Anonymous Referee #1

Received and published: 17 November 2015

First of all we thank Referee #1 for the very helpful comments and recommendations. We reply to the individual comments as follows:

Comment of Referee #1:
Minor technical issues: Pg 28225, top - It seems to me that the difference between TGM as measured by the 2537B and GEM as measured by the 2537X was low in all cases, but these data are not presented. Does the difference between these two measurements accurately represent GOM? What is the comparison between TGM-GEM and GOM as measured by the denuders? How accurate are the authors' estimation of GOM concentrations? I feel a bit more discussion should be devoted to this.

Reply:
It is possible, in principle, to determine the GOM concentration from the difference of TGM and GEM. But this can be expected to work well only for very cool and dry conditions like in Antarctica and the upper troposphere/lower stratosphere as shown by Temme et al., 2003 (ES&T 37, 22-31), Slemr et al., 2009 (ACP 9(6) 1957-1969), and Slemr et al., 2016 (AMTD; 1-25; doi:10.5194/amt-2015-376). Furthermore, by subtracting two big numbers (TGM, GEM) to get a small number (GOM) causes a uncertainty much higher than the expected value: as the Tekran instruments have a uncertainty of 12.5% or ~0.15 ng m^{-3}, the resulting uncertainty for GOM from the difference method would be ~200 pg m^{-3} (Gaussian error propagation) at an expected concentration of 2 to 100 pg m^{-3}. We decided, therefore, not to calculate GOM from the difference of the two Tekrans but taking denuder samples to get a rough idea of the GOM concentration. Due to critical comments of Referee #2 and as the focus of this paper are the vertical profiles and the found significant difference between the planetary boundary layer and the free troposphere, we decided to remove the results of the denuder samples. Therefore, we delete the text on page 28225 line 5 to 18. To clarify that for our measurements it is not possible to obtain GOM concentration from the difference method and because of a comment from Referee #2 we modified the text starting on page 28225 line 1 to:
"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 has been calculated by Weigelt et al. (2013) using two different approaches according to ISO 20988 type A6 and ISO 20988 Type A2. 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. Calculating GOM concentrations from the TGM and GEM difference (Temme et al., 2003a; Slemr et al., 2009; Lyman and Jaffe, 2011) is limited by its uncertainty (~150 pg m^{-3}) which is larger than the expected GOM concentrations (few tens of pg m^{-3}). Therefore, GOM concentrations are not presented."

Comment of Referee #1:
Pg 28228, line 15 - the authors state the differences in the means are significant but no p-value is given.

Reply:
For this and all other profiles the calculated significance level for the difference of PBL and FT was > 99.9%. In the revised version we give the p-values.

Comment of Referee #1:
Pg 28230, line 19 -"with the top" is an awkward phrase

Reply:
This sentence was changed to: "Since this profile was measured in the late morning (08:15 to 09:15 UTC; 10:15 to 11:15 local time), the PBL was found to be with 1750 – 1850 m a.s.l. rather shallow when compared to the previous profiles."

Comment of Referee #1:
Pg 28232, line 16 - this phrase begins awkwardly. The word "opposite" should be changed to "in contrast to"

Reply:
done

Comment of Referee #1:
Pg 28232, line 21 - if there is a clear jump in the FT to lower GEM concentrations, what does this say about the relative lifetime of GEM in the FT vs. the mixing time of the PBL–>FT. Would these observations suggest a shorter lifetime for GEM in the FT? Also, where does the missing Hg go? If GEM in the FT is _200 pg m3 lower than in the PBL and yet GOM is only _20 pg m3 at the top of the PBL, the balance must go somewhere or not all forms have been measured. Please comment.

Reply:
As shown by Murphy et al., 2006, 2007 (ES&T, 40(10), 3163–3167, 2006; JGR, 112(D4), D04203, 2007), oxidized mercury has the tendency to attach to small particles. As we did not measured particle bound mercury on ETMEP-2, we cannot do a mass closure.
However, the observed difference between PBL and FT does not originate from different life time and chemistry, but from mercury emissions on the ground and from the PBL dynamics. Mercury is emitted to the PBL by various sources. The PBL is somewhat decoupled from the FT due to dynamic processes like friction and convection processes (Stull, 1988). Therefore, the exchange between PBL and the FT is inhibited which results in a gradient between PBL and FT with higher concentrations in the PBL. The same applies for other gases such as CO and SO_2 (Figures 4 – 6) which are emitted on the ground. Currently we are preparing another manuscript dealing with measurements downwind a coal fired power plant. Beyond others, in this manuscript it will be shown that the plume of the power plant, containing elevated mercury concentration, is captured below the PBL top due to a small temperature inversion.
Further dynamically caused Hg gradients can be observed at the crossover from the troposphere to the stratosphere (tropopause inhibit air exchange from troposphere to stratosphere and stratospheric mercury concentration is lower; Slemr, et al., ACP, 9(6),

1957–1969, 2009; Lyman and Jaffe, Nature-Geos., 5(2), 114–117, 2011.) and from the northern to the southern hemisphere where the ITCZ acts as a dynamic barrier (Slemr et al., 1985 Atmos. Chem., 3(4), 407–434; Temme et al., 2003 AE, 37, 1889–1897).
We explained this in revised version as follows:
"… The sharp gradient at the PBL top is probably caused by atmospheric dynamics. Mercury is emitted to the PBL by various sources (Pirrone et al., 2010; Song et al., 2015). The PBL is somewhat decoupled from the FT due to dynamic processes like friction and convection processes (Stull, 1988). Therefore, the exchange between PBL and the FT is inhibited creating a gradient between PBL and FT with higher concentrations in the PBL. The same applies for CO and SO_2 (Figures 4-6) which are also emitted on the ground. Other dynamically caused mercury gradients can be found at the tropopause which inhibits exchange from the upper troposphere to the lower stratosphere (Slemr, et al., 2009; Lyman and Jaffe, 2011), and at the inter-tropical convergence zone (Slemr et al., 1985; Temme et al., 2003b) which inhibits transport from northern to southern hemisphere."

Anonymous Referee #2

Received and published: 2 November 2015

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, changes to the manuscript text are marked with green letters; 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 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.

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 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

Comment of Referee #2:
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 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 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…"

Comment of Referee #2:
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:
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 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 uncertainty 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, O_3, SO_2, NO) and are summarised together with instrument details in Table 2. CO and SO_2 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:
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/NO_2 provides information about the age of polluted air masses." was replaced by "Increased NO_x ($NO + NO_2$) 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 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, O_3, 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 O_3, 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:

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 O_3, 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 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:
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.

Mae Gustin:

Received and published: 2 November 2015

Comment of M. Gustin:
With no pyrolyzer in-line they cannot be sure their TGM measurement is TGM. They need to address this significant limitation. Assuming their Teflon inlet does not remove GOM is not a good assumption See Gustin et al 2013 RAMIX EST paper

Reply:
Sections related to GOM have been removed.
As described in the reply to the first comment of Referee #1 and the third general comment of Referee #2, in the PTFE coated inlet system only the core flow (without any wall contact) was sampled and directed through a PFA sample line towards the instruments. The flow rate in the 2.5 m long 7.7 mm wide (inner diameter) sample line was 25 l min^{-1} and therefore the 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 and under consideration of the instrumental limitation (uncertainty 12.5% or ~0.15 ng m^{-3}), the measured value represents TGM. Capture of GOM on 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).
The manuscript was updated as described in the reply to the corresponding comments of the two other Referees.

Comment of M. Gustin:
The significant limitations of the KCl denuder need to be discussed. See Gustin et al.2015 ACP paper

Reply:
The reviewer is correct, the section has been removed

Comment of M. Gustin:
A quartz wool trap will not quantitatively collect GOM and will be influenced by relative humidity.

Reply:
This method used by us has been published by Lyman and Jaffe (Nature Geoscience, 2012). We are aware that this has been questioned by recent work (Ambrose et al., 2015). However, since we do not use the difference of TGM and GEM to calculate GOM, we consider this point as not relevant in particular when taking the measurement uncertainty into account that has been explained in detail in the reply to the comments of Referee #1 and #2.

Comment of M. Gustin:
The authors need to read the recent literature cited in Gustin et al., 2015, and totally rethink their data.

Reply:
Thanks for the valuable advice.
Revisions related to TGM and GEM have been made and explained according to the more specific comments and recommendations by the two other referees.
All data related to the measurement of GOM by KCl coated denuders has been removed.

Comment of M. Gustin:
I think it is interesting that operationally defined TGM>GEM.

Reply:

We believe that is what should be expected if the inlet and the tubing transmit GOM. Our assumption of GOM transmission thus might be not as bad as claimed by the first comment of this reviewer.

Comment of M. Gustin:
Why do they discuss the Lumex measurement when they do not show data from this instrument?

Reply:
The reviewer is correct; the description of the Lumex instrument has been removed.

Finaly we like to point out that the wording of the whole text was improved by a native speaker. All changes to the Manuscript are indicated below using the Word track change tool.

Tropospheric mercury vertical profiles between 500 and 10,000 meters in central Europe

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Abstract

~~Measurements~~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. Consequently, only a few vertical Hg profile measurements have been reported since the 1970s. Besides the CARIBIC passenger aircraft observations, the

latest vertical profile over Europe was measured in 1996. Within the Global Mercury Observation System (GMOS) project four vertical profiles were taken on board research aircraft (CASA-212) in August 2013 in background air over different locations in Slovenia and Germany. Each vertical profile consists of at least seven 5 minute horizontal flight sections from 500 m above ground to 3000 m a.s.l.. Gaseous elemental mercury (GEM) ~~was measured with a Tekran 2537X analyser~~ and ~~a Lumex RA-915-AM. Total~~total gaseous mercury (TGM) was measured ~~using a~~ with Tekran 2537X and Tekran 2537B ~~analyser and gaseous oxidized mercury (GOM) was sampled onto 8 denuders for post flight analysis (one for each profile, three during the transfer flights, and two blanks).~~analysers. In addition to the mercury measurements, SO_2, CO, O_3, NO, NO_2, as well as basic meteorological parameters (pressure, temperature, relative humidity) have been measured. Additional ground based ~~speciated~~ mercury measurements at the GMOS master site in Waldhof (Germany) and measurements onboard CARIBIC passenger aircraft were used to extend the profile to the ground and upper troposphere, respectively.

No vertical gradient was found inside the well mixed boundary layer (variation by less than 0.1 ng~~.~~ m^{-3}) at different sites with GEM varying from location to location between 1.4 and 1.6 ng~~.~~ m^{-3} (STP; standard conditions: p = 1013.25 hPa, T = 273.15K). At all locations GEM dropped to 1.3 ng~~.~~ m^{-3} (STP) when entering the free troposphere and remained constant at higher altitudes. The combination of the vertical profile, measured on 21 August ~~21,~~ 2013, over Leipzig (Germany) with the CARIBIC measurements during ascent and descent to Frankfurt airport (Germany) at approximately the same time provide a unique central European vertical profile from inside the boundary layer (550 m a.s.l) to the upper free troposphere (10500 m a.s.l.) and shows a fairly constant free tropospheric TGM concentration of 1.3 ng~~·m^{-3} (STP). The highest GOM concentrations of up to 60 pg·m^{-3} (denuder samples) were found above the boundary layer during the transfer flights.~~ m^{-3} (STP).

1 Introduction

Mercury and its compounds are very toxic and, therefore, hazardous for human health and the environment (Selin, 2009). ~~Therefore it~~Consequently, mercury is on the priority list of many international agreements and conventions dealing with environmental protection and human health, including the United Nations Environment Program (UNEP) Minamata convention on mercury (www.mercuryconvention.org). Mercury is emitted to the atmosphere from a variety

of anthropogenic (e.g. coal and oil combustion) and natural sources (e.g. evaporation from ocean and lakes) (Pirrone et al., 2010). The most efficient transport pathway for mercury is the atmosphere (~~Filzgerald~~Fitzgerald et al., 1998). However, measurements of the vertical distribution of atmospheric mercury are rare, because airborne measurements are time consuming and expensive. Between 1978 and ~~2014~~2015 only seven campaigns performed airborne mercury measurements over Europe. Apart from the CARIBIC ~~dataset~~measurements (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container, ~~www.caribic-atmospheric.com),~~www.caribic-atmospheric.com) in the upper troposphere, the last European vertical profile of mercury was measured in June 1996. Table 1 summarises all European airborne mercury measurements known to us together with their key findings (including this study).

The GMOS 2012 measurement campaign at Mt. Etna (Global Mercury Observation System; www.gmos.eu~~; Weigelt et al., in prep.)~~) focused on volcanic emissions and ~~therefore~~ no vertical profile was measured. CARIBIC measurements focus on the tropopause region and ~~measures~~determine vertical profiles only above 6 km during ascent and descent from/to airports. During the four measurement campaigns over Europe between 1978 and 1996 a vertical gradient was found neither in the planetary boundary layer (PBL) nor in the free troposphere. This was expected, because most of the atmospheric mercury is in its elemental state Hg(0) with a long atmospheric life time of six months to one year (Lindberg et al., 2007). Due to the long lifetime, Hg is well mixed in the atmosphere. All ~~known~~ vertical profile measurements of Hg until 2009 were summarized by Swartzendruber et al~~.~~, (2009) (data are shown in Fig. 7 for comparison to this study). Hg vertical profiles were measured by Radke et al. (2007), Talbot et al. (2008), and Swartzendruber et al. (2006, 2008) in different locations over the Pacific Ocean and the US between 2002 and 2008. Vertical profiles over Canada were reported by Banic et al. (2003) for the period between 1995 and 1998. Friedli et al. (2004) report vertical profiles measured over Japan/Korea and China in ~~Spring~~spring 2001. In ~~this~~the Swartzendruber et al. (2009) summary, a paper by Ebinghaus and Slemr (2000) represents the only European vertical profile. ~~Recently,~~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~~(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., ~~1014).~~2014, Shah et al., 2015). Usually the GEM concentrations in the planetary boundary layer (PBL; ~~0-1~~ground to 1-3 km) were found to be the ~~same~~similar as in the lower free troposphere (FT). As mercury is emitted ~~from~~by sources on the ~~underlying surface~~ground, we would expect at least a slightly higher concentration inside the PBL compared to the FT. The absence of a vertical gradient inside the PBL and the FT is caused by the "fast" mixing velocity of Hg (hours to days), compared to the atmospheric life time (6 to 12 month) and the insufficient precision of the available mercury analysers to detect concentration gradients of less than 0.1 ng~~.~~ m^{-3}.

The European Tropospheric Mercury Experiment (ETMEP) was carried out in July/August 2012 (ETMEP-1) and August 2013 (ETMEP-2) to measure local emissions and to perform vertical profile measurements from inside the boundary layer to the lower free troposphere. In total 10 measurement flights were performed over Italy, Slovenia, and Germany with two small, flexible aircraft. The ETMEP-1 campaign focused on volcanic emissions as such and not on the investigation of vertical profiles. We report here the results of the ETMEP-2 campaign ~~five~~, which focused on vertical ~~profiles were carried out~~profile measurements over ~~Slovenia and Germany~~central Europe.

2 Measurement location and methodology

From ~~August~~ 19 to 22 August 2013, five ETMEP-2 measurement flights were carried out over central Europe (Fig. 1). After take-off on 19 August ~~19~~ at the aircraft's home base in Parma (northern Italy) the first vertical profile was measured in the early afternoon over the GMOS Master site "Iskraba" in Slovenia. Thereafter the second vertical profile was flown over Idrija (Slovenia), a former mercury mining area. On 21 August ~~21~~th, in the morning the transfer flight from Ronchi dei Legionari (north-east Italy) to Leipzig (central Germany) was used as the second measurement flight to obtain a central European horizontal profile inside or slightly above the boundary layer (flight 2). During this flight no vertical ~~profiles were~~profile was flown. After refuelling at Leipzig airport, the third flight was carried out on the same day. Within this flight, two vertical profiles were flown; the first one at noon downwind of a coal-fired power plant south of Leipzig (Lippendorf) and the second one ~~at~~in the early afternoon

over the Leipzig city-centre. With the fourth measurement flight on 22 August ~~22nd~~ (take-off in Leipzig), the fifth vertical profile was flown in the ~~forenoon~~late morning over the GMOS master site "Waldhof" (northern Germany), representing central European rural background air. Thereafter, the aircraft was refuelled at Leipzig airport and flown back to Parma on the same day. This last transfer flight (flight 5) was used to obtain a second central European horizontal profile slightly above the boundary layer. Here we present and discuss the vertical profiles over Iskraba, Idrija, Leipzig, and Waldhof. The ~~Lippendorf~~ vertical profile downwind of the Lippendorf coal fired power plant will be discussed in a separate paper (Weigelt et al., ~~in prep.).~~2016).

Each vertical profile consists of at least seven horizontal flight legs, lasting five minutes each. The altitude for the flight legs was chosen, starting inside the boundary layer at about 400 m above ground. For each vertical profile the highest flight level was 3000 m above sea level (a.s.l.). Each flight-level-change was performed within 2.5 minutes. Consequently, each vertical profile took 50 minutes~~. The~~, being representative for the transitory situation at a certain measurement location. The campaign ~~described above~~ was performed with a CASA 212 two engine turboprop aircraft (Fig. ~~2a). This aircraft is~~2a) operated by Compagnia Generale Ripreseaeree (http://www.terraitaly.it/). The CASA 212 has a maximum payload of 2.7 tons, allowing to carry the measurement instruments, different service instruments, the power supply, two pilots, and 5 operators. The aircraft normal cruising speed is 140 kn (~260 km~~·~~ h^{-1}). At this speed the maximum flight distance is ~1600 km. The maximum flight level of the unpressurized aircraft is 8500 m. As it was not possible to fly with oxygen masks, the maximum flight level for the ETMEP-2 campaign was limited to 10000 ft (~3000 m a.s.l.).

Previously, the CASA 212 was used as a research aircraft to carry remote sensing LIDAR systems (light detection and ranging), but not for *in situ* measurements. Therefore, the aircraft had no gas inlet. To transfer unbiased ambient air from outside the aircraft boundary layer to the measurement instruments, a gas inlet system has been developed and manufactured at the Helmholtz-Zentrum Geesthacht (Fig. 2b). The gas inlet was ~~specially~~ designed specifically for the cruising speed of the CASA 212. The air enters the inlet with a speed of about 260 km~~·~~ h^{-1} (~72 m~~·~~ s^{-1}). By expansion, the air velocity is reduced to about 15 km~~·~~ h^{-1} (~5 m~~·~~ s^{-1}). At 260 km~~·~~ h^{-1} about 120 l~~·~~ min^{-1} (ambient conditions) enters the inlet. In the centre of the expansion area the main sampling line starts~~·~~, taking only the core flow without contact with

inlet surface. All instruments pull their ~~measurement~~sample air from this main sampling line (all together about 25 l~~.~~ min^{-1}). The remaining 95 l~~.~~ min^{-1} are directed to the back of the inlet where the air speed is increased by a nozzle and the air exits. By replacing the inlet~~.~~ and outlet ~~nozzle~~nozzles with smaller or larger ones, this inlet system ~~is also suited~~can be adapted for other aircraft types with different cruising speed. In the expanded area (behind the main sample line) the air temperature (T), static pressure (p), and relative humidity (RH) are measured. To optimize for trace gas measurements and to avoid contamination, the whole inside of the inlet was coated with ~~Teflon~~PTFE and only ~~Teflon~~PFA tubes ~~(PFA)~~ were used for the sampling line. The outside of the inlet was copper coated to avoid electrostatic charging. The inlet body was mounted onto a 6 cm wide and 90 cm long telescope tube. This telescope tube was flexibly mounted into the aircraft fuselage. After take-off, the telescope tube was pushed down by ~40 cm from inside the aircraft, to ensure the inlet nozzle is outside the aircraft boundary layer. Before landing the telescope tube was pulled back into the aircraft fuselage. Inlet and telescope tube were equipped with controllable heaters to prevent icing. However, because the measurement flights were carried out in summer at altitudes below 3000 m a.s.l., it was never necessary to switch on the heating system. Inside the cabin the tubing from telescope tube to instruments (~2.5 m long 3/8'' main sample tube with PFA manifolds to instruments; residence time < 0.3 seconds) was not heated. The temperature inside the cabin was 18 to 30°C. Aerosol particles were filtered out at the instrument individual inlets by using PTFE membrane filter (pore size 0.2 µm). All data were ~~corrected for~~synchronized using individual instrument lag and response time ~~due to sampling tube length and instrument internal analysis~~.

For the campaign the aircraft was equipped with ~~three~~two mercury measurement instruments, ~~one Lumex RA-915AM,~~ a Tekran 2537B~~,~~ and a Tekran 2537X ~~–~~(cf. Tab. 2). ~~The high resolution Lumex RA-915 AM measures gaseous elemental mercury (GEM) with a raw signal temporal resolution of only 1 s. The measurement principle is based on atomic absorption spectroscopy (AAS) with Zeeman background correction. Due to the limited sensitivity however, the raw signal is noisy (about ± 4 ng·m^{-3}) and is dependent on pressure and temperature. As the aircraft cruising speed is about 72 m·s^{-1}, this highly resolved raw signal is very useful to detect small scale highly concentrated mercury plumes (concentration change > noise level). Therefore, Lumex data were used for data analysis but are not sown in the vertical profile plots. The Tekran 2537B and 2537X~~Both analysers are based on cold vapour atomic fluorescence spectroscopy (CVAFS) and can measure total gaseous mercury (TGM~~).~~.

Slemr et al., 2016). Because the CVAFS needs pre-concentrated samples, the Tekran analysers pre-amalgamate Hg from the sample air on solid gold cartridges and achieve a minimum temporal resolution of 150 seconds. For the ETMEP-2 flights a quartz wool trap was installed upstream the Tekran ~~2527X~~2537X analyser, removing only gaseous oxidized mercury (GOM) and aerosol particles with particle bound mercury (PBM) but no GEM from the air stream (cf. Lyman and Jaffe, 2011).

The Tekran 2537B analyser was operated as backup instrument without a quartz wool trap. ~~Although the Teflon made (PFA and PTFE) aircraft gas inlet system was not tested for GOM transmission efficiency, we expect nearly quantitative GOM transmission from the inlet to the instrument. Therefore, the Tekran 2537B measurement are believed to represent total gaseous mercury (TGM = GEM + GOM) concentrations. To estimate the concentration of GOM, additionally 8 manual denuder samples were taken (sampling time 1 hour or longer, sampling flow controlled using a mass flow controller). In parallel to the denuder samples two blank tests were performed by handling the denuders exactly the same way the samples were handled (denuder preparation, installation to sampling setup, storage, analysis), but without pulling sample air thru. After all flights had been finished, the denuders were analysed for their total GOM loadings in the laboratory. This method has a relatively high uncertainty of about ± 5 pg·m^{-3}. Nevertheless, additional information on the amount of GOM is obtained by that approach. During each vertical profile one denuder was used, whereas one denuder was loaded during the transfer flight Ronchi dei Legionari – Leipzig and two denuders were used along the transfer flight Leipzig – Parma. The blank tests were performed during the first vertical profile over Iskraba and the last vertical profile over Waldhof (see flight information and Fig. 1).~~ 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 has been calculated by Weigelt et al. (2013) using two different approaches according to ISO 20988 type A6 and ISO 20988 Type A2. 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. Calculating GOM concentrations from the TGM and GEM difference (Temme et al., 2003a; Slemr et al., 2009, Lyman and Jaffe, 2011) is limited by its uncertainty (~150 pg m^{-3}) which is larger than the expected GOM concentrations (few tens of pg m^{-3}). Therefore, GOM concentrations are not presented.

For the identification and characterization of different air masses carbon monoxide (CO), ozone (O_3), sulphur dioxide (SO_2), nitric oxide (NO), nitric dioxide (NO_2), and the basic meteorological parameters temperature (T), pressure (p), and relative humidity (RH) were measured simultaneously at high temporal resolution~~. Instrument details are summarised in Table 2.~~ (cf. Table 2). Uncertainties of these parameters were calculated according to the individual instrument uncertainty given by the manufacturer and the calibration gas accuracy (CO, O_3, SO_2, NO) and are summarised together with instrument details in Table 2. CO and SO_2 can be used for the identification of city plumes and plumes of power stations, respectively~~.~~ (Parrish et al., 1991; Klemp et al., 2002; Jaffe et al., 2005, Slemr et al., 2014). O_3 can be used to characterize upper tropospheric/lower stratospheric air or to explain oxidation processes~~. A~~ (Zahn and Brenninkmeijer, 2003). Increased NO_x ($NO + NO_2$) mixing ratio ~~of NO/NO_2 provides information about the age of polluted air masses.~~can indicate combustion plumes (Ambrose et al 2015; Weigelt et al., 2016), too. Usually FT air is ~~much~~ dryer than PBL air (Spencer and Braswell, 1996) and, therefore, the RH measurements can distinguish these two air masses. ~~Model~~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 ~~were~~has been calculated every 150 s along the aircraft flight tracks ~~for additional information.~~according to the CARIBIC scheme (http://www.knmi.nl/samenw/campaign_support/CARIBIC/). These calculations are based on meteorological analysis data from the European Centre for Medium-Range Weather Forecasts (ECMWF) and the TRAJKS trajectory model (Scheele et al., 1996).

Before take-off all instruments were warmed up for at least 45 minutes, using an external ground power supply. During the starting of the engines the power was interrupted for less than 3 minutes. Since 45 minutes were too short to stabilize the Tekran 2537 internal permeation source, these instruments were calibrated directly after each measurement flight before the engine shut down. All data were recalculated, using the post flight calibration. The pressure in the fluorescent cells of both Tekran instruments was kept constant using upstream

pressure controllers at the exits of the cells. This eliminated the known pressure dependence of the response signal (Ebinghaus and Slemr, 2000; Talbot et al., 2007). ~~The Lumex analyser has a much shorter warm up time of less than 10 minutes and was, therefore, calibrated before take-off.~~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. The CO instrument calibration takes 60 seconds and was, therefore, performed during the measurement flights every 20 minutes. The O_3, SO_2, NO, NO_2 instruments have a fairly constant signal response and were thus calibrated before and after the ETMEP-2 measurement campaign with external calibration gases. The factory calibration was used for the pressure, temperature and relative humidity sensors. The measurements were synchronized using their individual lag and response times. Please note that all mercury (TGM~~,~~ and GEM~~, and GOM~~) concentrations are reported at standard conditions (p = 1013.25 hPa, T = 273.15K). At these standard conditions 1 ng~~.~~ m^{-3} corresponds to a mixing ratio of 112 ppqv (parts per quadrillion by volume).

3 Results

The first vertical profile was measured on 19 August ~~19~~, 2013 from 11:15 to 12:15 UTC over the GMOS Master site "Iskraba" (Fig. 1). As Iskraba is located in mountainous terrain, the lowermost flight ~~leg~~level was ~~performed~~ at 1000 m a.s.l.. The measurements are summarised in Fig. 3. The squares represent the constant flight level measurement points (2 measurements with 2.5 minutes each). The stars represent the measurements while climbing between two flight levels (2.5 min average). The data, represented by squares are thus more significant and the data illustrated as stars do provide additional information of the vertical structure. Please note that the RH and the air temperature (T) are plotted with high temporal resolution (1 s) in the ~~right most~~rightmost panel. RH increases with increasing altitude and shows no step change to lower RH which would identify the top of PBL. Hence, the whole profile in Fig. 3 was flown within the PBL. The ~~mercury~~ measurements indicate a very constant mercury concentration without any vertical gradient for TGM and GEM. With 1.44 ng~~.~~ m^{-3} the whole column average TGM concentration was somewhat below the northern hemispheric background concentrations of 1.5 - 1.7 ng~~.~~ m^{-3} (Lindberg et al., 2007) but was comparable with the August 2013 monthly median of 1.41 ng~~.~~ m^{-3} at Mace Head/Ireland (Weigelt et al., 2015) and a median concentration of 1.40 ng~~.~~ m^{-3} of all vertical profiles over Tennessee, USA,

in 2012-2013 (Brooks et al., 2014). With 1.38 ng~~·~~ m^{-3} the column averaged GEM concentration was only slightly lower than TGM but this difference is smaller than the combined uncertainties of both instruments and thus insignificant. ~~The manual denuder sampling (integral value, representative for the whole boundary layer over Iskraba) gave a GOM concentration between 1.9 and 13.2 pg·m^{-3}, which is smaller than the GOM concentration which can be resolved by the TGM – GEM differential measurement. This was the second lowest GOM concentration measured on all ETMEP-2 flights with the manual denuder sampling technique (Tab. 3). No ground-based reference data for Iskraba were available due to technical reasons. Furthermore, Lumex instrument data were not available due the instrument failure.~~No ground-based reference data for the GMOS Iskraba site were available due to technical reasons. Besides mercury, neither CO, nor O_3, NO, and NO_2 mixing ratios indicate a significant vertical gradient. Only the SO_2 mixing ratio increased from 1000 to 1500 m a.s.l. and remained constant ~~there above~~at higher altitudes. In general the measurements thus showed that the air over Iskraba was well mixed within the PBL.

After the ~~experimental flights~~flight over Iskraba ~~were~~was completed, the second vertical profile was flown on the same day about 80 km northwest over the former mercury mining area "Idrija". Until the 1990s, Idrija was the second largest mercury mine in operation worldwide (Grönlund et al., 2005). This profile was measured between 12:25 and 13:25 UTC (Fig. 4). Due to the mountainous terrain the seven horizontal fight legs were performed within the altitude range 1350 m to 3150 m a.s.l.. On the contrary to Iskraba, the uppermost flight leg over Idrija was flown above the PBL, in FT air. This is clearly indicated by a significantly reduced RH (the ~~right most~~rightmost panel in Fig. 4). The boundary layer top was found at 2850 to 2900 m a.s.l..

Compared to Iskraba, the mercury concentration over Idria was with 1.5 to 1.6 ng~~·~~ m^{-3} (GEM) and 1.6 to 1.7 ng~~·~~ m^{-3} (TGM) about 10 to 15% higher. ~~With 18.0 to 28.8 pg·m^{-3}, also GOM (manual denuder sampling) was found to be significantly higher than over Iskraba.~~ The elevated mercury concentrations might be caused by increased emission from the soil around Idrija due to the legacy of the former mining activity. However, as over Iskraba no vertical GEM or TGM concentration gradient was observed inside the PBL. It should be noted that above the PBL the GEM and TGM concentrations were found to be significantly lower (GEM: 1.23 ng~~·~~ m^{-3}; TGM: 1.32 ng~~·~~ m^{-3}; $p = 0.999$). Ozone, CO, NO_2, and SO_2 mixing ratios behave similarly, although NO_2 and SO_2 show a small gradient within the PBL with slightly

decreasing mixing ratios with increasing altitude. At 2700 m a.s.l. near the top of the PBL, all trace gas mixing ratios start to decrease and the mixing ratios at 3150 m a.s.l. in the FT are the lowest of the whole profile. O_3 and CO mixing ratios decrease by about 20% when entering FT, NO_2 by about 60% and SO_2 drops essentially to the detection limit. This step in mixing ratio at the PBL top indicates that FT air is separated from the PBL air due to slow air mass exchange. Nitrogen oxide (NO) shows no vertical gradient from inside the PBL to the FT. It should be noted the NO mixing ratios are close to the instrument's detection limit and might be not representative or have at least a large uncertainty. -The stars at 2900 m a.s.l. represent a mixture of the PBL and FT air, explaining the concentrations are between the PBL and FT air concentration (e.g. GEM 1.~~2~~3 ng~~.~~ m^{-3} and TGM 1.~~3~~4 ng~~.~~ m^{-3}).

On 21 August ~~21~~, 2013, two vertical profiles were measured over central Germany in the area of the city of Leipzig (Fig. 1). The first profiling was carried out downwind of a coal-fired power plant and is the subject of another paper (~~Bieser~~Weigelt et al., ~~in prep~~2016.). Thereafter, the second profile was flown between 11:10 UTC and 12:10 UTC over the city centre of Leipzig (population 500,000). The Leipzig profile was flown upwind of the power plant and was taken as a reference for the profile downwind of the ~~coal-fired~~ power plant measurements. The profile is shown in Fig. 5. The lowermost flight level over Leipzig was 450 m above ground (600 m a.s.l.) and the highest one was 3020 m a.s.l..

From ~~August~~ 21 to 23~~,~~ August 2013, additionally four CARIBIC ~~measurement~~ flights were performed aboard a passenger aircraft (Lufthansa airbus A340-600) from Frankfurt/Germany to Caracas/Venezuela and Vancouver/Canada and back. Among other instruments (Brenninkmeijer et al. 2007), the CARIBIC system carries a Tekran 2537A mercury analyser, measuring ~~the~~ TGM along the flight track with a temporal resolution of 600 s (Ebinghaus et al. 2007; Slemr et al. 2014~~).~~; Slemr et al., 2016). On 21 to 23 August ~~21 – 23,~~ 2013, a high pressure system dominated the weather over Germany and Western Europe when the ETMEP-2 and the CARIBIC measurements were carried out. The wind direction in the free troposphere (3-10 km) was west to northwest and the forward- and backward trajectory analysis showed that both the ETMEP-2 and CARIBIC aircraft sampled about the same air mass (see Fig. S-1, ~~supplement).~~supplementing information). 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 allows supplementing and comparing the ETMEP-2 Leipzig TGM vertical

profile with the independent CARIBIC measurements during ascent/descent from/to Frankfurt airport, only some 350 km apart. 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.. Stratospheric CARIBIC measurements (with O_3 > 80ppb) are not shown.

The ETMEP-2 measured RH vertical profile identified the PBL top over the city centre of Leipzig at 2200 to 2250 m a.s.l.. While the first five ETMEP-2 horizontal flight legs were flown inside the PBL, the last two legs were performed in FT air. Again, inside and above the PBL no vertical gradient was apparent for GEM, TGM, O_3, CO, NO, and SO_2, indicating well mixed air masses. Only for NO_2 a negative vertical gradient was found inside the PBL, but not above. Inside the PBL the average GEM and TGM concentration was 1.50 and 1.55 ng~~·~~ m^{-3}, which is in between the concentrations found inside the PBL over Iskraba and Idrija. The FT GEM and TGM concentration over Leipzig was ~~measured to be~~ 1.2 to 1.3 ng~~·~~ m^{-3}. Similar concentrations were also found in the FT air over Idrija (Fig. 4), Waldhof (Fig. 6, flight leg five and six), as well as during the transfer flights Ronchi dei Legionari – Leipzig and Leipzig – Parma (not shown). ~~The GOM concentration from denuder samples along the Leipzig profile was 1 pg·m^{-3} (lower detection limit) to 10.6 pg·m^{-3}, representing the lowest measured concentration along all flights (cf. Tab. 3).~~

The CARIBIC and ETMEP-2 FT data match very well~~.~~ (Fig. 5). The average TGM concentration is 1.23 ng~~·~~ m^{-3} for the ETMEP-2 and 1.30 ng~~·~~ m^{-3} for CARIBIC dataset. This means that the measurements carried out in this study (August 2013) revealed no vertical ~~GEM~~TGM gradient ~~is apparent~~ in the entire FT over Central Europe. Inside the PBL the GEM and TGM concentration ~~is~~was found to be about 20% higher. 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 O_3, and 0,05 ppb for NO ~~measured aboard CARIBIC match the ETMEP-2 measurements very well, supporting~~(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. Consequently, the combined ETMEP-2 and CARIBIC data set provides to the best of our knowledge the first complete vertical mercury profiles from inside the PBL to the upper FT.

The last vertical profile was flown on 22 August ~~22,~~ 2013~~,~~ over the GMOS master site "Waldhof" (Fig. 6). Since this profile was measured in the ~~forenoon~~late morning (08:15 to

09:15 UTC; 10:15 to 11:15 local time), the PBL was found to be with ~~the top at~~ 1750 – 1850 m a.s.l. rather shallow when compared to the previous profiles. Thus only the first four flight legs were flown inside the PBL and the remaining three were above. As measured during all previous vertical profiles, again a significant difference between PBL and FT air was apparent for GEM and TGM concentrations, and CO, NO, and SO_2 mixing ratios. The two lower FT flight legs indicated typical GEM and TGM concentrations of 1.27 and 1.19 ng~~·~~ m^{-3} (1950 m a.s.l.) and 1.22 and 1.22 ng~~·~~ m^{-3} (2490 m a.s.l.), respectively. However, in the uppermost flight level at 3030 m a.s.l. GEM and TGM concentrations were ~~with~~ 0.99 and 0.98 ng~~·~~ m^{-3}, respectively, i.e. about 25% lower. Furthermore, in that layer not only the GEM and TGM concentrations, but also the CO and O_3 mixing ratios were about ~ 25% lower. At the same time RH was with 66.6 % substantially higher and SO_2 with 1.1 ppb slightly higher. Five day backward trajectories (Fig. S-2, ~~supplement~~supplementing information) suggest that the air from this uppermost flight leg originated from the subtropical east Atlantic (about 30°N, 25°W). On the contrary, the air measured during all lower flight legs (in PBL and FT air) came from north Canada (north of 60°N, west of 50°W).

Inside the PBL the GEM and TGM concentrations were with 1.93 and 1.95 ng~~·~~ m^{-3}, respectively, the highest in the uppermost flight leg (1470 m a.s.l.). Similarly, the CO mixing ratio was also elevated and the SO_2 raw signal indicated some short peaks to 1.5 ppb (not shown). The coincidence of elevated GEM and TGM concentrations with elevated CO and SO_2 mixing ratios was probably caused by a combustion plume. Below this plume again a fairly constant profile was measured for GEM (1.66 ng~~·~~ m^{-3}), TGM (1.73 ng~~·~~ m^{-3}), CO (121.4 ppb), O_3 (52.4 ppb), and NO (at detection limit). Only NO_2 and SO_2 mixing ratios increased towards the ground from 1.1 and 1.1 ppb, at 962 a.s.l. to 1.7 and 1.6 ppb at 429 m a.s.l., respectively.

GEM concentration measured by the speciation unit at the ground at the Waldhof site was with 1.92 ng~~·~~ m^{-3} somewhat elevated. ~~Concurrently measured concentrations of GOM (3.6 pg·m^{-3}) and particle bound mercury (PBM, 7.8 pg·m^{-3}) were somewhat elevated too.~~ The Waldhof three-year-average (2009-2011) GEM concentration is 1.~~0 pg·m^{-3} for GOM and 6.3 pg·m^{-3} for PBM~~61 ng m^{-3} (Weigelt et al., 2013). With 2.0 ppb the ground based NO_2 mixing ratio follows the increasing gradient toward the ground. On the contrary the Waldhof NO mixing ratio was significantly higher (1.0 ppb), and O_3 (36.4 ppb) and SO_2 (1.0 ppb)

mixing ratios were somewhat lower than the airborne measurements. The measured air temperature and pressure however matched very well.

~~The GOM concentration from the manual denuder sampling was calculated to be between 24.6 and 37.3 pg·m^{-3}, which is much higher than the ground based measured concentration. This mismatch is probably caused by the different air masses that have been sampled. While the ground based measurement represent only air from the lower PBL which are directly influenced by dry deposition, the airborne sampling represents the entire air column from inside the PBL to the lower FT. Vertical GOM profiles reported by Brooks et al. (2014) show clearly a tendency to lower GOM concentrations at the lowest altitudes. Except Iskraba, all denuder samples were taken to more than 17% of the sampling time above the PBL. The three denuder samples taken on the transfer flights between Italy and Germany do represent mainly FT air. For all three denuders a relatively high GOM loading of 18.4 – 65.6 pg·m^{-3} was found (Tab. 3). These GOM concentrations are in reasonable agreement with ~ 20-110 pg·m^{-3} measured in August 2012 at altitudes up to 6 km by Brooks et al. (2014) over Tennessee, USA. It is assumed that above the PBL the GOM concentration is higher because less aerosol surface is available to condense the GOM onto, the RH is usually lower, and the radiation flux is higher (less humidity results in fewer clouds and less light scattering. Furthermore, solar radiation is scattered and reflected at the PBL cloud top and is partly scattered back above the PBL). All these conditions favour elevated GOM concentrations with a maximum at altitudes between 2 and 5 km (Brooks et al., 2014). Within future studies more detailed GOM vertical profiles with a better vertical resolution should be carried out.~~

4 Conclusions

~~Opposite~~In contrast to most of the previously reported vertical profiles, we always observed a significant difference between PBL and FT air (Fig. 7, p = 0.999). While the FT GEM and TGM background concentration over central Europe was ~~measured to~~ ~ 1.3 ng~~.~~ m^{-3}, 10-30~~-~~% higher GEM and TGM concentrations were found in the PBL. The sharp gradient at the PBL top is probably caused by atmospheric dynamics. Mercury is emitted to the PBL by various sources (Pirrone et al., 2010; Song et al., 2015). The PBL is somewhat decoupled from the FT due to dynamic processes like friction and convection processes (Stull, 1988). Therefore, the exchange between PBL and the FT is inhibited creating a gradient between PBL and FT with higher concentrations in the PBL. The same applies for CO and SO_2 (Figures 4-6) which are

also emitted on the ground.. Other dynamically caused mercury gradients can be found at the tropopause which inhibits exchange from the upper troposphere to the lower stratosphere (Slemr, et al., 2009; Lyman and Jaffe, 2011), and at the inter-tropical convergence zone (Slemr et al., 1985; Temme et al., 2003b) which inhibits transport from northern to southern hemisphere.

Besides ~~this abrupt jump~~the strong concentration gradient at the PBL top, at all sampling locations, neither in the boundary layer, nor in the free troposphere a clear vertical gradient was apparent. This is in agreement with most of the vertical profiles obtained elsewhere (Swartzendruber et al., 2009; Brooks et al., 2014~~).~~, Shah et al., 2015). Vertical profiles with pronounced decreasing GEM concentrations with increasing altitude were reported by Radke et al. (2007) and Brooks et al. (2014), but only for spring month April, May, and June. These are the months with the strongest stratosphere to troposphere ozone flux in the northern hemisphere (Olsen et al., 2004) and the anomalous vertical profiles with strong vertical GEM gradients ~~are probably~~may be related to it. In summer months GEM and TGM are homogeneously distributed inside the PBL and FT. The combination of ETMEP-2 measurements over Leipzig with CARIBIC measurement over Western Europe (Fig. 5) gives a unique vertical profile from 0.5 km (lower PBL) to 10.5 km (upper FT). From above the PBL to the FT top the TGM background concentration is on average 1.3 ng~~·~~ m^{-3}.

~~During all vertical profiles, as well as during the transfer flights between Slovenia, Germany, and Italy denuder samples were taken in PBL- and FT air. The analysis of the denuders for GOM indicated an increased GOM concentration above the PBL. As this is a region favouring the generation of GOM (low particle surface (in comparison to PBL), low humidity, and high actinic fluxes from top and below (reflection at PBL top)), this finding is reasonable. The vertical distribution and the range of observed GOM concentrations reported here are in agreement with measurements by Brooks et al. (2014). Considering a GOM concentration between 1.0 and 65.5 pg·m^{-3} (Tab. 3) and an average FT GEM concentration of 1.3 ng·m^{-3}, the ratio of GOM to GEM is 0.1 to 5.0%. Note however the large uncertainty of the measured GOM concentrations of ±5 pg·m^{-3}. Therefore, more detailed GOM vertical profiles with a better vertical resolution should be carried out in the future.~~

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).

Acknowledgements

Measurements were carried out as part of the European Tropospheric Mercury Experiment (ETMEP) within the Global Mercury Observation System project (GMOS; www.gmos.eu). GMOS is financially supported by the European Union within the seventh framework programme (FP-7, Project ENV.2010.4.1.3-2). Special thanks to Compagnia Generale Ripreseaeree (http://www.terraitaly.it/) in Parma/Italy and the pilots Oscar Gaibazzi and Dario Sassi for carrying out the measurement flights. Furthermore we ~~like to~~ thank the whole IAGOS-CARIBIC team (www.caribic-atmospheric.com) for carrying out the measurement flights. Last but not least we thank the German Federal Environmental Agency (Umweltbundesamt) and the Waldhof team for the ground based measurements at the Waldhof site.

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Tables

Table 1: Summary of all known European airborne atmospheric mercury measurements until December 2014.

Time	Location	Altitude	Key finding	Literature
1978-1981	Central Europe	6 -12 km	• no vertical gradient	Slemr et al., (1985)
1981	West of Göteborg	up to 3 km	• decrease with altitude proportional to pressure decrease → no vertical gradient when transferring to STP conditions	Brosset (1987)
June 1988	Eastern Lithuania	???	• concentration proportional to pressure at sampling altitude → no vertical gradient when transferring to STP conditions	Kvietkus ~~et al.~~ (1995)
June 1996	Eastern Germany	0.5 – 3.75 km	• no vertical gradient • increased concentration observed near source region up to ~2 km altitude	Ebinghaus and Slemr (2000)
since 2005	Europe and global (CARIBIC Project)	6-12 km	• ~~cf. GMOS Deliverable D5.1, D5.2, and D5.4~~long term monitoring in UT and LS (trend analysis) • large scale plume identification	Slemr et al. (2009, 2014) www.caribic-atmospheric.com
July/August 2012	Mt. Etna volcano (Southern Italy)	0-4 km	• no/low gaseous mercury emission from Mt. Etna volcano	~~Weigelt et al (in prep.)~~www.gmos.eu
August 2013	Central Europe (Slovenia and Germany)	0-3 km 6-11 km	• significant difference between boundary layer and free troposphere, but no vertical gradient inside individual layers	this study

Table 2: List of instruments, installed into the CASA 212 research aircraft. The acronyms are: GEM = gaseous elemental mercury; GOM = gaseous oxidized mercury; CO = ~~Carbon Monoxide~~carbon monoxide; O_3 = ~~Ozone~~ozone; SO_2 = ~~Sulphur~~sulphur dioxide; NO = ~~Nitric~~nitric oxide; NO_2 = ~~Nitric~~nitric dioxide.

Parameter	Instrument name	Temporal resolution	Uncertainty	Lower detection limit
~~GEM~~	~~Lumex RA-915AM (modified, T-stabilised by Lumex company)~~	~~1 sec (raw signal)~~	~~±4 ng/m³ (1 s raw signal) ±0.25 ng/m³ (120 s average)~~	~~0.5 ng/m³ (120 s average)~~
GEM	Tekran: 2537X (with upstream quartz wool trap)	150 s	~~±0.1 ng·m^{-3}~~ ± 12.5% of reading	0.1 ng·m^{-3}
GEM + unknown amount of ~~GOM*~~GOM[a]	Tekran 2537B	150 s	~~±0.1 ng·m^{-3}~~ ± 12.5% of reading	0.1 ng·m^{-3}
~~GOM~~	~~manually denuder samples~~	~~2600 to 3600 s~~	~~±5 pg·m^{-3}**~~	~~1 pg·m^{-3}~~
CO	Aero Laser AL5002	1 s	~~±1 ppb~~±3% of reading	1.5 ppb
O_3	Teledyne API 400A	10 s	±~~0.5~~2% of reading	0.6 ppb
SO_2	Thermo: 43C Trace Level	10 s	±~~3~~4% of reading	0.2 ppb
NO NO_2	Teledyne API M200EU	10 s 10 s	±10% of reading	0.05 ppb
Pressure	Sensor Technics CTE7001	1 s	±1% of reading	0 mbar
Temperature	LKM Electronic DTM5080	1 s	±0.13°C	-50°C
Relative Humidity (RH)	Vaisala HMT333	8 s	±1.0% RH (0-90% RH) ±1.7% RH (90-100% RH)	0%
GPS data (3d position, speed, heading)	POS AV	1 s	±5 m (horizontal~~)***~~)[b] ±15 (vertical~~)***~~)[c]	---

*[a] The aircraft inlet system transmission efficiency for GOM was not tested.

~~** Difference of the two blank tests~~

***[b] The GPS accuracy is dependent on the number of satellites. The given numbers are estimated values.

~~Table 3: Results of the manual denuder samples during all ETMEP-2 measurement flights in 2013 over central Europe. GOM data were corrected for denuder blank test, additionally performed over Iskraba/Slovenia and Waldhof/Germany.~~

Date	Location	Profile character (relative sampling time in PBL* and FT** air	analysed GOM concentration [pg·m^{-3}]
2013-08-19	Iskraba/Slovenia	vertical (100% PBL; 0%FT)	1.9 - 13.2
2013-08-19	Idrija/Slovenia	vertical (83% PBL; 17% FT)	18.0 - 28.8
2013-08-21	Ronchi dei Legionari/Italy to Leipzig/Germany	horizontal (20% PBL; 80% FT)	18.4-24.0
2013-08-21	Lippendorf/Germany	vertical (76% PBL: 24% FT)	7.0-15.7
2013-08-21	Leipzig/Germany	vertical (61% PBL; 39% FT)	1.0*** - 10.6
2013-08-22	Waldhof/Germany	vertical (54% PBL; 46% FT)	24.6-37.3
2013-08-22	Leipzig/Germany to Parma/Italy 1 (central- and south Germany)	horizontal (0% PBL; 100% FT)	55.4-65.6
2013-08-22	Leipzig/Germany to Parma/Italy 2 (south Germany and Alps)	horizontal (0% PBL; 100% FT)	22.1-31.1

* planetary boundary layer (PBL)

** free troposphere (FT)

***If a concentration was found to be below the method lower detection limit of 1.0 pg·m^{-3}, the lower detection limit is given.

Figures

Flight 1 (19.08.2013)
Flight 2 (21.08.2013)
Flight 3 (21.08.2013)
Flight 4 (22.08.2013)
Flight 5 (22.08.2013)

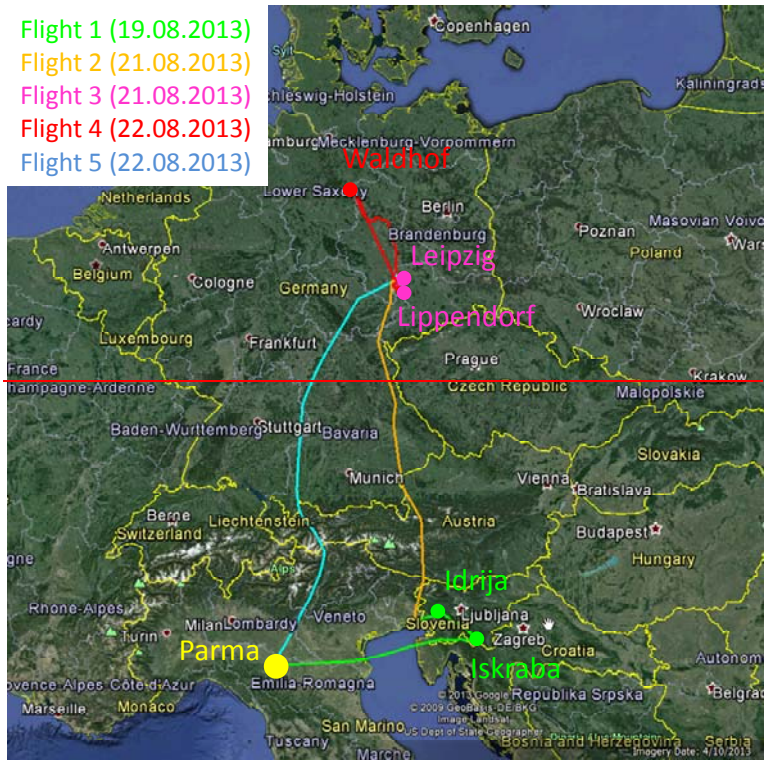


Figure 1: Flight tracks of the European Tropospheric Mercury Experiment part 2 (ETMEP-2) research flights in August, 2013. Flights are separated by the flight track colour. The home base of the used aircraft was Parma/Italy. Over Waldhof, Leipzig, Lippendorf, Idrija, and Iskraba vertical profiles were flown. ~~The underlying map was taken from Google Earth.~~

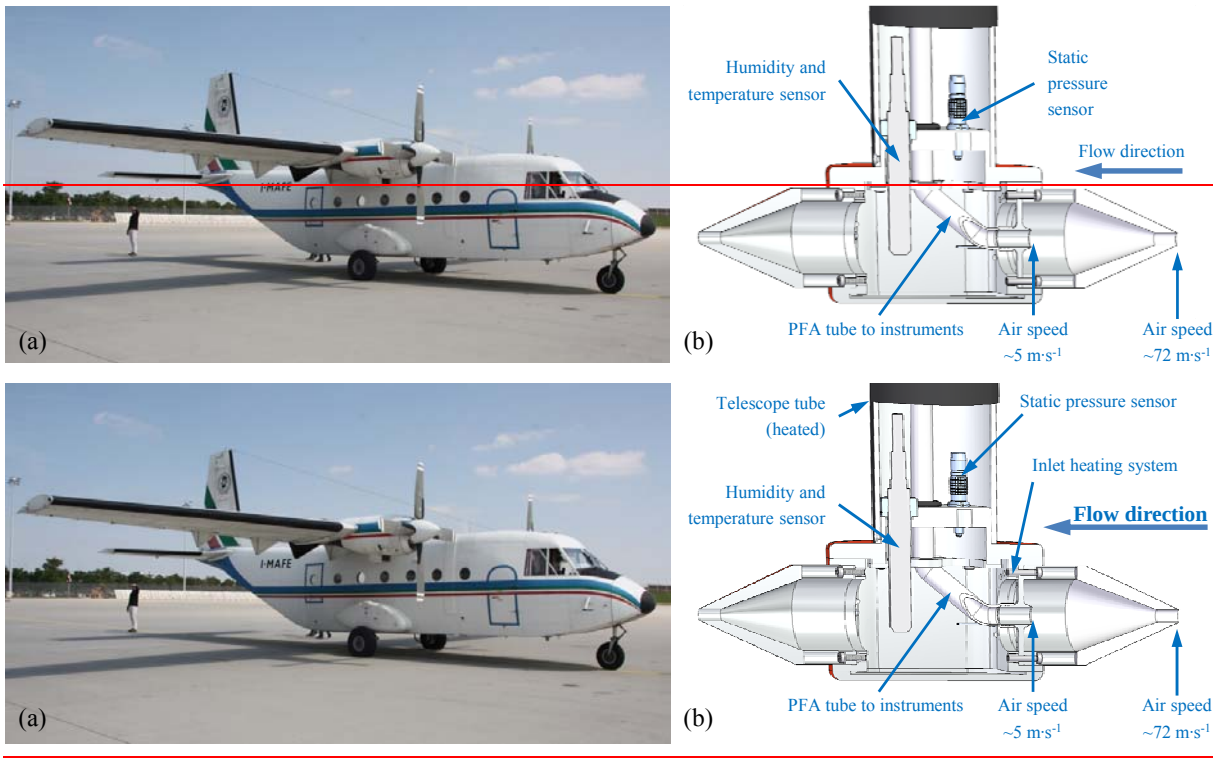
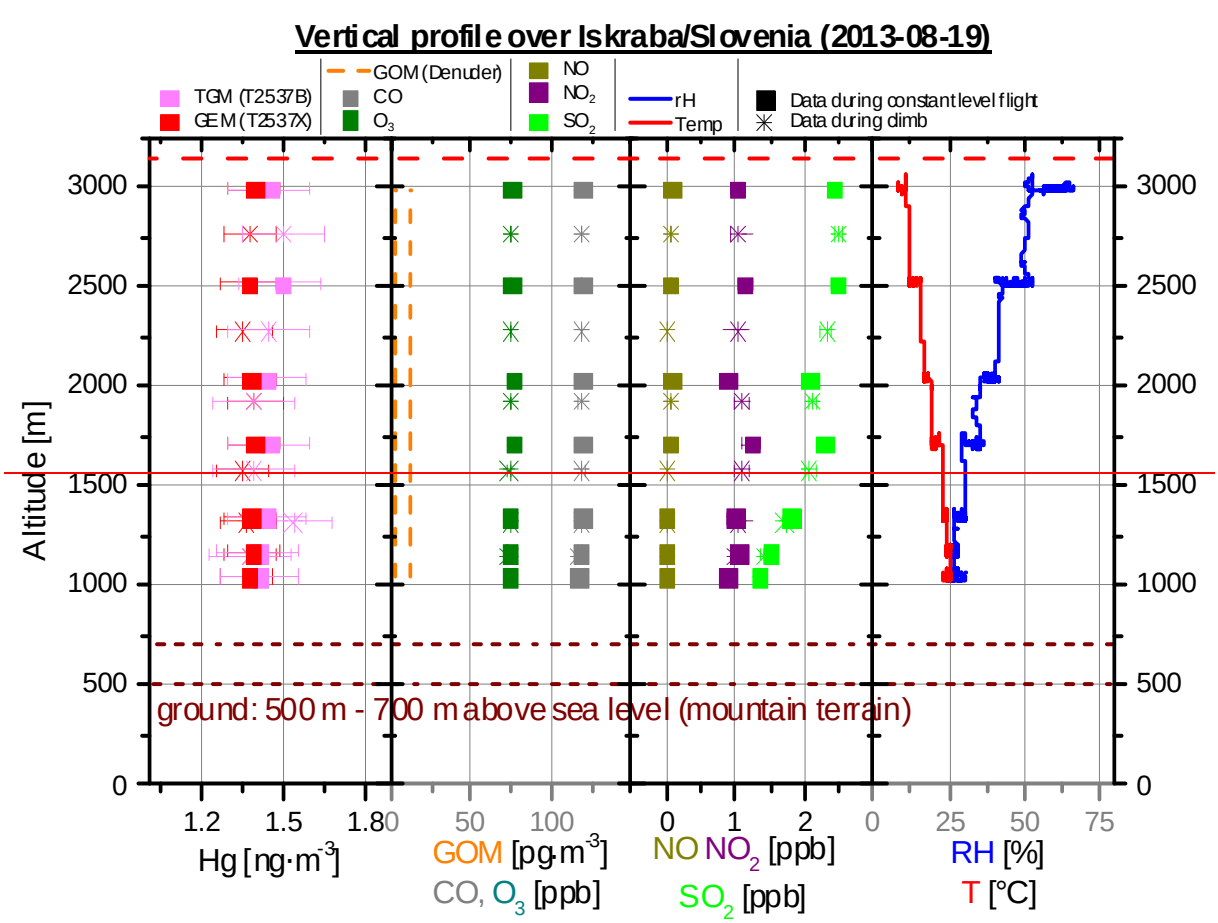
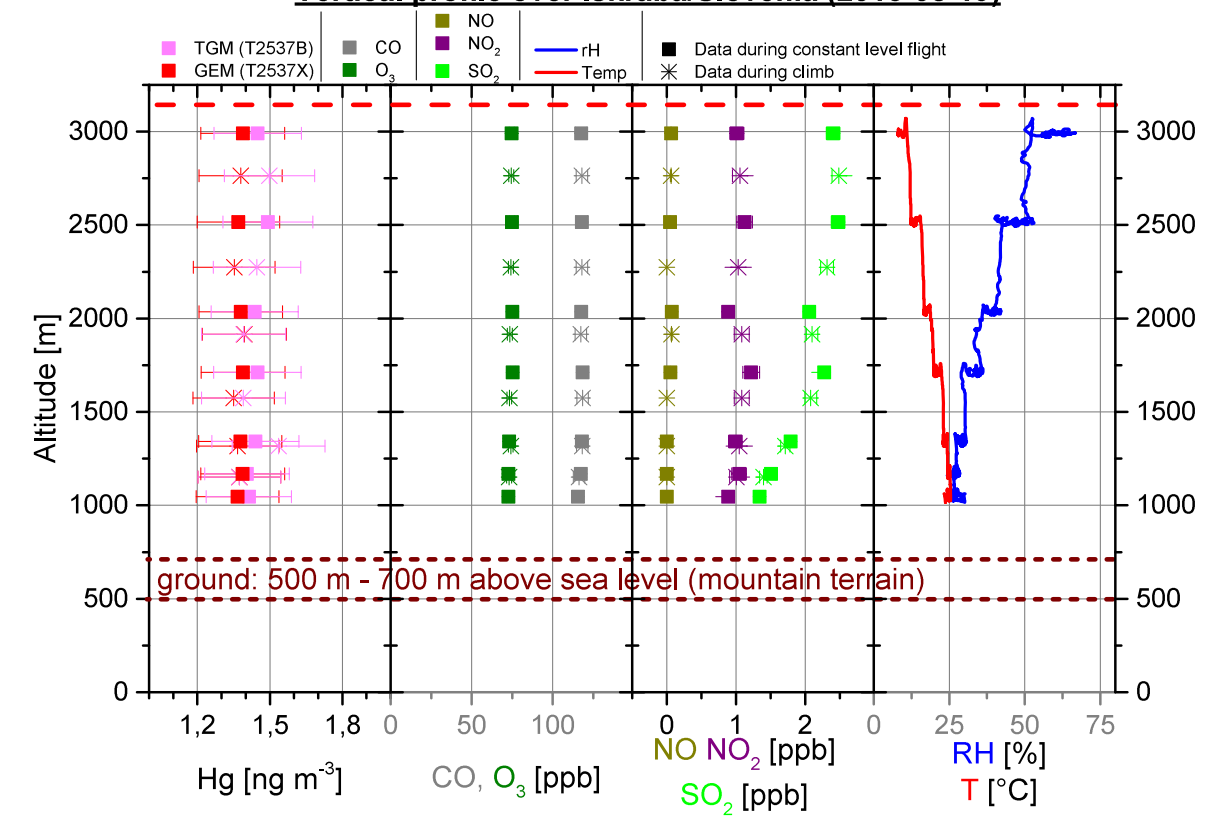


Figure 2: For the ETMEP-2 campaign in August 2013 the CASA 212 (a) from the Italian company Compagnia Generale Ripreseaeree (http://www.terraitaly.it/) was equipped with specially designed and manufactured PTFE coated trace gas inlet (b).

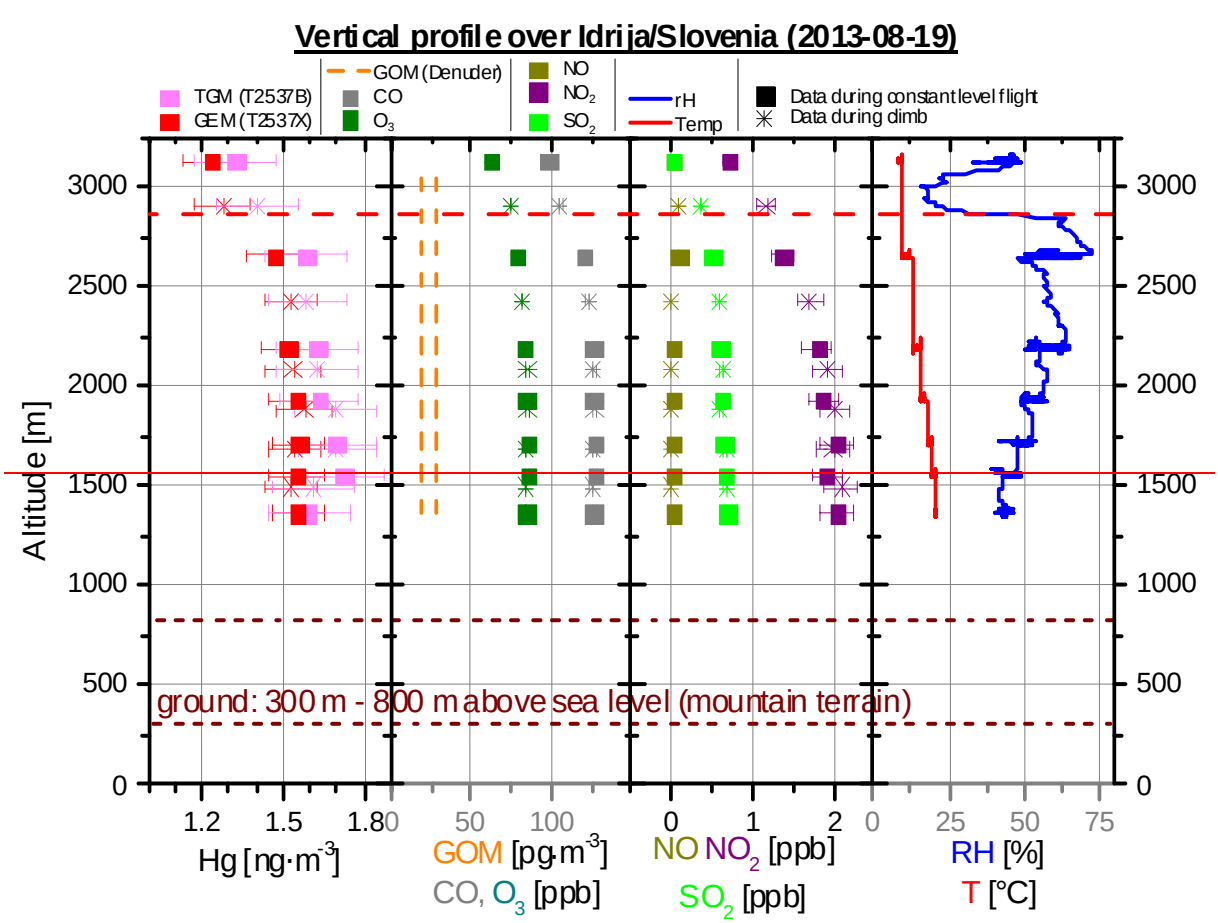

Vertical profile over Iskraba/Slovenia (2013-08-19)
TGM (T2537B)
GEM (T2537X)
GOM (Denuder)
CO
O3
NO
NO2
SO2
rH
Temp
Data during constant level flight
Data during climb
Altitude [m]
ground: 500 m - 700 m above sea level (mountain terrain)
Hg [ng·m-3]
GOM [pg·m-3]
CO, O3 [ppb]
NO NO2 [ppb]
SO2 [ppb]
RH [%]
T [°C]

1

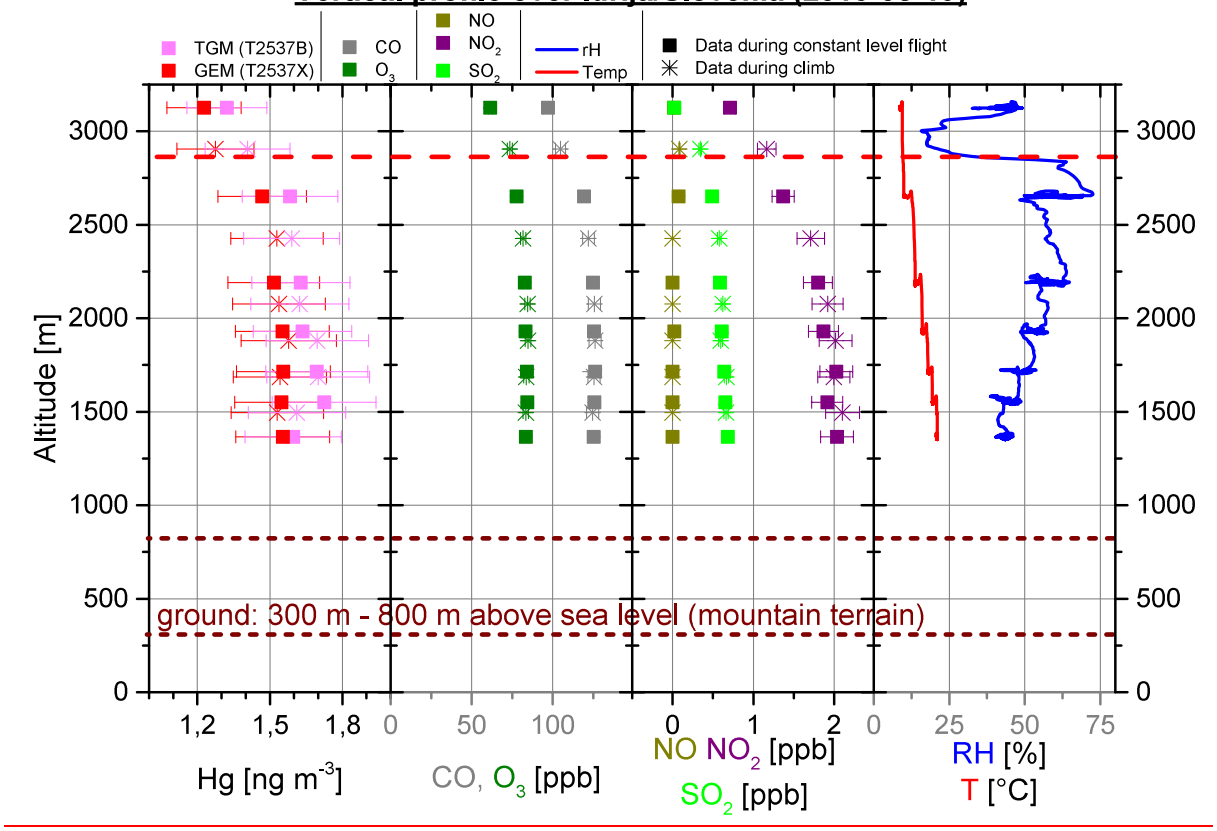

Vertical profile over Iskraba/Slovenia (2013-08-19)
TGM (T2537B)
GEM (T2537X)
CO
O3
NO
NO2
SO2
rH
Temp
Data during constant level flight
Data during climb
Altitude [m]
ground: 500 m - 700 m above sea level (mountain terrain)
Hg [ng m-3]
CO, O3 [ppb]
NO NO2 [ppb]
SO2 [ppb]
RH [%]
T [°C]

2

Figure 3: Vertical profile, measured on 19 August ~~19,~~ 2013 from 13:17:30 to 14:07:30 (local time) over the GMOS master site "Iskraba" (45.561°N, 14.858 °E, elevation: 530 m a.s.l.; mountain terrain). Squares represent 300 s averages with horizontal flight leg; stars indicate 150 s averages during climbing between two neighbouring flight legs. ~~Data indicated as squares are more reliable than the data indicated with stars. GOM was sampled onto a denuder during the whole profile. Two blank measurements were performed at the beginning and at the end of the ETMEP-2 campaign. Therefore the given GOM concentration (high concentration with consideration of low blank and vice versa) is an average over the whole air column.~~ The red dashed line indicates the planetary boundary layer (PBL) top, which is not representative here because all measurements were performed below the boundary layer top. GEM and TGM concentrations are given at standard conditions (p=1013.25 hPa, T=273.15 K).

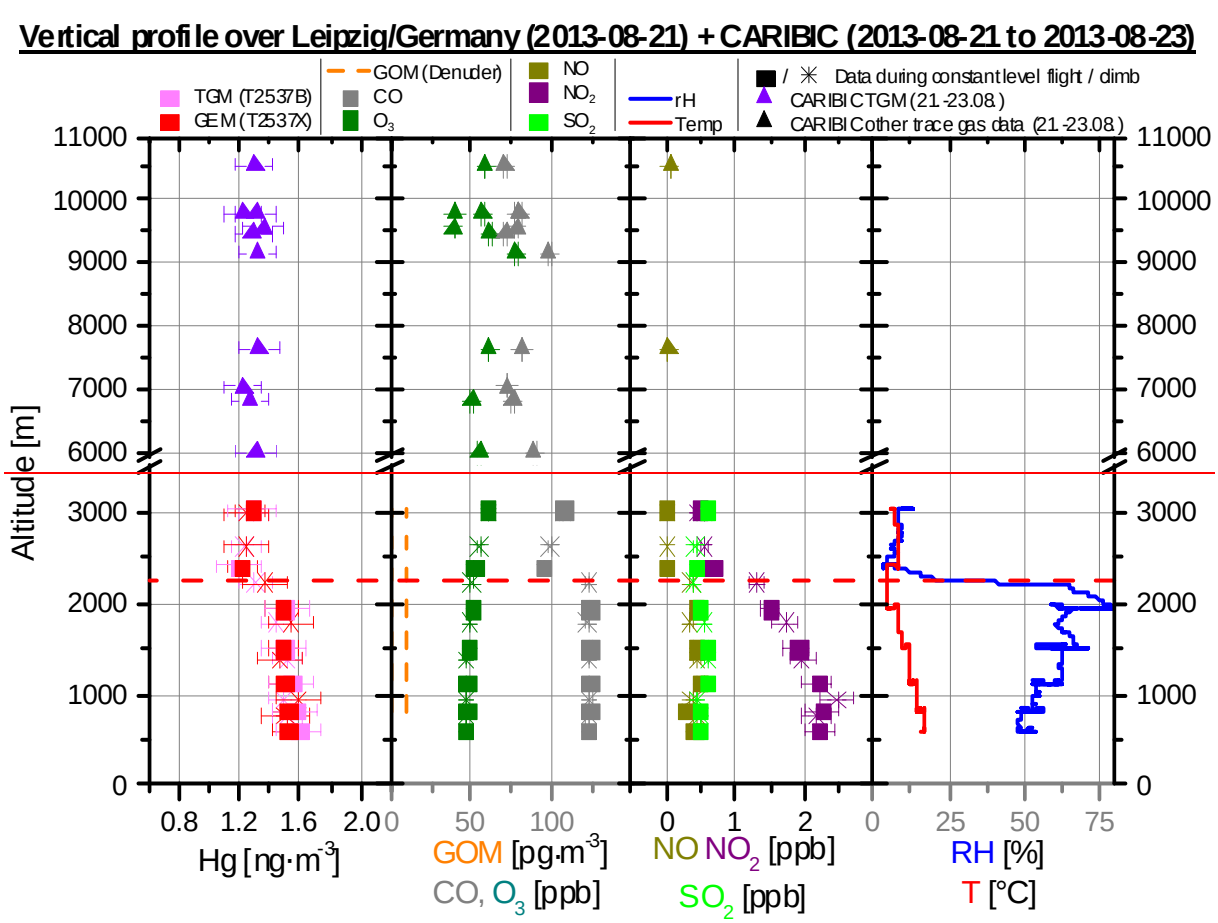

Vertical profile over Idrija/Slovenia (2013-08-19)
TGM (T2537B)
GEM (T2537X)
GOM (Denuder)
CO
O3
NO
NO2
SO2
rH
Temp
Data during constant level flight
Data during climb
Altitude [m]
ground: 300 m - 800 m above sea level (mountain terrain)
Hg [ng·m-3]
GOM [pg·m-3]
CO, O3 [ppb]
NO NO2 [ppb]
SO2 [ppb]
RH [%]
T [°C]

1

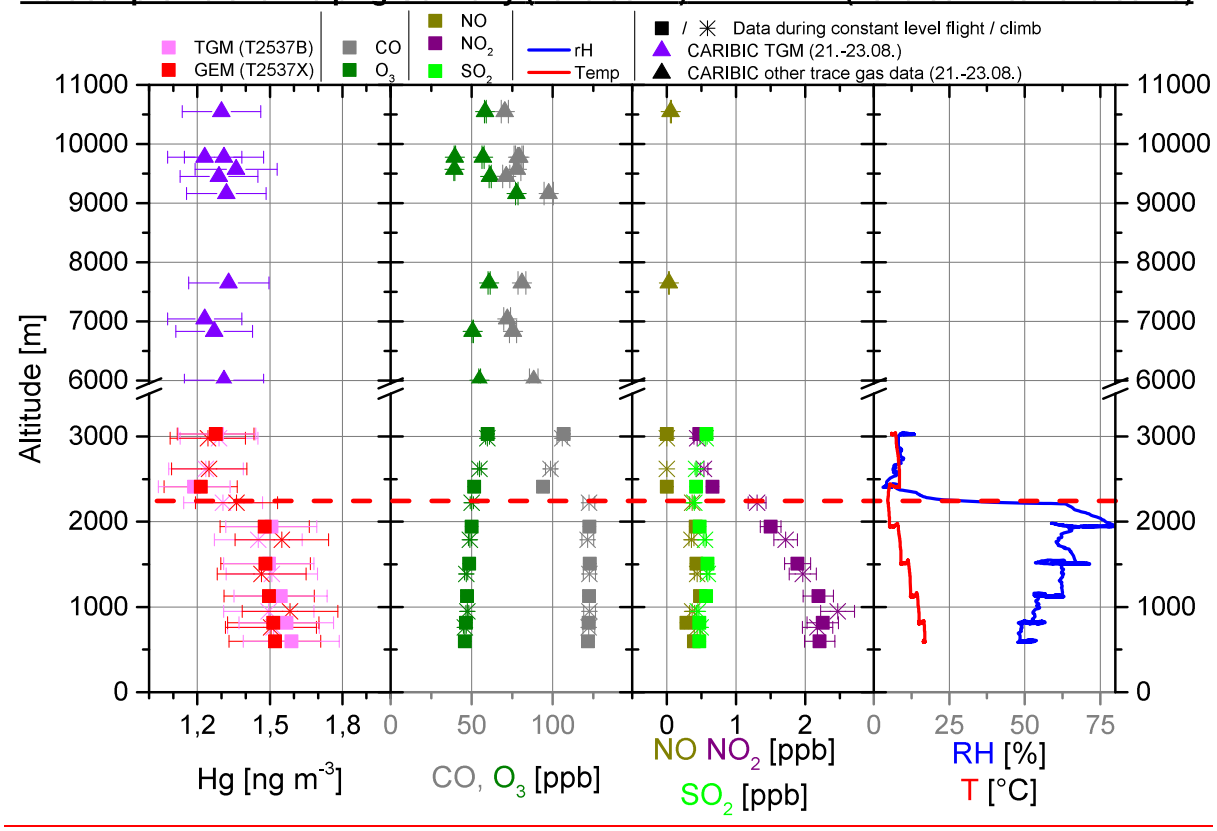

Vertical profile over Idrija/Slovenia (2013-08-19)
TGM (T2537B)
GEM (T2537X)
CO
O3
NO
NO2
SO2
rH
Temp
Data during constant level flight
Data during climb
Altitude [m]
ground: 300 m - 800 m above sea level (mountain terrain)
Hg [ng m-3]
CO, O3 [ppb]
NO NO2 [ppb]
SO2 [ppb]
RH [%]
T [°C]

2

Figure 4: Same as Fig. 3, but for the former mercury mining area “Idrija” (45.000°N, 14.022 °E, elevation: 330 m; mountain terrain up to 800 m). The profile was measured on 19 August ~~19,~~ 2013 from 14:30:00 to 15:20:00 (local time). The PBL top (red dashed line) was determined to be at 2850 to 2900m a.s.l.. TGM and GEM concentrations are given at standard conditions (p=1013.25 hPa, T=273.15 K).

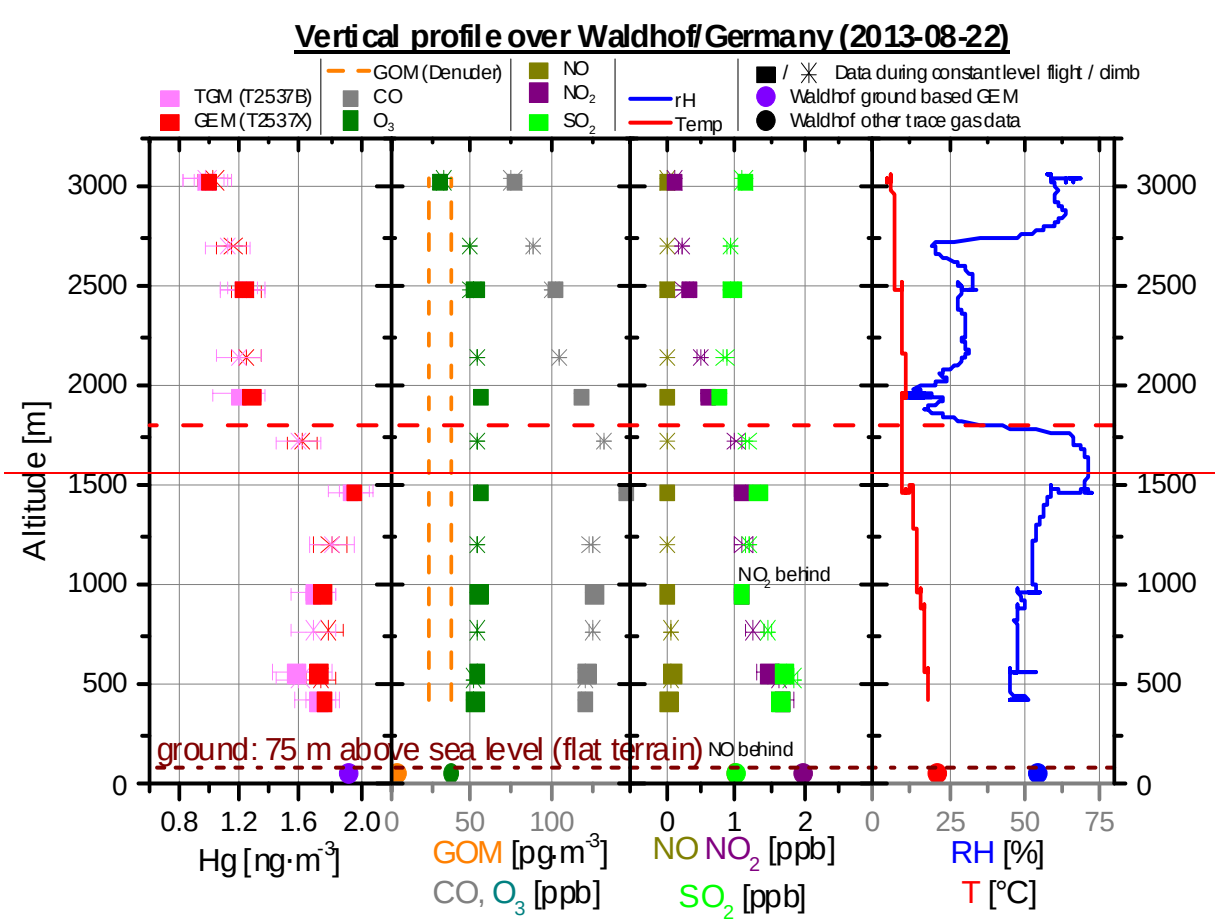

Vertical profile over Leipzig/Germany (2013-08-21) + CARIBIC (2013-08-21 to 2013-08-23)
TGM (T2537B)
GEM (T2537X)
GOM (Denuder)
CO
O3
NO
NO2
SO2
rH
Temp
/ Data during constant level flight / climb
CARIBIC TGM (21.-23.08.)
CARIBIC other trace gas data (21.-23.08.)
Altitude [m]
Hg [ng·m-3]
GOM [pg·m-3]
CO, O3 [ppb]
NO NO2 [ppb]
SO2 [ppb]
RH [%]
T [°C]

1

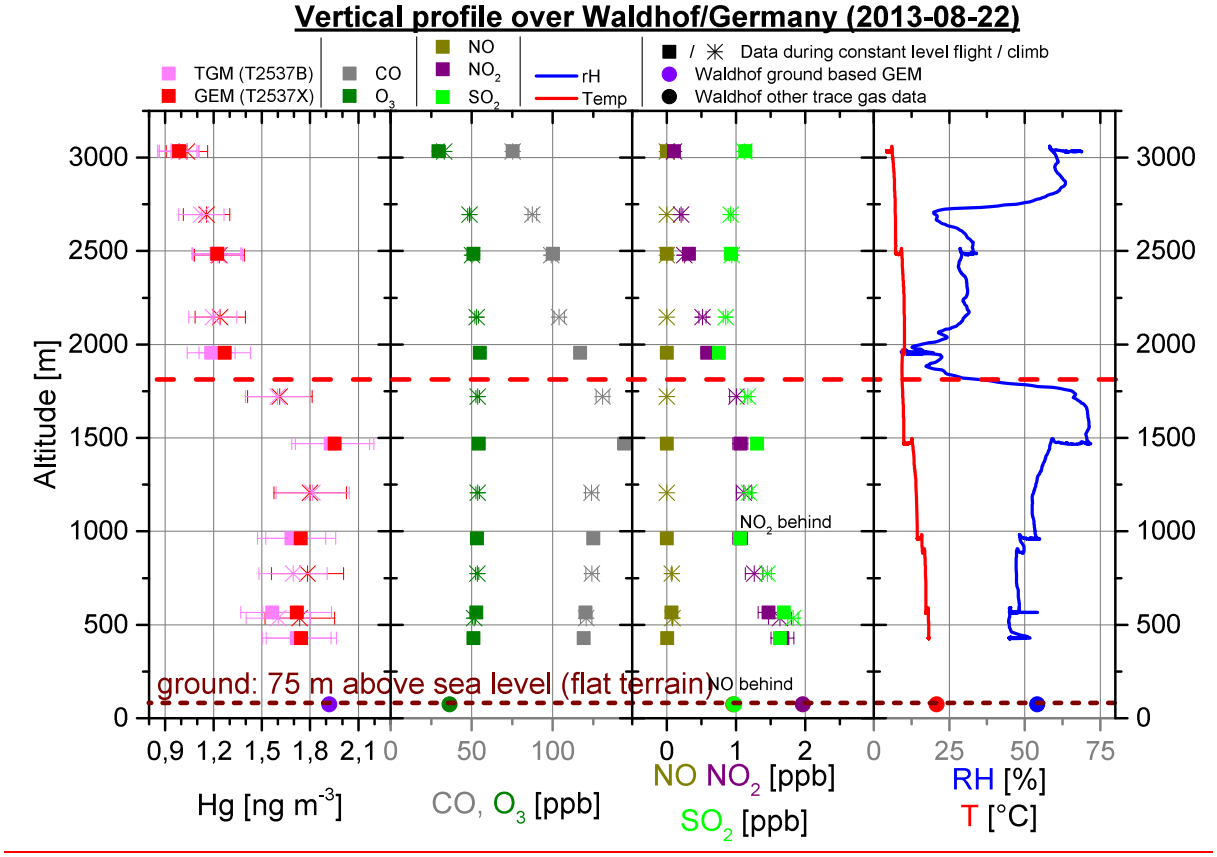

Vertical profile over Leipzig/Germany (2013-08-21) + CARIBIC (2013-08-21 to 2013-08-23)
TGM (T2537B)
GEM (T2537X)
CO
O3
NO
NO2
SO2
rH
Temp
/ Data during constant level flight / climb
CARIBIC TGM (21.-23.08.)
CARIBIC other trace gas data (21.-23.08.)
Altitude [m]
Hg [ng m-3]
CO, O3 [ppb]
NO NO2 [ppb]
SO2 [ppb]
RH [%]
T [°C]

2

Figure 5: Vertical profile, measured within the ETMEP-2 campaign on 21 August ~~21,~~ 2013 from 13:15:00 to 14:07:30 (local time) over the city centre of Leipzig/Germany (51.353°N, 12.434 °E, elevation: 125 m, flat terrain) and from 21-23 August ~~21-23,~~ 2013 over Western Europe (east of 0 °W; CARIBIC). While the ETMEP-2 data were averaged for 300 s (squares) and 150 s (stars), the CARIBIC data (triangles) represent 600 s averages. The plots have the same structure as Fig. ~~4~~3. The PBL top (red dashed line) was determined to be at 2200 to 2250 m a.s.l.. Please note, Y-axis is broken between 3500m and 6000m. TGM and GEM concentrations form ETMEP-2 and CARIBIC measurements are given at standard conditions (p=1013.25 hPa, T=273.15 K).

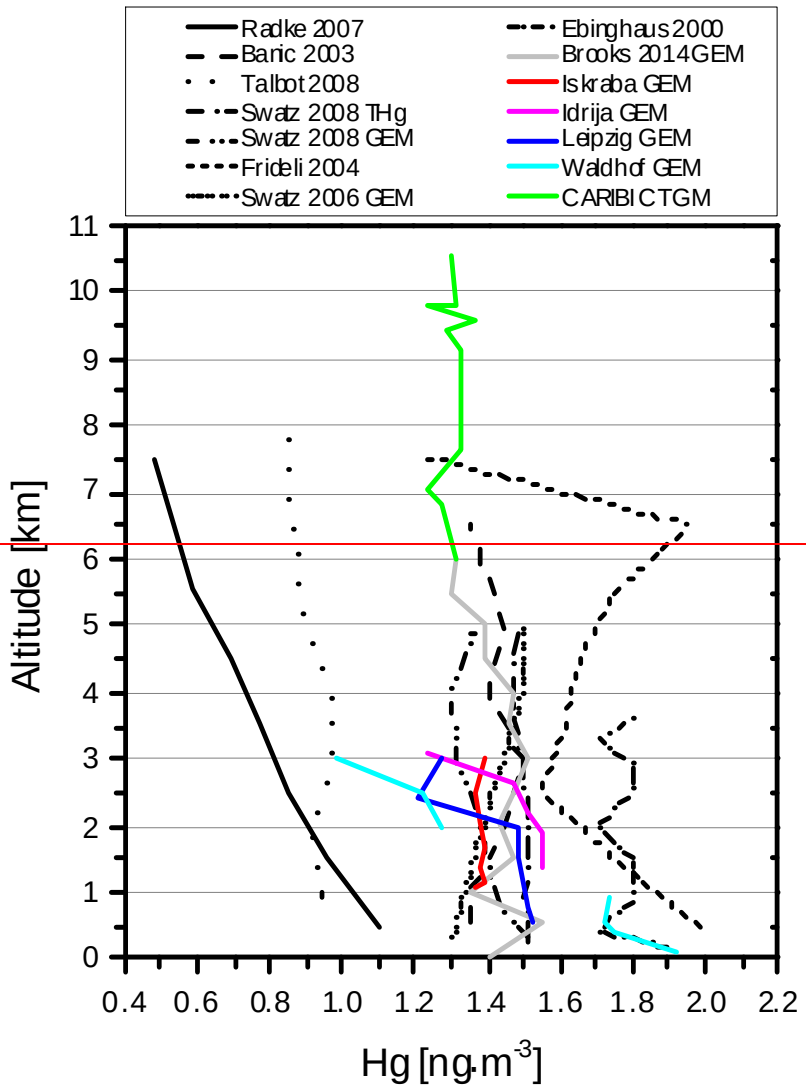

Vertical profile over Waldhof/Germany (2013-08-22)
TGM (T2537B)
GEM (T2537X)
GOM (Denuder)
CO
O3
NO
NO2
SO2
rH
Temp
/ Data during constant level flight / climb
Waldhof ground based GEM
Waldhof other trace gas data
Altitude [m]
NO2 behind
NO behind
ground: 75 m above sea level (flat terrain)
Hg [ng·m-3]
GOM [pg·m-3]
CO, O3 [ppb]
NO NO2 [ppb]
SO2 [ppb]
RH [%]
T [°C]

1


Vertical profile over Waldhof/Germany (2013-08-22)
TGM (T2537B)
GEM (T2537X)
CO
O3
NO
NO2
SO2
rH
Temp
/ Data during constant level flight / climb
Waldhof ground based GEM
Waldhof other trace gas data
Altitude [m]
NO2 behind
NO behind
ground: 75 m above sea level (flat terrain)
Hg [ng m-3]
CO, O3 [ppb]
NO NO2 [ppb]
SO2 [ppb]
RH [%]
T [°C]

2

Figure 6: Same as Fig. ~~4~~3, but over the GMOS master site Waldhof/Germany (52.801°N, 10.756 °E, elevation: 75 m, flat terrain). The profile was measured on 22 August ~~22,~~ 2013 from 10:22:30 to 11:17:30 (local time). The PBL top (red dashed line) was determined to be at 1750 to 1850 m a.s.l.. Additionally the data measured at the same time at the ground based site "Waldhof" are plotted. TGM and GEM concentrations are given at standard conditions (p=1013.25 hPa, T=273.15 K).


Radke 2007
Baric 2003
Talbot 2008
Swatz 2008 THg
Swatz 2008 GEM
Frideli 2004
Swatz 2006 GEM
Ebinghaus 2000
Brooks 2014GEM
Iskraba GEM
Idrija GEM
Leipzig GEM
Waldhof GEM
CARIBIC TGM
Altitude [km]
Hg [ng.m-3]
0
1
2
3
4
5
6
7
8
9
10
11
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2

1

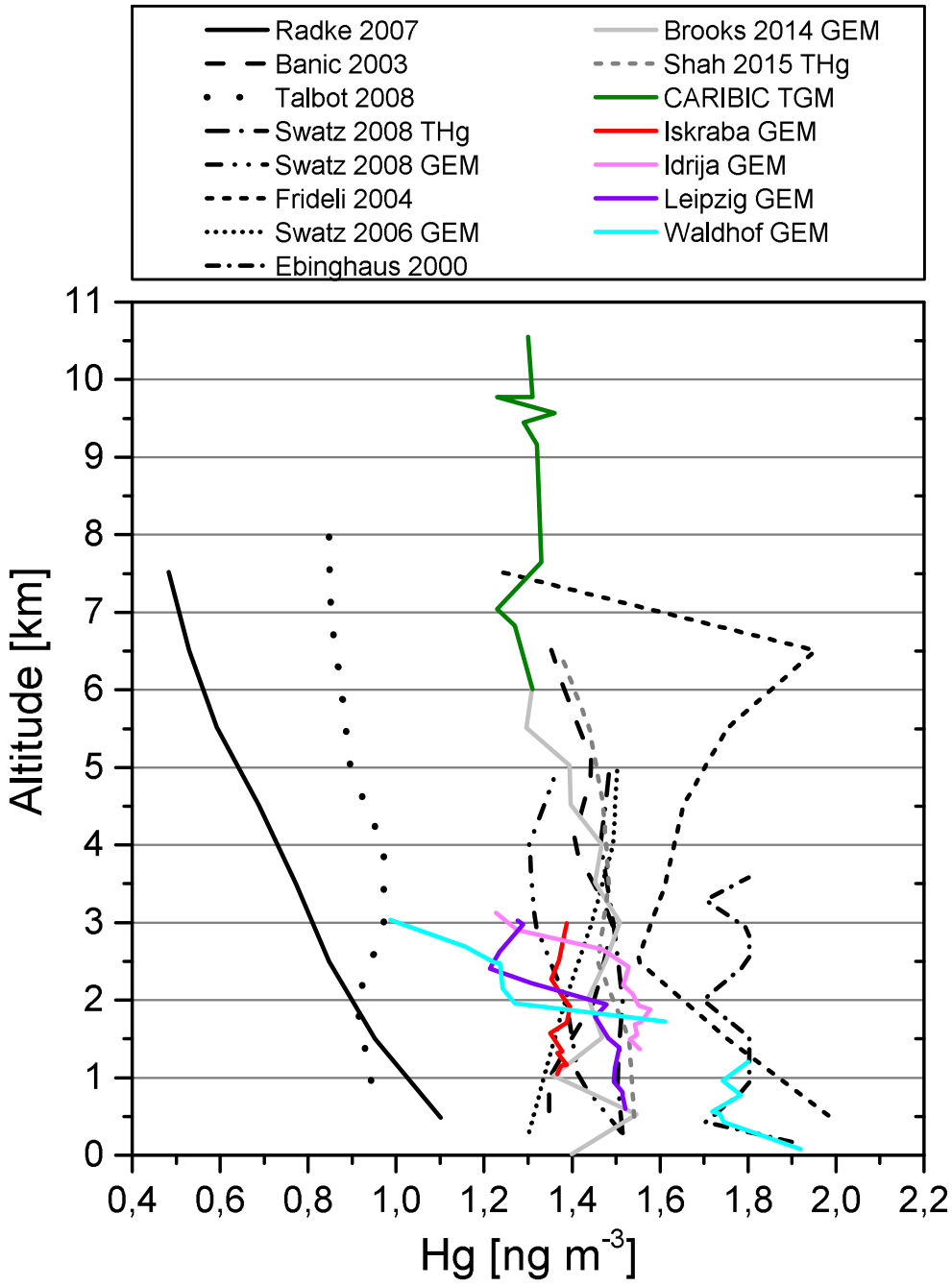


Figure 7: Comparison of known vertical gaseous mercury profiles (THg, TGM and GEM). Data plotted in black were taken from ~~Swatzendruber~~Swartzendruber et al., (2009). Data in grey represent the August measurement from Brooks et al., ~~(2014).~~(2014) and the averaged data from Shah et al., (2015). Coloured data represent ETMEP-2 data (Fig. 3-6). The Waldhof 1.47 km ~~fight~~flight leg average was removed for this plot, because ~~of~~it was probably measured inside a plume ~~measurement~~of polluted air (cf. discussion to Fig. 6).