Atmos. Chem. Phys. Discuss., 15, C8824–C8828, 2015
www.atmos-chem-phys-discuss.net/15/C8824/2015/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Tropospheric mercury vertical profiles between 500 and 10 000 m in central Europe" *by* A. Weigelt et al.

Anonymous Referee #2

Received and published: 2 November 2015

Review of ACP-2015-551 "Tropospheric mercury vertical profiles between 500 and 10,000 meters in central Europe"

Overview: This manuscript reports vertical profile measurements of atmospheric mercury and other trace gases over Europe during August 2013. This study is important given that the scientific community has relatively little data describing the vertical distribution of mercury (and mercury species) in the atmosphere, which plays a very important role in determining the transport and cycling of mercury. That being said, there are several substantial limitations to this dataset that the authors do not adequately discuss, and several assumptions that they make which need significant clarification before this manuscript could be considered for publication.

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General comments:

First, the vertical profiles are comprised of only 5-minute long horizontal flight sections (at least seven sections per flight). However, the mercury analyzers only have a temporal resolution of 2.5 minutes. As such, while the flights cover altitudes ranging from the boundary layer into the lower free troposphere (3000 m asl), there are only 2 mercury measurements recorded at each altitude. The authors assume that these two data points are representative of the concentration at the measurement altitude, but with only n=2 this assumption seems highly questionable. The authors do not discuss the limitations or uncertainty associated with this small sampling frequency at any point in the manuscript. For example, are the authors certain that the analyzers had fully equilibrated to the new sampling altitude before the first of these two measurements began? How does this sampling method compare to the other published vertical profiles that are cited throughout the manuscript? These kinds of issues must be discussed and the authors need to address how representative these 2 measurements per altitude segment actually are.

Second, the authors report GOM measurements collected with KCl-coated denuders. However, there are now numerous papers discussing recovery issues with KCl-coated denuders and possible interferences, resulting in potentially low recoveries of GOM (e.g. Lyman et al., 2010; Gustin et al., 2013; McClure et al., 2014; Jaffe et al., 2014). If the authors are going to present GOM data collected with KCl denuders they need to acknowledge these studies and discuss their data in the context of them. That being said, the GOM data they do present consists of one denuder for a single vertical profile. Thus there is a single GOM measurement for each profile. This information does not seem to be very informative given that several studies have reported higher concentrations of GOM in the free troposphere than in the boundary layer. A single denuder sample combines the boundary layer and free tropospheric concentrations into a single measurement. Thus is it highly unclear what the authors aim to show with this information. Consequently I suggest they not include the GOM data in this

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manuscript, or at least minimize their discussion of these results as they are not very meaningful.

Also with regards to the mercury sampling methods, it is not entirely clear what the TGM measurements actually represent. They offer no information to prove that GOM or PBM were effectively transported through the unheated inlet and sample line (which could have resulted in loss of oxidized Hg compounds to the walls of the tubing or inlet). They also did not include any mechanism for converting these forms of oxidized mercury to the elemental form that the Tekran analyzer quantifies. Thus there is no information or data to confirm that in fact this measurement channel truly quantified TGM and not just GEM. The authors need to address this more fully. In contrast, for the GEM analyzer they used a quartz wool trap to remove oxidized mercury compounds which has been published in other studies as an effective method (Lyman and Jaffe, 2012) but was also shown to liberate GOM at high WV mixing ratios (Ambrose et al. 2013) – the authors should discuss whether this effect may have impacted their GEM measurements at any point during boundary layer measurement segments. Also, if the TGM measurements are in fact TGM, why not compute the difference between TGM and GEM measurements on each flight as an additional way of quantifying oxidized Hg (GOM + PBM)?

Lastly, with respect to other airborne Hg measurements and vertical profiles of Hg species, the authors should also review and cite the recent manuscript by Shah et al. (ACPD, 2015).

Specific comments:

Abstract: At the start of the abstract the authors should address WHY vertical profiles of atmospheric Hg are needed.

Page 3, Lines 14-15: “All known vertical profile measurements prior to 2009. . .” (Here should also discuss Shah et al., 2015)

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Page 4, Lines 6-7: Only 4 vertical profiles are actually discussed in the manuscript. The fifth will reportedly be discussed in a different manuscript.

Page 5, Lines 30-33: Is it true then that the inlet and sample lines were not heated at all? This is different from other mercury sampling methods including those from aircraft. Could any mercury have been lost to the walls of the inlet or sample tubing?

Page 6, Lines 23-25: See above for concerns about GOM transmission. What evidence or citations could be offered to be more conclusive about GOM transmission through the sample lines?

Pages 6-7, Lines 32 and 1: Here and for all other measurements the authors need to discuss measurement precision and uncertainty in much more detail. What uncertainty values do they associate with each measurement and how were these values obtained?

Page 7, Line 10: what does "high temporal resolution mean"? What was the actual sampling frequency for each measurement?

Page 7, Lines 11-18: This discussion needs references.

Page 7, Lines 17-18: Later the authors refer to forward trajectories too but they are not mentioned here. How do they reconcile the combination of forward and backward trajectories?

Page 10, Line 3: Earlier it was stated that the forthcoming manuscript about the profile downwind of the power plant is being organized by Weigelt et al. (Page 4, Lines 27-28) but here it says Bieser et al.

Page 10, Lines 14-18: The evidence offered is not conclusive enough to confirm that the two aircraft, flying at very different altitudes, sampled the same air mass. Only wind direction is cited as evidence. It seems that the authors could compare the other trace gas measurements and meteorological measurements from the two aircraft to offer more support for this assumption. Also, are the authors using CARIBIC measurements

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just from August 21 (the day when the ETMEP-2 profile over Leipzig took place) or are they using data from August 21-23? More details on how the CARIBIC and ETMEP-2 data were combined are needed.

Page 11, Lines 6-7: The statement that "no vertical GEM gradient is apparent in the entire FT over Central Europe" seems like a very strong statement to conclude just from one vertical profile. This statement should be revised and rephrased based on the information actually available from this study.

Page 12, Lines 8-9: Concentrations of 3.6 pg/m3 and 7.8 pg/m3 are very small (even for GOM denuder measurements) and should not be referred to as "somewhat elevated".

Page 12, Lines 16-32 and Page 13 Lines 1-2: Here is one place where more discussion of the limitations of GOM denuder sampling should be provided. As stated above, a single GOM concentration representing an entire vertical profile is not a very useful piece of information. Also, the concentrations observed here, while comparable to those measured by Brooks et al. (2014) are much lower than those reported by Lyman and Jaffe (2012) or by Shah et al. (2015) in the free troposphere. This needs much more discussion (or, as previously suggested, the GOM denuder measurements could be excluded entirely as they do not add much to the overall understanding of the vertical distribution of Hg species).

Figure 1: This figure is impossible to read in black and white. A different map should be used which can be easily interpreted either in color or in grayscale.

Figures 3-6: What do the error bars represent for each data point? As previously mentioned, a discussion of uncertainty analysis is needed in the Methods section.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 28217, 2015.