through the sample and reference cells?

5) The configuration of the roof-top measurements is not clear. On page 5658 it states that two PMTs were used for roof sampling, while on page 5670 it appears only one PMT was used for the ambient measurements. This should be clarified in the text and in the schematic figure.

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