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Comment

Interactive comment on “A cavity ring-down spectroscopy sensor for measurements of gaseous elemental mercury – Part 1: Development for high time resolution measurements in ambient air” by A. Pierce et al.

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Author Responses

Referee 1 (R1.): The authors present a further development of a laser based system for fast measurement of elemental mercury in air described initially by Fain et al. (2010). A system for automatic wavelength locking and stabilization of the laser wavelength has been developed. Measurement of the differential absorption using an on/off-line tun-

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ing of the wavelength has been implemented. Ozone interference has been solved by thermal decomposition of ozone in the air sample. Instrumental challenges due to the temperature fluctuations, ozone interference, and frequency conversion efficiency are discussed. The paper is well organized and written. From the perspective of a physicist the presented work might be impressive. From the perspective of an atmospheric scientist who would welcome any improvement in the measuring techniques, the work is disappointing since the resulting detection limit of 0.35 ng m⁻³ with an integration time of 5 min is comparable with the performance of the portable commercial instrument based on atomic absorption spectroscopy with Zeeman background correction (Lumex, mentioned by Fain et al. (2010) but not here) and is worse than that of the Tekran instrument which with 5 min sampling time has a detection limit of ~0.1 ng m⁻³. The objectives of the work as stated by Fain et al. (2010) were to develop a technique suitable for micrometeorological flux measurements, i.e. capable of fast (~10 Hz and more) measurements at ambient levels (~2 ng m⁻³). The presented performance falls far behind this objective and after another two years of development even behind the detection limit of 0.1 ng m⁻³ with 10 s resolution reported by Fain et al. (2010) for an instrument whose improvement is the subject of this work. This being according to the Table 1 of Fain et al. (2010) the 7th attempt on GEM detection by CRDS, I would expect a short discussion of the fundamental limits of the CRDS technique for this application. The authors could then compare their results with this benchmark and discuss the ways to get near it. Without such discussion the conclusion of “more of the same”, i.e. better temperature control, better laser, ozone scrubber, appears to be rather clueless. I also wonder what the content of the announced Part 2 might be which cannot be presented in this paper.

Response: We would like to clarify that the current sensor and associated measurements presented in this manuscript are vastly different from those presented in Faïn et al. (2010). Most importantly, in Faïn et al. we presented a laboratory prototype that required manual wavelengths scans to quantify Hg absorption. We here present the substantial and important developments and advancements for in-situ real-time

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measurements of GEM in ambient air, including automated wavelength control, signal acquisition and processing, and inlet configurations to reduce interferences. We originally separated our manuscripts into two parts, the first part was meant to extensively discuss advances made to the sensor (current manuscript) and a Part 2 which would present detailed ambient air measurements. However upon review of the referee comments we have decided to improve on the organization of the current manuscript and now include all measurements that we intended to provide in Part 2 into this manuscript. This should address the reviewer's concern as we will thereby discuss in detail the advantages of using the CRDS techniques for GEM measurements, the limitations in background ambient air measurements, and comparison to other systems (including the Lumex).

In regards to the critique on system sensitivity, it is important to note that in Fain et al., the sensitivity was reported as $3 \times \text{SE}$ (standard error) while here we report a sensitivity of $3 \times \sigma$ (standard deviation, see comparison table in R1.C1.). While of course it would always be desirable to have better instrument sensitivities, we will clarify in our revision that this is the best sensitivity so far achieved by CRDS technology and that the current sensitivity allows for characterization of GEM patterns not feasible with other, slow-response sensors.

Comments (C#.): R1.C1. In section 3.2 the different methods of background correction are discussed without mentioning the Zeeman background correction as realized successfully in the commercial Lumex instrument for measurement of ambient mercury. Neither is Lumex instrument mentioned in Section 3.5 in which the preliminary field performance is compared with other instruments. At least the latter should be added to put the presented results into perspective.

Response: A paragraph and a table will be added to section 3.5 that compare our current system with other systems for measuring GEM. These comparisons were originally intended to be discussed in Part 2. Specifically, the following section will be added to the paper to address R1.C1.:

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“A series of GEM measurement techniques have been developed and discussed in the literature (Comparison Table). The technique most used in research and ambient air monitoring is based on cold-vapor atomic fluorescence spectroscopy. The Tekran 2537 analyzer has been tested in various inter-comparison studies (Ebinghaus et al., 1999; Munthe et al., 2001; Pandey et al., 2011; Schroeder et al., 1995), showing excellent sensitivity (0.1 ng m^{-3} (3σ) over 5 min) and stability in laboratory and ambient air measurements (Tekran, 2009). Other techniques used include a portable atomic absorption spectroscopy system using Zeeman background correction with a sensitivity of 2 ng m^{-3} over 1 sec; measurements by this system have been made in laboratory and ambient air (OhioLumex, 2012). Another system is based on differential absorption lidar (DIAL) with a sensitivity of $0.5\text{--}2 \text{ ng m}^{-3}$ over 5 to 10 sec in laboratory air and factory plume measurements (Edner et al., 1989). Also, a sequential two photon laser induced fluorescence (LIF) spectrometer with a 10 Hz laser system and sensitivity of 0.15 ng m^{-3} (3σ) for 10 sec has been employed for laboratory air and ambient air measurements (Bauer et al., 2002; Bauer et al., 2003). Additional CRDS systems, with sensitivities ranging from 2.19 to 27 ng m^{-3} , operate at $10\text{--}50 \text{ Hz}$ and have been used to measure GEM in in laboratory air, inert gas, or flue gas with high GEM levels (Carter, 2004; Faïn et al., 2010; Jongman et al., 1995; Spuler et al., 2000; Tao et al., 2000). The system presented in Faïn et al. (2010) that preceded the system presented here was the only CRDS system so far that provided preliminary background ambient air GEM measurements; these measurements, however, were limited to a few single measurements and were performed using manual wavelength scans over the GEM absorption spectrum and thereby did not allow for real-time GEM measurements. Microwave induced plasmas (MIP)-CRDS with 20 Hz repetition rate and sensitivities that ranged from 400 to 1841 ng m^{-3} over 2 to 5 sec were used for measurements of GEM in argon gas (Duan et al., 2005; Wang et al., 2005); and cavity-enhanced absorption spectroscopy (CEAS) with a sensitivity of 66 ng m^{-3} over 10 sec (3σ) was used for measurements of GEM in a static cell (Darby et al., 2012). Very few of these systems, however, have been adapted for GEM concentration measurements under real-time,

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ambient air conditions. When comparing our results to techniques used previously, the sensitivity of our current CRDS system (3σ ; 1.9 ng m⁻³ at 10 sec time resolution, and 0.5 ng m⁻³ at 2.5 min time resolution) compares well to these other techniques (range of 0.1-1841 ng m⁻³ over time resolutions of 0.1 sec to 5 min)."

R1.C2. The on/off-line tuning does not remove completely the ozone interference. The authors rightly explain that this might be partly because of the very high absorption by ozone leaving too few photons left for measurement. But it could also be due to differential absorption of ozone for the on/off wavelengths which could be measured directly with mercury free air containing defined mixing ratios of ozone. Such measurement combined with ozone measurement would perhaps enable an exact correction for ozone interference. Because of the problems with ozone pyrolysis mentioned below in point 5 this might be a preferable solution to the ozone interference.

Response: We tested O₃ interferences using O₃ spikes in Hg-free air as well as using natural background O₃ levels in ambient air measurements to assess reasons for the O₃ interferences. However, while the response of the differential CRDS measurement to O₃ can be fitted by a linear regression (see Figure 7 of current manuscript), the predictive value of this regression only accounts for about 2/3 of the variability in O₃ concentrations ($r^2 = 0.66$). Correcting O₃ interference by this regression, hence, would add significant noise to measurements in ambient air, and we therefore decided to remove O₃ rather than correct data for these interferences.

However, we agree with the reviewer that another possible reason for O₃ interferences (aside from changes in signal power, I₀) may include different O₃ absorption of the online and offline measurement wavelengths (although this is expected to be very small given the extremely narrow GEM absorption line, the broad absorption spectrum of O₃, and the small wavelength detuning [0.003 nm]). In the revised manuscript, we will clarify these points in section 4.2.

R1.C3. Fig. 6 shows that $\sim 1^\circ\text{C}$ change in instrument temperature causes 30% change

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in differential extinction. The text in Chapter 4.3 reads as if this problem were solved by a foam enclosure which reduced the temperature fluctuations to $<1^{\circ}\text{C}$. As Fig. 6 shows apparently the state with the foam enclosure it can illustrate an improvement but hardly a solution of this problem.

Response: Yes, temperature fluctuations during ambient air measurements cannot be fully eliminated by a foam enclosure but are greatly reduced, which we will clarify in the revised manuscript. Please note that other environmental variables also slightly affect our measurements; to account for these, we perform multiple linear regressions using these variables (i.e., temp, RH, pressure) and back-correct measurements if these variables are significantly related. A conversion factor (number of Mm^{-1} per 1 ng m^{-3}) is then calculated based on the regression of corrected differential extinctions and GEM concentrations measured by a Tekran Hg analyzer over corresponding 2.5 min measurement intervals. Final CRDS GEM concentrations are then calculated based on these conversion factors. This information will be added to section 3.3 to clarify these issues and to further explain our data processing steps.

R1.C4. The authors suspect the temperature dependence to be due to the temperature sensitive elements of the cavity but discuss it in Chapter 4.3 in terms of absolute and differential extinctions, i.e. spectroscopical properties. This might be misunderstood by the readers.

Response: We will clarify this discussion.

R1.C5. The removal of ozone interference by pyrolysis poses two problems which are not addressed. First, particulate mercury will be released at high temperature (see Rutter and Schauer, Atmos. Environ. 41, 8647-8657, 2007) and the resulting and already present reactive gaseous mercury will be at least partly pyrolysed to GEM (Lyman and Jaffe, Nature Geoscience 5, 114-117, 2012). Consequently, it will not be GEM which will be measured with ozone pyrolysers and this should be mentioned in the text. Secondly, upstream pyrolyser will make the measurements with high temporal

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resolution difficult because of its residence time.

Response: Our inlet configuration prior to entering the pyrolyzer consists of a 0.2 μm pore size Teflon filter and a 5 m unheated Teflon line; inlets of this configuration don't efficiently transmit RGM or PHg (Brunke et al., 2010; Moore et al., 2013). Further, because we operate our system at flow rates of 8 lpm, we calculate transmission time of only about 2 seconds from the end of the sample line injection to the cavity. We further addressed to what degree the cavity and inlet configuration affect high-frequency concentration fluctuations by cospectral analysis of air drawn through the cavity and measurements by a 3D anemometer at the system inlet. This analysis indicates that cavity measurements can be made up to a frequency of about 0.45 Hz; this analysis will be part of a subsequent manuscript discussing the first deployment of this sensor for Eddy Covariance GEM flux measurements.

R1.C6. The authors present absolute and differential extinctions. For people not familiar with the technique it would be helpful to know what Hg absorption coefficient they use for calculating the mercury concentrations. As the locking wavelength does not coincide exactly with the maximum of the atmospheric absorption other absorption coefficient than its literature value has to be used. Or did they calibrate the instrument? If so, how?

Response: We will clarify that reviewer 1 is correct; we don't use the literature value for the absorption coefficient, as explained in Faïn et al. (2010). CRDS differential absorption measurements are compared to GEM concentrations measured by a Tekran 2537 analyzer at 2.5 min averaging time to calculate a conversion factor (Mm^{-1} per 1 ng m^{-3} GEM). This is necessary because the absorption coefficient changes over time, which we attribute to long-term drifts in alignment, signal strength, and mirror reflectivity – this will be clarified in the revised manuscript.

Our wavelength locking is extremely close to the peak absorption value as is shown in Figure 2 and will be clarified in Section 3.2. In Figure 2a we show that the peak absorp-

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tion of the Hg200 isotope external Hg cell we use to lock the laser is $<0.001\text{nm}$ from the peak of the ambient air GEM absorption. Please keep in mind that the absolute wavelength numbers shown in Figure 2 include uncertainties of the laser output (within $\pm 0.03\text{ nm}$). This is why we use an external Hg cell to position the wavelength as close as possible to the peak absorption line regardless of what wavelength the laser reads which is not accurate enough to locate the GEM absorption peak (FWHM of 0.005 nm). Due to this laser wavelength error and laser drift over time, the external Hg cell is used to maintain the laser wavelength on the Hg absorption peak.

Referee 2 (R2.): The paper discusses a cavity ring-down spectroscopy sensor to measure gaseous elemental mercury. The ultimate goal is to develop a sensor with faster time resolution than the available standard – 2.5 min – and thus enable new observations (e.g., mercury cycling.) Refinements to a laboratory prototype were made (e.g., improved line locking) and the system was integrated into a field portable laboratory container. Ambient air tests were performed which included inter-comparisons with other sensors. The paper clearly describes the instrument improvements over the previous prototype. It was well-written, the scientific methods and assumptions were valid, and the experiments were sufficient to support conclusions. However it hard to say that “substantial” conclusions were reached. More work is needed to stabilize the instrument and deal with ozone, which is a major interference. It is unclear why the ambient air measurements are to be fully discussed in a part 2 of the paper (i.e, only preliminary data was shown).

Response: As discussed in the response to reviewer 1, we will add extensive measurements conducted in ambient air that we originally intended to discuss in a second part to the current manuscript. This will greatly improve the discussion of current performance and CRDS limitations for measurement of GEM.

Comments (C#.): R2.C1. The authors should reference the laser-based fast-time-response mercury sensor development work done at Sandia National Laboratories in 2007-2008. A few references are listed below but more detailed

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literature search could be done. <http://www.sandia.gov/remote-sensing/applications-caseStudies/mercury.php> <http://144.206.159.178/ft/CONF/16410985/16411002.pdf>
Alexandra A. Hoops, Thomas A. Reichardt, Dahv. A. V. Kliner, Jeffrey P. Koplow, and Sean W. Moore, Detection of mercuric chloride by photofragment emission using a frequency-converted fiber amplifier, Applied Optics, Vol. 46, Issue 19, pp. 4008-4014 (2007) <http://dx.doi.org/10.1364/AO.46.004008>

Response: As discussed above (R1.C1.), we will add a detailed table and discussion to compare our system to other measurement techniques published in the literature. We will also add the work from Sandia National Laboratories (although this work is focused more on HgCl₂ as opposed to GEM).

R2.C2. In addition to high-time resolution, the goal is to create an instrument capable of continuous and automated measurements of GEM in ambient air. The authors should discuss how this could be achieved – or on what time scales – with a flashlamp pumped Nd:YAG and dye laser system. Beyond a demonstration of the proof-of-principal, this laser system could not be fully automated and run continuously for a month (e.g. technical personnel would needed for bi-monthly flash-lamp changes at 50Hz, dye lifetime would need to be considered, etc.)

Response: More details on this was intended to be provided in Part 2 but will now be included in the current manuscript. We will show that this system is capable of being deployed in the field in a trailer, but the referee also is correct in that it cannot run for months straight and must be manned. We will discuss that the system can be run continuously for at least ten hours; that flash lamps must be changed after 30 million shots, or about 7 days of continuous run time; and that dye must be changed every two weeks with heavy use (5-8 hours a day 5 days a week).

R2.C3. In this referee's option – incremental improvement to the prototype was demonstrated but substantial progress over what is in the literature was not shown.

Response: When reviewing the table included in R1.C1. it is our opinion that with this

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CRDS system we have made substantial progress over any previous attempt to use CRDS technology for measurement of GEM, and that compared to other techniques our time resolution and sensitivities are high. We further present extensive direct measurements of GEM by the CRDS system in ambient air (as opposed to measurements in flue gas, pure N₂, or synthetic air), and discuss important interferences and issues that have not been documented by other studies. We will further include a detailed figure (See Spike Figure) that shows an example of the high temporal resolution and the advantages for characterization of GEM concentration patterns and dynamics.

Referee 3 (R3.): This is an interesting paper and the authors have done a very careful job in improving the reliability and performance of their GEM measurement instrument. As I read the paper, however, I definitely had the impression that this is far instrument is still far from a field-ready sensor. Considerable care and expertise are required to perform the measurements, and even then there are some issues such as the effect of temperature fluctuations that are not completely understood and that still affect the accuracy and precision of the measurements. On the whole though, I support publication of the manuscript. A couple of minor revisions are suggested:

Response: See response and our clarifications above.

Comments (C#.): R3.C1. One very interesting aspect of the manuscript was the fast piezoelectric tuning of the dye laser wavelength, on and off resonance with GEM absorption lines at 25 Hz. It is unclear from the manuscript how this was implemented. Is this an option offered by Sirah or was this a custom modification performed by the authors. A diagram to provide more information on the piezoelectric tuning element is strongly recommended.

Response: The piezo electric tuning element was custom-supplied by Sirah; it is mounted in the dye laser and used to tune a Littrow grating of the dye laser resonator in smaller increments than can be achieved with only the laser grating tuning. We will clarify this as well as the programming and control to maintain frequency conversion

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efficiencies that was custom-programmed and developed during the project in Section 3.2.

R3.C2. What was the time period between dye changes? Dyes that are pumped with the 355-nm Nd:YAG output typically last on the order of hours, which would seem to be a major obstacle to the development of a field instrument.

Response: As mentioned in R2.C2., dye is changed every two weeks during heavy use (5-8 hours a day 5 days a week) and changed once a month during light use (1-4 hours a day 3-4 days a week). This procedure is relatively simple and can be performed by a trained lab technician within a couple of hours, so this is not a problem from field deployment of the sensor.

R3.C3. Is there some reason not to scan the dye laser wavelength over GEM absorption lines and record the absorption spectrum? In many ways this would simplify the instrument, eliminating the need for the wavelength locking cell and the fast piezoelectric tuning, for example. The authors should discuss why scanning measurements were not performed.

Response: In Fain et al. 2010, manual scans across the GEM absorption lines were performed to determine GEM concentration. However, this scanning procedure takes 5-10 minutes (depending on scan step sizes) so it did not allow for high time resolution (25 Hz) measurements. The differential measurement technique we implemented in this system, on the other hand, allows for baseline measurements to be made every other laser pulse so that data can be continuously corrected for baseline drifts at 25 Hz. This will be clarified in the revised manuscript in section 3.2.

References:

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Interactive comment on Atmos. Meas. Tech. Discuss., 5, 8995, 2012.

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Comparison Table: Sensors used for detection of GEM

Product/type	Detection limit (3 σ e in ng m ⁻³)	Response time	Made in?	Measurement method	Source
Zeman mercury analyzer RA-VIS	2	1 sec	Ambient air	Atomic absorption spectrometer with Zeeman background correction	(OhioLumes, 2012)
Tekran 2537B	0.1	5 min	Ambient air	Cold vapor atomic fluorescence spectrometry	(Tekran, 2009)
Lidar	~ 0.5 -2	5-10 sec	Lab air, Factory plume	Differential absorption lidar (DIAL)	(Edner et al., 1989)
LIF	0.15	10 sec	N ₂ buffer gas	Sequential two photon laser induced fluorescence spectrometry	(Bauer et al., 2002; Bauer et al., 2003)
CRDS	27	3sec	Lab air	BBO crystal frequency-doubled, pulsed dye laser (line width of 0.1 cm ⁻¹) pumped (10 Hz) by a frequency-tripled Nd:YAG laser at 355 nm	(Jongman et al., 1995)
CRDS	4.5	75 sec	Lab air, Perm source and N ₂	Quanta-Ray GCR-16 Nd:YAG laser pumping a PDL-3 dye laser with 10 Hz repetition rate, BBO frequency doubled (0.11 cm ⁻¹ line width)	(Spuler et al., 2000)
CRDS	24	unspecified	Argon	Nd:YAG laser pumping a tunable dye laser frequency doubled (0.1 cm ⁻¹ line width)	(Tao et al., 2000)
CRDS	~ 90	10 sec	Flue gas	Frequency-tripled Alexandrite laser, seeded with a single mode, external-cavity diode laser, UV output line width 0.006 cm ⁻¹	(Carter, 2004)
(Microwave Induced Plasmas) MIP-CRDS	~ 400	5 sec	Argon	alternative plasma sources for CRDS measurement of GEM (tube-shaped MIP source) using Nd:YAG laser with 20Hz repetition rate pumping a dye laser (line width 0.08 cm ⁻¹)	(Duan et al., 2005)
(Microwave Induced Plasmas) MIP-CRDS	~ 1841	2-5 sec	Argon	alternative plasma sources for CRDS measurements, Nd:YAG laser with 20Hz repetition rate pumping a dye laser frequency doubled (line width 0.08 cm ⁻¹)	(Wang et al., 2005)
CRDS	2.19	0.1 sec	Ambient Air	Nd:YAG laser pumping a tunable dye laser (0.0019 nm line width)	(Fain et al., 2010)
CEAS	66	10 sec	Injection into static cell	Cavity-enhanced absorption spectroscopy, Hg-Ne pencil lamp	(Darby et al., 2012)

*Definition of detection limit not specified (i.e., not necessarily 3 σ e)

Fig. 1.

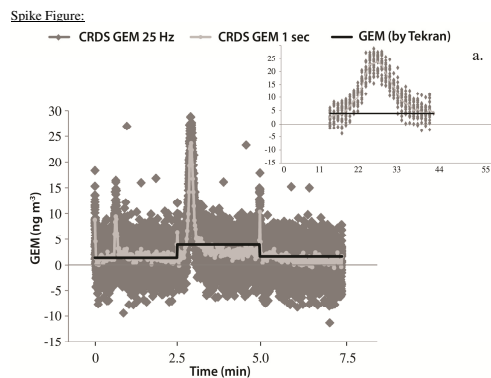
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High-resolution CRDS measurements with short GEM spike additions to ambient air, and comparison to measurements using a Tekran Hg analyzer. CRDS measurements are shown at 25 Hz and 1 sec time resolutions, while Tekran measurements are shown at 2.5 min resolution. A) 4 ng m⁻³ spike. Inset shows only the spike area.

Fig. 2.