Atmos. Chem. Phys. Discuss., 15, C12538–C12542, 2016
www.atmos-chem-phys-discuss.net/15/C12538/2016/

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.

andreas.weigelt@bsh.de

Received and published: 19 February 2016

Reply to comments of anonymous Referee #1

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-3Âň, the resulting uncertainty for GOM from the difference method would be ∼200 pg m-3Âň (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 ($\sim$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 SO2 (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 SO2 (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."

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.