**Atmospheric
Chemistry
and Physics**
Discussions

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.

F. Slemr (Referee)

franz.slemr@mpic.de

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The authors review at first the analytical techniques available for the measurement of mercury species. They present experimental evidence that the Tekran speciation technique, currently the only one used for routine speciation measurements, is probably substantially underestimating gaseous oxidised mercury (GOM) concentrations and possibly also that of particulate bound mercury (PBM). In the second part they mostly use ratios of measured to modelled concentrations to substantiate this claim.

The paper reveals signs of hasty writing and needs a thorough editing before it can be

published in a final version. Some conclusions are questionable and a more precise wording is also needed at times. On balance, however, I think that the paper is useful and should be published after substantial revisions.

1. General comments

The title crows about successes of which I, after some 30 years of activity in this field, am not much aware. I concede that the models have improved quite a lot and phenomena such as polar depletion events have been discovered and largely explained, but that is not what the paper is about. The review deals mainly with technique for speciated mercury measurements and despite some new techniques the fundamental analytical problems have not been solved. The oxidation mechanism is still an open question, mostly because the final products have not been identified yet. The results of rather rare GOM and PBM intercomparisons still may deviate by a few hundred percent and even the GEM measurement, for which the authors claim "relative confidence", may deviate by 20% (Aas, 2006) and even recently by almost 30% (Gustin et al., 2013) when run at the same site. Is the title not too sanguine under these circumstances? Would it not be more proper to use a more modest title without the word "successes"? If the authors persist on "successes" than it should be accompanied by "failures".

A review like this has been presumably written for a broader community than mercury specialists. Therefore, I think that non-specialist readers would benefit from the review more if chapter 2 had some introduction outlining general principles and problems of the Hg analytics, such as listed below:

a) The analytical problem: GEM mercury concentrations in ambient air are on the order of a few ng m-3, GOM and PBM concentrations are usually two to three orders smaller.

b) Mercury is usually detected by atomic absorption (AAS) or atomic fluorescence spectroscopy (AFS). Both techniques detect, by their physical nature, only Hg atoms, i.e. GEM. GOM and PBM have thus to be converted to GEM for their detection.

c) The sensitivity of AAS and AFS is, with exception of laser techniques, not sufficient for direct measurements of GEM, GOM, and PBM. Consequently, mercury species have to be preconcentrated.

d) Gold surface is almost universally used to preconcentrate GEM, GOM, and with a special design (gold coated quartz wool) even PBM. Mercury compounds are converted to GEM during their thermodesorption from gold adsorbers. Consequently, an AAS or AFS instrument combined with a preconcentration on a gold adsorber will provide TGM (GEM + GOM) or TM (GEM + GOM + PBM) concentrations.

e) In the absence of methods for determination of individual GOM and PBM compounds, the current speciation techniques are based on specific enrichment of GEM, GOM and PBM. Differential techniques for GOM, PBM or both, such as measuring the difference between TGM and GEM, are subject to large uncertainties due to the subtraction of large numbers.

f) GOM is believed to be sticky in sampling lines. Consequently, the sampling system for GOM has to be designed to prevent wall losses.

g) GOM and PBM are in temperature dependent equilibrium. Specific PBM sampling has to take account of this, in addition to the usual precautions to prevent size dependent particle losses. As it might be difficult to achieve the separation of PBM and GOM without disturbing the equilibrium, RM (i.e. PBM + GOM) measurements might be more accurate than the sum of specific PBM or GOM measurements.

Passive sampling techniques are developed for other purposes than active sampling techniques and have their special problems. For this reason I would recommend to treat them in a separate sub-chapter. Chapter 2 could then have two sections: one with active sampling techniques and the other with the passive ones. Alternatively three chapters would do: active automated, active manual, and passive techniques.

GOM and PBM concentrations measured currently with the Tekran system are roughly

consistent with the widely accepted atmospheric mercury lifetime of 0.5 – 1.5 years. Almost all of the evidence presented in this review suggests that GOM and possibly PBM measured by Tekran speciation system are substantially underestimated. As GOM and PBM are readily rained and washed out, higher GOM and PBM concentrations imply substantially shorter lifetime. Perhaps the modeller coauthors should say something about this contradiction.

2. Specific comments

Abstract: Concerning the priorities in the second but last sentence I think that the word "calibration" is not properly used. What we need are systems to produce test GOM and PBM mixtures to determine sampling and conversion efficiencies and to carry out intercomparisons with spiked air. "Calibration" in a narrower sense means to me the calibration of the AAS or AFS detectors which is no problem. The questionable use of "calibration" became obvious when talking about a special PBM calibration system. As with all other elements on particles we are talking about the aerosol elemental composition. It should be no problem (and it has already been done) to produce substrates with a known Hg content. Certified materials such as fly ash are available. The problem with the PBM measurements is, to my opinion, not their calibration but a sampling problem. To solve it test mixtures are needed.

I am also sceptical about the "quantitative correction factor for biased GOM and PBM data". The discussion in this review shows clearly that there will not be a one correction factor but many of them, depending on the sampling system configurations, ozone and humidity interferences, filter loadings, etc., which are only partly under retrospective control. In addition, how can we determine quantitative correction factors with GOM and PBM intercomparison results varying by several hundred percent. My first priority would be to get a decent agreement of GOM and PBM measurements in several multi-technique intercomparisons.

Introduction, 3rd paragraph: "Measuring speciated Hg in the atmosphere.." should be

preceded by some statement about the Hg species, their importance and occurrence.

Section 2.1.2 Lumex: The performance assessment here underrates, to my opinion, the potential of the instrument in several aspects:

a) The instability of the instrument is mostly due to temperature drifts. Temperature control of the sensitive parts of the instrument by the company has already brought substantial improvements. Were the measurements reported in the Supplement made already with the improved version?

b) A detection limit of 1 ng m-3 can be improved by signal averaging over a longer periods. If averaged over the sampling time of Tekran, a detection limit of a few tenths of ng m-3 can be achieved.

c) The instrument can be periodically calibrated using a permeation source such as used for internal calibration of the Tekran instruments. This is not available commercially but it can be done.

Section 2.1.3 Gardis: Measures total mercury if GOM and PBM get to the gold traps. It should be mentioned that Gardis amalgamates mercury twice, opposite to only once by the Tekran instrument. This might reduce some interferences such as passivation encountered when using the Tekran instruments.

Section 2.1.4 UMHERZ: The description needs more details about how TGM and GEM are measured. The reference Gustin et al. (2013) does not contain any information about the principle of the UMHERC instrument. Thus either a brief description is needed or a pertinent reference.

Section 2.1.5 DOHGS: The description of the instrument is poorly worded and misleading: The original KCl denuder removed only GOM but not PBM. The denuder was replaced by quartz wool which captures GOM and almost all PBM. To measure TGM in the second channel GOM and PBM are pyrolysed using quartz chips and later quartz wool. "pyrolysed quartz wool" does not make sense. The appraisal of the instrument

would also gain from a better wording. Because GOM +PBM usually represent only a few percent of TGM, the major problem is the uncertainty of the difference of two large numbers (TGM – GEM). I also think that sensitivity is a secondary issue. Primarily it is the precision of the large GEM and TGM concentration measurements which determine the uncertainty of their difference.

Section 2.1.6 Laser systems are essentially atomic absorption or fluorescence systems and as such measure only GEM. If GOM or PBM are to be measured, they have to be converted to GEM.

Section 2.2: I find the term "integrated" misleading because automated Tekran system also integrates over a period of at least 2.5 minutes. "Manual techniques" would be a better term because it would contrast these methods to the automated ones.

Section 2.2.1: Gold is the most frequently used and best studied preconcentration material and thus should be mentioned in the first place. It is known to collect GEM and GOM and as a plug of gold coated quartz wool also most of PBM. By converting GOM and PBM to GEM during the thermodesorption the measurements with gold represent TGM or even TM.

Desorption of GOM from carbon sampler probably needs recollection on gold or a pyrolyser for conversion to GEM detectable by AAS and AFS.

Section 2.2.2, Mist chamber for GOM: According to the description of the mist chamber by Stratton and Lindberg (1995) the sampled air goes directly into the chamber without any particle filter. Such technique would thus measure GOM + PBM. The same applies to the mist chamber used by Sheu and Mason (2001). Therefore, the title of this section is misleading.

Section 2.2.2, UNR active system for GOM: What does ". . . two in-series Teflon filter packs" mean? Teflon filters or Teflon holders of filters? Are these really made of Teflon or PFA?

Section 2.3: I agree with the statement that the GOM measurements are not calibrated but disagree with the same statement for PBM. If properly sampled, PBM on some substrate can be analysed by thermodesorption or digestion by a calibrated AAS or AFS instrument. The problems with PBM measurements are thus not related to calibration but to the sampling technique. No special calibration technique for PBM is needed as is not needed for the determination of any other element on particles.

Section 3.1: What do the authors mean by "covered" and "uncovered lines"? A protection against sucking in rain droplets belongs to a good laboratory practice and does not need to be mentioned.

There is a simple answer for the question in the title: if GOM quantitatively gets to the gold traps of Tekran and these are not passivated it will be measured. This should be mentioned at the outset.

The paragraph about the passivation of the gold surface is not clear. If the surface is passivated it should be also passivated to the same degree to Hg from the internal permeation device. This would lead to less precise but still accurate results. Please clarify. The sentence about the use of the pyrolyser is wrong. To avoid problems with the GOM transmission through the sampling line the pyrolyser has to be placed at the inlet of the sampling system. As such it would pyrolyse also PBM. That means that TM will be measured in this configuration, not TGM.

Section 3.2.1, page 3790, last paragraph: "..was collected in activated charcoal scrubbed air, which removes O3 and water vapour." It is the charcoal and not the air which removes O3 and water vapour. In addition, activated charcoal also removes all sorts of organic compounds which might interfere with GOM collection. Consequently, experiments of this sort are necessary but not sufficient.

Section 3.3, 2nd paragraph: "Known analytical challenges….temperature artifacts.." – if the authors mean temperature dependent GOM/PBM equilibrium than they should state it clearly.

Reading the discussion about the GOM breakthrough through the KCl denuder and its interference with the PBM measurements I wonder why very low PBM concentrations, frequently under the detection limit, are routinely being measured by Tekran systems. One would expect that the sticky GOM passing through the denuder will be at least partly captured by the PBM filter.

Section 5, 1st paragraph on page 3801: "a quantitative and trusted correction factor to apply for affected measurements" is to my opinion an illusion – see my comment to Abstract.

Section 6: In the title of this section I would replace "technical" by a more specific "analytical".

The list of "outstanding issues" reads as a shopping list. The issues should be ordered according to their importance to prevent this.

I would put the identification of the GOM and PBM chemical compounds on the first place because as the final oxidation products they are the keys to resolve the question of Hg chemistry. Secondly, if we know the compounds we can develop specific methods to generate test mixture for them. Thirdly, known physico-chemical properties of known substances will facilitate the judgment about their sampling and analytical artefacts.

On the second place I would put activities to achieve a decent agreement between measurements of each mercury species by several (at least two, preferably three and more) physico-chemically different techniques in intercomparisons using ambient and spiked air. Only then we can claim the results to be accurate. This crucial issue is not mentioned at all.

The issue of "A standard, field deployable calibration system" needs rewording. What we really need are systems to produce test atmospheres for study of sampling efficiencies and artifacts, conversion efficiencies, etc., and to carry out intercomparisons with spiked ambient air. The analysis itself is almost always based on AAS or AFS detection

which can be easily calibrated. This issue should be perhaps put on the third place.

The issue about "Improvements of the Tekran.." contains a statement that a pyrolyser is needed if TGM is to be measured. This is not correct because it has to be a pyrolyser at the inlet to prevent GOM losses in the tubing. Since such pyrolyser will also pyrolyse PBM, TM will be measured. The major improvement could be the development of a technique to measure RM, see next issue.

The statement that "the Tekran 1130/1135 system is configured. . ...is the best method to measure these two compounds" is at odds with the discussion in this review and should be deleted. I agree with the statement that RM measurements may be more accurate then separate GOM and PBM measurements – see my proposal for the introduction of the section 2. A technique for reliable RM measurements by Tekran should thus be developed. The rest of this issue about promising specific techniques and surrogates to correct for deficiencies only dilutes the message and should be deleted.

The issue about correction factors is to my opinion unattainable – see my comments to Abstract – and should thus be deleted.

The issue about the identifying the major reduction and oxidation pathways is to my opinion redundant. It is already covered by the issue about the identification of individual GOM and PBM compounds.

The issue about the passive sampling: Passive sampling is mentioned frequently in the text and this may lead to the impression that it may substantially contribute to the solution of the analytical problems discussed in this review. I think that the decisive answers such as the identification of the individual compounds will be delivered by active techniques. This should not detract from the role of passive techniques as a cheap alternative to expensive active techniques, once the analytical problems discussed in this review are solved.

Table 1: As mentioned before I would prefer a division between active and passive sys-

tems, with active ones perhaps subdivided between automated and manual. Detection limits depend on the sampling time and should be thus stated with it. Tekran 2537: with a pyrolyser at the inlet TM will be measured, not TGM. Lumex: 1 ng m-3 detection limit can be substantially lowered by signal averaging – see comment in the text. I disagree with Lumex being only "good for industrial applications". It has been successfully applied for aircraft measurements as well because it is fast. Please consider also other comments to Lumex.

3. Supplement

TGM vs GEM comparison: Soda lime is known to capture GOM. Consequently, only GEM can be measured with soda lime trap and a filter. Please correct! Does the sentence on lines 59-61 means that Tekran measures TGM or what does it mean? Please clarify.

Detailed discussion on the potential for different forms in the air of Florida: The authors probably mean "different compounds"? "These papers" are mentioned in the first sentence – which papers? The detailed discussion here does not mention one fundamental problem: the use of surrogate surfaces to estimate or measure dry deposition is questionable. According to Hicks (1986) "it is difficult to interpret results obtained by collection devices having surfaces different from nature". This reference is old but still valid. Consequently, surrogate surface techniques have been abandoned in almost all fields of atmospheric chemistry. Surrogate surfaces e.g. cannot measure bidirectional fluxes, such as have been reported for mercury (Lindberg et al., 1998; Zhang et al., 2009). The models usually consider bidirectional fluxes but have their specific parameterisation problems. Can such shaky ground carry the sophisticated discussion in this section?

Detailed discussion of the RAMIX data: This section is largely redundant because the results of RAMIX experiment were already published in a series of paper in Environmental Science and Technology. Only new insights, if there are any, should be

discussed here.

Detailed discussion of atmospheric chemistry: I do not see any new insights in addition to Hynes et al (2009). If it is so, this section can be deleted.

PBM detailed information: The sentence on lines 209 – 211 is not clear: if the first filter is the quartz fiber filter then please write it so to avoid misunderstanding. "The latter" probably means KCl-coated quartz fiber filter but it is not clear what it is comparable to – TGM, GOM, PBM measurement?

If DOHGS system uses quartz wool to capture GOM then it is almost certain that quartz fiber filter will capture at least some GOM.

Details on the sampling configuration in Weiss-Penzias et al. (2003): One important detail is omitted: the configuration also contained a soda lime trap to prevent gold cartridge passivation. Soda lime removes GOM.

4. Editorial comments

Page 3779, line 24: " …a difficult and technical undertaking" What do the authors mean by the word "technical"? All measurements are technical undertakings.

Page 3781, line 15: The temperature of 350°C for thermodesorption of Hg from gold surface seems to me to be too low. Please check.

Page 3782, line 6: The correct wording would be: "The Lumex instrument uses atomic absorption spectrometry with Zeeman background correction."

Page 3783, line 7: Please state here that GOM + PBM = RM.

Page 3784, line 6: Please be more specific: "The former system is a … . and the latter operates on…"

Page 3789, line 4: "…mentioned that the passivation…"

Page 3789, line 21: "…interference in the collection" probably better

Page 3790, line 3: "where" without capital letter

Page 3790, line 17: "These data demonstrate that…"

Page 3792, line 17: "..indicated that

Page 3792, last paragraph: Here suddenly RM, i.e. GOM + PBM, appears in a chapter about GOM intercomparisons. Is it correct?

Page 3793, line 15: Again RM collection efficiency appears in a chapter about PBM. Please check.

Page 3794, line 7: "polarizability" – probably means "polarity"?

Page 3794, line 18: "rejuvenatable"? – does it mean "regenerated" or simply "freshly cleaned"

Page 3795, line 10: "it is likely that…"

Page 3795, line 14: "If you assume that.."

Page 3796, line 15: "It is possible that this oxidant is N2O5… . "

Page 3801, line 1: Measurements may be erroneous, models are usually not in the same sense as measurements. Models may deviate from reality by unsuitable grid sizing, subscale process parameterisation, missing processes, erroneous reaction rate constants, etc., but mostly not by computational errors. Please find a more suitable word for "model errors".

Page 3801, line 26: ppq are "mixing ratios", not "concentrations"

Supplement, line 72: "This indicates that at times…"

Supplement, line 196: "…that PBM had a bimodal size distribution"

5. References:

Aas, W (ed.).: Data quality 2004, quality assurance, and field comparisons,

EMEP/CCC-Report 4/2006, NILU, Kjeller, Norway 2006.

Gustin, M.S., Huang, J., Miller, M.B., Peterson, C., Jaffe, D.A., Ambrose, J., Finley, B.D., Lyman, S.N., Call, K., Talbot, R., Feddersen, D., Mao, H., and Lindberg, S.E.: Do we understand what the mercury speciation instruments are really measuring? Results of RAMIX, Environ. Sci. Technol., 47, 7295-7306, 2013.

Hicks, B.B.: Measuring dry deposition: Re-assessment of the state of the art, Water, Air Soil Pollut., 30, 75-90, 1986.

Lindberg, S.E., Hanson, P.J., Meyers, T.P., and Kim, K.-H.: Air/surface exchange of mercury vapor over forests – the need for a reassessment of continental biogenic emissions; Atmos. Environ. 32, 895-908, 1998.

Sheu,G.-R., and Mason, R.P.: An examination of methods for the measurements of reactive gaseous mercury in the atmosphere, Environ. Sci. Technol., 35, 1209-1216, 2001.

Stratton, W.J., and Lindberg, S.E.: Use of a refluxing mist chamber for measurements of gas phase mercury(II) species in the atmosphere, Water Air Soil Pollut., 80, 1269-1278, 1995.

Zhang, L., Paige Wright, L., Blanchard, P.: A review of current knowledge concerning dry deposition of atmospheric mercury, Atmos. Environ., 43, 5853-5864, 2009.

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