

Interactive comment on “Successes and challenges of measuring and modeling atmospheric mercury at the part per quadrillion level: a critical review” by M. Sexauer Gustin et al.

A. Hynes

ahynes@rsmas.miami.edu

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The comments of both referees provide a substantial critique of the manuscript however I would like to draw attention to points that relate to work from my research group. I should make clear that this does not indicate agreement with sections of the manuscript that I do not address.

The paper states: “2.1.6 Laser systems Two laser systems have been developed for measurement of GEM (Pierce et al., 2013 Bauer et al., 2002, 2010). One is a cavity ring down system and the other operates on the principle of laser-induced fluores-

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cence. Both are calibrated using Tekran[®] data. These do not currently have the ability to measure GOM. The cavity ring down instrument has interferences with ozone (Ashley Pierce, Ph.D. Candidate, UNR, personal 10 communication, 2014). During RAMIX these two instruments were deployed and could only be operated when trained personnel were present. Given the current sensitivity and electrical power use of these instruments (a small city) they are best applied in the lab.”

The paper fails to note that the laser-induced fluorescence system operated by my research group successfully sampled on 18 days, typically sampling for between 4 and 6 hours. The longest period of continuous sampling lasted for 26 hours. Over this 18-day period we sampled from the RAMIX manifold and, in addition at the end of the campaign we sampled ambient air independently, including true in-situ sampling on the roof of our mobile lab. We also attempted to measure RGM by pyrolyzing the sample air and measuring the difference between Hg(0) and TGM.

The instrument requires trained personnel to operate, as do most of the instruments that are currently deployed for ultra-sensitive analysis of trace atmospheric species. The operation of this instrument as deployed at RAMIX and with further modifications at the University of Miami is described in detail in a recent paper by Bauer et al., [2014]. Ironically Professor Gustin is listed in the acknowledgements, she received the paper after publication and I'm at a loss as to why the authors fail to cite the paper. The suggestion that the power requirements of this instrument are “those of a small city” are utterly ludicrous and speak to the authors ignorance of instrumentation that has been deployed and advanced our measurement of trace atmospheric species including OH, NO_x and now mercury. The only component of the system deployed at RAMIX that had a significant power requirement was a Nd-Yag laser that draws 10 amps at 220 V, i.e. ~ 2000 watts. A instrument that used similar principles, i.e. sequential two photon laser induced fluorescence and that utilized two more powerful driver Nd-Yag lasers (requiring higher electrical power) and two tunable excitation sources was deployed for measurement of NO_x on the NASA DC8 during multiple NASA flight campaigns (see

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for example Bradshaw et al. [1999]).

As currently deployable our instrument is unique in its ability to address some of the current issues in the atmospheric chemistry of mercury. 1) It monitors Hg(0) in-situ at atmospheric pressure and composition. Although an air sample can be drawn into a fluorescence cell for analysis this is not necessary since the technique operates in the open air. 2) It does not detect oxidized mercury so this does not have to be removed prior to analysis. 3) The sensitivity and temporal resolution is considerably better than any other instrument that has been deployed to measure Hg(0). Currently, the achievable detection sensitivity is $\sim 15 \text{ pg m}^{-3}$ ($\sim 5 \times 10^4 \text{ atoms cm}^{-3}$, $\sim 2 \text{ ppq}$) at a sampling rate of 0.1 Hz i.e. averaging 100 shots with a 10 Hz laser system. 4) Addition of a pyrolysis channel will allow the simultaneous measurement of total mercury and Hg(0) with high temporal resolution.

Supplement “Detailed discussion of Atmospheric Chemistry”

To describe the discussion of the Hg(0) O₃ as a “Detailed discussion of Atmospheric Chemistry’ seems inappropriate and the brevity of the section is problematic. Tossell [2003] actually found that HgO was unbound with respect to reactants while Shepler and Peterson [2003] reported that HgO was bound by approximately 17 kJ mol⁻¹. Using the 17 kJ binding energy makes the reaction to form HgO exothermic by 93 kJ/mole $\text{Hg}(0) + \text{O}_3 \rightarrow \text{HgO} + \text{O}_2$ (1) $\Delta H = 93 \text{ kJ mol}^{-1}$

Hynes et al. [2009] did not calculate a rate for this reaction, rather we calculated a rate for the reverse reaction using a calculated equilibrium constant, the principle of detailed balance and the rate coefficient reported by Pal and Ariya [2004], $7.5 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This gave a rate coefficient of $3.1 \times 10^{-4} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reverse process i.e. $\text{HgO} + \text{O}_2 \rightarrow \text{Hg}(0) + \text{O}_3$ (-1) This is at least six orders of magnitude faster than any physically reasonable rate coefficient. It implies that the rate coefficient for reaction (1) must be SLOWER than $1 \times 10^{-25} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ making it of no possible significance in the atmosphere.

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We discussed the work of Hall [1995], Pal and Ariya [2004] and Summer et al. [2005] but not the work of Rutter et al. [2012] which had not been published.

We noted that “Calvert and Lindberg [2005] suggest that reaction might proceed via an addition reaction to produce a weakly bound molecule with a binding energy of $\sim 16 \text{ kJ mole}^{-1}$. Such an addition complex would have no exothermic dissociation routes but it might diffuse to the reaction walls.” and later “If the reaction does proceed in the gas phase it must be via the formation of a weakly bound complex that is likely reversible since no exothermic decomposition pathways are accessible. In the laboratory experiments such a complex could diffuse to the reactor surface to form solid mercuric monoxide, possibly via oligomer formation.” and finally “The combination of complex gas phase kinetics coupled with contributions from heterogeneous reactions could certainly explain the very large differences in the rate coefficients obtained in the recent studies of this reaction. However oxidation based on such a mechanism is unlikely to be of any significance in the atmosphere. At typical atmospheric concentrations a very small fraction of the Hg(0) would be present as adduct and the chances of heterogeneous removal would not be significant.

To re-emphasise, while the formation of a weakly bound adduct of O₃ and Hg(0) might explain the results of laboratory studies it cannot be of any importance in the real atmosphere.

With regard to the suggestion that reaction might occur via isomerization of such an adduct we noted: “Tossell states that a stable van der Waals complex of Hg and O₃ exists but gives no value for a binding energy and also notes that the isomerization of this species to OHgO₂, as suggested by Calvert and Lindberg, is unlikely since it is endothermic but again quantitative thermodynamic data is not provided.” It should also be noted that Calvert and Lindberg make clear that an OHgOO can only produce HgO(s) if this species collides with an aerosol or other solid surface. “However, if only homogeneous reactions are available to the HgO₃ species (no aerosols or nearby surfaces), then decomposition in pathway (d) in Fig. 1 would likely be followed by

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reaction (f) to regenerate Hg and ultimately, ozone.”

Pathway (d) is the reaction $\text{HgO} \rightarrow \text{Hg} + \text{O}$ (d) followed by (f) $\text{O} + \text{O}_2 \rightarrow \text{O}_3$ (f)

In other words this process CANNOT produce gas phase oxidized mercury.

The manuscript refers to HgO as a possible component of gaseous oxidized mercury but this species cannot exist in the atmosphere as a covalently bound diatomic molecule if one accepts the most recent values of the HgO binding energy.

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