

## ***Interactive comment on “Programmable thermal dissociation of reactive gaseous mercury – a potential approach to chemical speciation: results from a field study” by C. Tatum Ernest et al.***

**Anonymous Referee #2**

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### **1 General Comments**

The manuscript describes the use of thermal desorption technique in order to try to gain an insight into the chemical composition of the oxidised mercury compounds which are collected when using denuder sampling techniques. Atmospheric oxidised Hg is fundamental in the cycling of Hg, because oxidised Hg makes up the major part of Hg deposited (both dry and wet deposition) from the atmosphere to terrestrial and aquatic ecosystems. Therefore understanding the chemical composition of the species which are sampled on denuders and often simply referred to collectively as RGM (Reactive Gaseous Mercury) is a pressing research objective. The lack of knowledge of the na-

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ture of RGM is one of the major obstacles in understanding the atmospheric Hg cycle and in modelling the atmospheric dispersion, chemistry and deposition of Hg. The manuscript's objective therefore addresses an extremely relevant scientific question. Unfortunately what it does not do is provide any concrete answers. The field campaign measurements and subsequent analysis are described in the manuscript as a 'proof of concept' experiment, which is not a problem, however the lack of conclusions is. An abstract which concludes with the sentence "*The PTD profiles from these samples were compared with PTD profiles of HgCl<sub>2</sub>*", already gives the impression that the concept was not proved. In fact the abstract is lacking in results or conclusions.

Although the manuscript describes a novel approach to an important problem, and presents an imaginative field measurement campaign which addresses a relevant issue, namely the speciation of Hg in coal fired power plant plumes, the manuscript fails to reach substantial conclusions (point 3, of the manuscript review criteria). The point being 'substantial', the Conclusions state

*"The profiles of the stack and plume samples are consistent with HgCl<sub>2</sub> being the chemical form of the sampled RGM".*

While this adds weight to the generally held opinion that it is indeed HgCl<sub>2</sub> which is emitted from coal fired power plants, it is difficult to describe it as a substantial conclusion. It is also the only conclusion, and comes with a caveat regarding the fact that HgCl<sub>2</sub> and HgBr<sub>2</sub> are indistinguishable using this technique.

### **2 More Specific comments**

#### **2.1 Concerning the References**

There really are very few references. A lot of work on Hg in Florida has been carried out over the past 10-20 years but no mention of this made (the University of Michigan School of Public Health and more recently the University of Nevada, Reno, have been

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involved). This is not referenced.

There are a number of recent articles discussing the efficiency of KCl denuders to sample RGM (and possible problems associated with them when O<sub>3</sub> is present in high concentrations). Some alternative methodologies are starting to be used. These are not mentioned.

Some recent modelling studies have lent weight to the idea that although a high proportion of total Hg present in the stack is oxidised, this proportion is reduced dramatically by reduction processes in the plume itself so that the net emissions are higher in Hg<sup>0</sup> than most emission inventories suggest. This is not mentioned either.

I have made a short list of some examples at the end of my comments.

There is no mention of the global importance of anthropogenic Hg emissions, or the upcoming (at the time of submission) Minamata Convention, or indeed the significant proportion of Hg emissions which derive from coal combustion. As coal combustion is a major energy source in a number of economies which are experiencing sustained growth, perhaps some comment would have been appropriate.

Of the references that are cited one is in preparation, and therefore at the time of my writing unavailable, one is a PhD thesis which is available on the internet however given that it is nearly 300 pages long, some indication of which chapter and section the authors are referring to would have been useful. Another of the references, Landis et al., 2009, appears to be a conference presentation, but I was unable to find the proceedings.

Some example references Kos et al. (2012); Lyman et al. (2010); Lyman and Jaffe (2011); Sexauer Gustin et al. (2012); Sherman et al. (2012); Zhang et al. (2012a,b)

## 2.2 Experimental description

The section describing the sampling and the different types of tubular denuder employed becomes a little confusing at certain points. I would suggest a summary

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table giving the number and denuder type used for the laboratory calibration profiles (with flow rates), and also for the different stack, "close-in" and "further-out" samples which were taken. If this were somehow combined with which samples were analysed by using "oven 1" and which using "oven 2" the description could be shortened considerably and the whole would be easier to follow. For example towards the end of section 2.3 the authors state that a total of 20 uncoated tubular denuder samples were obtained, but, were these quartz of Pyrex, etched or unetched? I think sections 2.3 to 2.8 could be reduced to about half their present length and certainly more clear and precise than in the present form.

## 2.3 Differences between these results and those described in the Thesis

There seems to be some contradiction between the results obtained here and those presented in the PhD Thesis. The use of uncoated denuders is described in the thesis in section 7.4.5; here problems were encountered when ramping the oven temperature for the typical annular denuder (usually used with a KCl coating), because of uneven heating, due to the shape of the denuder. Thus an uncoated Pyrex tube is used instead of the annular denuder. The results obtained show a clear difference in the thermal decomposition profiles of HgBr<sub>2</sub> and HgCl<sub>2</sub>. Section 3.5 of the manuscript clearly states that the PTD profiles of the compounds are identical, when using a constant temperature ramp between 50 and 500C. Why not use a temperature ramp that can distinguish between them as in the thesis? It also appears from figure 7.24 of the thesis that the first evidence of thermal decomposition of both compounds was observed above 200C. This does not appear to tally with the profiles from the "oven 1" and "oven 2" profiles in the manuscript, where the onset of decomposition appears to occur at a lower temperature. I think if one of the author's own references appears to contradict the results presented, then some explanation is required.

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### 3 Summary

The experience gained in this study appears to have led to a recognition of some of the difficulties in using this technique, and also to an understanding of how the choices of type of denuder (etched or not), and heating cycle can influence the results. I imagine that in future a note of the direction of the gas flow during sampling will be made as this seems to be important too. However, this represents part of the learning curve in a new technique, and as such deserves mention in the experimental section of an article which describes the 'perfected' or 'improved' implementation of the technique. Such an article appears to be in preparation and a foretaste is given in section 3.5, and in the last two figures of the supplementary material. I have serious doubts that the work described here warrants publication as an article in its own right.

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