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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.

A. Weigelt et al.

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Reply to comments of anonymous Referee #2

We'd like to thank Referee #2 for the fitting and detailed comments. However, we wonder about the page and line numbers given in the review, because this seems not to be related to the ACPD layout of our manuscript. However, we found the sections the referee's general and specific comments were related to and reply to them as follows. Please note, given page and lines are related to the discussion paper layout.

Comment of Referee #2:

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 tempo-

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ral 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.

Reply:

Yes, Referee #2 is correct - we performed only two measurements at each flight level of each profile plus one measurement during each flight level change and the whole profile took almost an hour. We have done so to quickly capture the transitory situation. If we would have sampled longer at each flight level, the uncertainty introduced by PBL dynamics might impair the representativeness of the vertical distribution.

We agree that a short measurement gives only a snapshot of the current situation at a certain location. The two measurement points at a certain flight level represent an average over a flight distance of 21.6 km (300 sec with 72 m/s). The concentrations measured during the change of the flight level (stars in Fig. 3-6) represent an average of the air between two flight levels and always match the constant level flight concentrations. As we found the same concentration for each altitude step in each region we measured (except the difference between boundary layer and free troposphere) and the measured PBL concentrations match the northern hemispheric background concentrations of 1.5 - 1.7 ng m-3 (Lindberg et al., 2007), we believe that our measurements are representative for background conditions in central Europe. The good

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agreement to the CARIBIC measurements in the free troposphere further supports the assumption that our measurements are representative for a larger area. Concerning the technical question to the equilibration of the analysers:

As described in the manuscript we used pressure controller (Bronkhorst) to stabilize the pressure in the optical cell of the instruments. Temperature in the cabin was quite constant and so during flight level change only the measurement flow has to adjust to the new condition. Usually this takes only few seconds. In addition, the sampling flow rate is integrated over the sampling period and the mercury concentration is calculated with this integral. Consequently, any flow rate variations are considered for.

To clarify this we added the following text at different sections of the manuscript:

Page 28223 line 1: "...each vertical profile took 50 minutes, being representative for the transitory situation at a certain measurement location."

Page 28226 line 13: "...This eliminated the known pressure dependence of the response signal (Ebinghaus and Slemr, 2000; Talbot et al., 2007). During profiling the temperature in the cabin was relatively constant. Sampling flow rate responds to changing altitude within a few seconds and flow rate fluctuations are accounted for by the integration of flow rate over the sampling interval."

Page 28233 line 5: new section: "Although the profile measurements were carried out within a short period, we believe that they are representative for summer conditions in central Europe. We measured similar concentrations at all flight levels of all measurement locations (except the above discussed PBL-FT difference) and they agree with the well established northern hemispheric background concentration of 1.5 - 1.7 ng m-3 (Lindberg et al., 2007)."

The section starting on page 28233 line 6 was deleted due to the second general comment of Referee #2

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

Reply:

We had intensive discussions with a Norwegian and an Italian expert working on emission inventories. Both stressed that our GOM measurements are of high relevance for emission inventories. However, because the GOM measurements are not the main focus of this paper and under consideration of the justified criticism to the uncertainty of denuder GOM measurements resulting from the recent publications, we decided to remove the GOM measurement results from the manuscript. Eventually, our measurements of higher GOM in the FT compared to the PBL only confirm the results of recent publications.

In the manuscript all GOM related text as well as Table 3 were deleted.

Comment of Referee #2:

Also with regards to the mercury sampling methods, it is not entirely clear what the

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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)?

Reply:

As mentioned in our reply to the first comment of Referee #1, the instrument precision does not allow us to estimate/calculate GOM concentration below 200 pg m-3 from the difference between TGM and GEM. Other limitations of the difference approach have to be considered as well. Particle bound mercury (PBM) was not measured, because with an inlet system optimized for trace gases, it is very difficult to sample quantitatively aerosol particles (Brenninkmeijer et al., 2007: ACP 7, 4953–4976; Slemr et al., 2016 AMTD; 1-25; doi:10.5194/amt-2015-376). Aerosol particles entering the inlet system are removed by the quartz wool trap and/or the PTFE filters in front of the individual Tekran inlets.

As written on page 28224 lines 3-6, the inlet system was equipped with a heating system to prevent icing, but it was not switched on. In Figure 2b the heating system was not show, so we modified this figure for the revised version. With respect to GOM

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transmission to the instrument we point out that in the PTFE coated inlet system only the core flow (without any wall contact) was flown through a PFA sample line towards the instruments. The flow rate in the 2.5 m long 7.7 mm wide (inner diameter) PFA sample line was 25 l min-1 and therefore the sample air residence time below 0.3 seconds. An international field intercomparison (Ebinghaus et al., 1999, Atmos. Env. 33, 3063-3073) has concluded that under these conditions the measured value represents TGM. The capture of GOM by the gold traps and its conversion to GEM during the thermal desorption is discussed by Slemr et al. (2016 AMTD; 1-25; doi:10.5194/amt-2015-376).

We clarified this in the manuscript as follows:

Figure 2b: The figure was modified to indicate the heating system, too. In the caption the phrase “PTFE coated” was added.

Page 28223 Line 19: “. . .line starts, taking only the core flow ore flow without contact with inlet surface.”

Page 28224 Line 8: “. . .manifolds to instruments; residence time < 0.3 seconds)”

Page 28225 Line 1-5: “The Tekran 2537B analyser was operated as backup instrument without a quartz wool trap. The PFA and PTFE made gas inlet and tubing system was not tested for GOM transmission efficiency. However, the residence time of the sampled air in the PFA tubing connecting the inlet and the instruments is shorter than 0.3 seconds. An international field intercomparison (Ebinghaus et al., 1999) has concluded that under such conditions mercury measurements represents TGM (TGM = GEM + GOM). The capture of GOM by the gold traps and its conversion to GEM during the thermal desorption is discussed by Slemr et al. (2016). Consequently, we believe our Tekran 2537B measurements approximate TGM concentrations with an uncertainty of 12.5%. The uncertainty. . .”

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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).

Reply:

The Shah et al., (2015) paper is a very important contribution for knowledge mercury cycling and speciation in the troposphere, however it was not available when we submitted this manuscript. In the revised version the Shah et al. paper is referenced and their averaged vertical profile (Fig. 2a) is included for comparison in Fig. 7 of our manuscript. The text on page 28221 lines 10-15 was changed as follows:

"... In 2014 Brooks et al. (2014) reported speciated mercury vertical profiles measured over USA over a period of almost one year from August 2012 to June 2013. Recently, Shah et al., (2015) published total Hg (THg) and oxidized Hg (Hg(II)) vertical profiles measured over the south eastern USA between 1 June and 15 July 2013. The August measurement from Brooks et al., (2014) and the averaged data from Shah et al., (2015) are shown in Fig. 7 as well. Except for large vertical GEM gradients reported by Radke et al. (2007) and in April, May and June by Brooks et al. (2014), no pronounced GEM vertical gradients were observed by other researchers in other months (Swartzendruber et al., 2009; Brooks et al., 2014, Shah et al., 2015). Usually..."

The caption to Fig. 7 was updated as follows: "...Data in grey represent the August measurement from Brooks et al., (2014) and the averaged data from Shah et al., (2015)..."

Specific comments:

Comment of Referee #2:

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

Reply:

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The start of the Abstract was changed to: “The knowledge of the vertical distribution of atmospheric mercury (Hg) plays an important role in determining the transport and cycling of mercury. However, measurements of the vertical distribution are rare, because airborne measurements are expensive and labour intensive. . . .”

Comment of Referee #2:

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

Reply:

done (see reply to general comment 4 of Referee #2)

Comment of Referee #2:

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.

Reply:

This is correct, a manuscript is in preparation and will be submitted soon. This was already mentioned in the discussion paper (page 2822 lines 21-23): “Here we present and discuss the vertical profiles over Iskraba, Idrija, Leipzig, and Waldhof. The Lippendorf vertical profile downwind the coal fired power plant will be discussed in a separate paper (Weigelt et al., 2015c).”

Comment of Referee #2:

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?

Reply:

We had a heating system for the inlet and the telescope tube to prevent icing (Fig

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2b was updated to indicate this). Because the measurement flights were carried out in summer at altitudes below 3000 m a.s.l., it was not necessary to switch it on (cf. temperature profiles in Figs.3-6).

As already explained in detail in the reply to the general comment 3 of Referee #2, even we did not tested our inlet system for Hg transmission efficiency we believe we did measure TGM, because:

a) all parts which had contact to measurement air was made of or coated with PTFE and PFA,

b) in the inlet only the core flow was taken,

c) the residence time in the PFA tube was less than 0.3 seconds,

d) an international field intercomparison (Ebinghaus et al., 1999, Atmos. Env. 33, 3063-3073) has concluded that under these conditions and under consideration of the instrumental limitation the measured value represents TGM.

The text in the manuscript was changed as indicated in the reply to the general comment 3.

Comment of Referee #2:

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?

Reply:

see detailed reply to the specific comment above and general comment 3

Comment of Referee #2:

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 uncer-

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tainty values do they associate with each measurement and how were these values obtained?

Reply:

Page 6-7, lines 32 and 1 (submitted file) corresponds to page 28225 lines 12-13 in the discussion paper layout and was deleted in the revised version due to the second general comment of referee #2.

Measurement uncertainty of the mercury analyser has been calculated by Weigelt et al., (2013) using two different approaches according to ISO 20988 type A6 and ISO 20988 Type A2 to be 12.5 and 12%, respectively. This uncertainty complies with the quality objective of the EU air quality directive 2004/107/EC. The instrumental setup in the aircraft was almost identical and therefore we expect the uncertainty to be very similar. This explanation has been already included in the revised version due to the first minor technical issue of Referee #1.

According to the uncertainty of the other parameters we added the following text to page 28225 line 22:

" . . .high temporal resolution. Uncertainties of these parameters were calculated according to the individual instrument uncertainty given by the manufacturer and the calibration gas accuracy (CO, O3, SO2, NO) and are summarised together with instrument details in Table 2. CO and SO2 can be. . .."

In Table 2 for GEM, GEM+GOM and CO we changed the given uncertainty from absolute values to % of reading, to be comparable to the other trace gases.

Comment of Referee #2:

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

Reply:

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Temporal resolutions for all individual measured parameter are summarized in Table 2. We added “(cf. Table 2)” to that sentence.

Comment of Referee #2:

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

Reply:

Following references have been added:

Parrish et al., 1991; Klemp et al., 2002; Jaffe et al., 2005; Slemr et al., 2014; Zahn and Brenninkmeijer, 2003; Ambrose et al., 2015; Weigelt et al., 2016 (this was Weigelt et al., 2015c in the discussion paper); Spencer and Braswell, 1996; Slemr et al., 2016

The sentence “A ratio of NO/NO2 provides information about the age of polluted air masses.” was replaced by “Increased NOx (NO + NO2) mixing ratio can indicate combustion plumes (Ambrose et al 2015; Weigelt et al., 2016), too.”

Comment of Referee #2:

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?

Reply:

Forward and backward trajectory calculation has been carried out according to the CARIBIC scheme (http://www.knmi.nl/samenw/campaign_support/CARIBIC/).

The Manuscript page 28225 line 28 to page 28226 line 2 has been changed as follows: “. . . For additional information model meteorological data like potential vorticity, equivalent potential temperature, relative- and specific humidity, cloud cover, cloud water content, 3 dimensional wind vector, as well as five day backward and two day forward trajectories has been calculated every 150 s along the aircraft flight tracks according to

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the CARIBIC scheme (http://www.knmi.nl/samenw/campaign_support/CARIBIC/). . .”

Comment of Referee #2:

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.

Reply:

This was an error in the submitted manuscript and was already corrected during the proof reading process for the ACPD file. Weigelt et al., 2015b (now 2016) is correct.

Comment of Referee #2:

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 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.

Reply:

In the section thereafter on page 2830 lines 12-14 it is written, that the trace gases CO, O3, and NO measured aboard CARIBIC match the ETMEP-2 measurements very well, which supports the notion that the same FT air mass was sampled during the CARIBIC and ETMEP-2 flights. The difference was only 20 ppb or 20% for CO, 0,2 ppb or < 1% for O3, 0,05 ppb for NO (difference in % is not given because both values are close to zero). Because we do not want to forestall this result, in the section mentioned by Referee #2 we argued with the meteorological conditions and backward- and forward trajectory calculations. In the manuscript we clarified this as follows:

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Page 28229 line 17: ". . .supplement). As it will be shown below with the discussion of Fig. 5, the trace gases measured aboard both aircraft match very well, which supports the notion that the same FT air mass was sampled during the CARIBIC and ETMEP-2 flights. This. . . "

Page 28230 lines 11-14: ". . .Furthermore the other trace gases measured on both aircraft match very well, too. The difference was only 20 ppb or 20% for CO, 0,2 ppb or < 1% for O3, and 0,05 ppb for NO (difference in % is not given because both values are close to zero). As indicated above, this agreement further supports the notion that the same FT air mass was sampled during the CARIBIC and ETMEP-2 flights. . .."

Concerning the second part of the comment: We combined CARIBIC (21 to 23 August) and ETMEP (23 August) data by analysing them independently and plotting them in the same graph, as both measurements are related to the same standard conditions (STP: p= 1013 hPa, T=273 K). In the manuscript we clarified this as follows:

Pahe 28229 lines 20-21: ". . .For this extension only free tropospheric CARIBIC measurements from 21 to 23 August 2013 east of 0°E are additionally plotted in Fig. 5, providing a vertical profile extending from 600 to 10500 m a.s.l... . ."

Caption to Fig. 5: ". . . TGM and GEM concentrations form ETMEP-2 and CARIBIC measurements are given at standard conditions (p=1013.25 hPa, T=273.15 K)."

Comment of Referee #2:

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.

Reply:

The reviewer is correct; the sentence on page 2823 lines 10-11 has been rephrased to: ". . . This means that the measurements carried out in this study (August 2013) revealed

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no vertical GEM gradient in the entire FT over Central Europe. . . .”

Comment of Referee #2:

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”.

Reply:

The sentence has been deleted due to the exclusion of the denuder sample results.

Comment of Referee #2:

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).

Reply:

This section has been deleted due to the exclusion of the denuder sample results.

Comment of Referee #2:

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.

Reply:

Figure 1 was changed to be interpreted either in colour or in grayscale

Comment of Referee #2:

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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.

Reply:

A discussion explaining the error bars was implemented in the method section (see reply to third general and sixth specific comment of Referee #2). In Figures 3-6 GOM was removed due to exclusion of the denuder samples.

Finaly we like to point out that the wording of the whole text was improved by a native speaker.

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

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