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

A. Weigelt[1,*], R. Ebinghaus[1], N. Pirrone[2], J. Bieser[1,3], J. Bödewadt[1], G. Esposito[2], F. Slemr[4], P.F.J. van Velthoven[5], A. Zahn[6], and H. Ziereis[3]

[1] {Helmholtz-Zentrum Geesthacht (HZG), Institute of Coastal Research, Geesthacht, Germany}

[2] {National Research Council (CNR), Institute of Atmospheric pollution Research, Rende, Italy}

[3] {Deutsches Zentrum für Luft- und Raumfahrt (DLR), Institute of Atmospheric Physics, Oberpfaffenhofen, Germany}

[4] {Max-Planck-Institute for Chemistry (MPI-C), Department of Atmospheric Chemistry, Mainz, Germany}

[5] {Royal Netherlands Meteorological Institute (KNMI), Chemistry and Climate Division, De Bilt, Netherlands}

[6] {Karlsruhe Institute of Technology (KIT), Institute of Meteorology and Climate Research, Karlsruhe, Germany}

[*] {now at: Federal Maritime and Hydrographic Agency (BSH), Hamburg, Germany}

Correspondence to: A.Weigelt (Andreas.Weigelt@bsh.de), R. Ebinghaus (Ralf.Ebinghaus@hzg.de)

Abstract

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) and total gaseous mercury (TGM) was measured with Tekran 2537X and Tekran 2537B 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 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 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).

1 Introduction

Mercury and its compounds are very toxic and, therefore, hazardous for human health and the environment (Selin, 2009). 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 (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 2015 only seven campaigns performed airborne mercury measurements over Europe. Apart from the CARIBIC measurements (Civil Aircraft for the

Regular Investigation of the atmosphere Based on an Instrument Container, 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) focused on volcanic emissions and no vertical profile was measured. CARIBIC measurements focus on the tropopause region and 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 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 2001. In the Swartzendruber et al. (2009) summary, a paper by Ebinghaus and Slemr (2000) represents the only European vertical profile. 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 GEM concentrations in the planetary boundary layer (PBL; ground to 1-3 km) were found to be the similar as in the lower free troposphere (FT). As mercury is emitted by sources on the 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, which focused on vertical profile measurements over central Europe.

2 Measurement location and methodology

From 19 to 22 August 2013, five ETMEP-2 measurement flights were carried out over central Europe (Fig. 1). After take-off on 19 August 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, 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 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 in the early afternoon over the Leipzig city-centre. With the fourth measurement flight on 22 August (take-off in Leipzig), the fifth vertical profile was flown in the 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 vertical profile downwind of the Lippendorf coal fired power plant will be discussed in a separate paper (Weigelt et al., 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, being representative for the transitory situation at a certain measurement location. The campaign was performed with a CASA 212 two engine turboprop aircraft (Fig. 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 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 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 nozzles with smaller or larger ones, this inlet system 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 PTFE and only PFA tubes 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 synchronized using individual instrument lag and response time.

For the campaign the aircraft was equipped with two mercury measurement instruments, a Tekran 2537B and a Tekran 2537X (cf. Tab. 2). 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 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. 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 (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 (Zahn and Brenninkmeijer, 2003). Increased NO_x (NO + NO_2) mixing ratio can indicate combustion plumes (Ambrose et al 2015; Weigelt et al., 2016), too. Usually FT air is dryer than PBL air (Spencer and Braswell, 1996) and, therefore, the RH measurements can distinguish these two air masses. 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/). 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). 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) 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, 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 level was 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 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 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. 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 at higher altitudes. In general the measurements thus showed that the air over Iskraba was well mixed within the PBL.

After the flight over Iskraba 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 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. 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 1.3 ng m^{-3} and TGM 1.4 ng m^{-3}).

On 21 August, 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 (Weigelt et al., 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 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 21 to 23 August 2013, additionally four CARIBIC 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 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 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, 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 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 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 TGM gradient in the entire FT over Central Europe. Inside the PBL the GEM and TGM concentration 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 (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 2013 over the GMOS master site "Waldhof" (Fig. 6). 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. 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 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, 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. The Waldhof three-year-average (2009-2011) GEM concentration is 1.61 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.

4 Conclusions

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 ~ 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 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 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}.

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 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 (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	• 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	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; O_3 = ozone; SO_2 = sulphur dioxide; NO = nitric oxide; NO_2 = nitric dioxide.

Parameter	**Instrument name**	**Temporal resolution**	**Uncertainty**	**Lower detection limit**
GEM	Tekran: 2537X (with upstream quartz wool trap)	150 s	± 12.5% of reading	0.1 ng m^{-3}
GEM + unknown amount of GOM[a]	Tekran 2537B	150 s	± 12.5% of reading	0.1 ng m^{-3}
CO	Aero Laser AL5002	1 s	±3% of reading	1.5 ppb
O_3	Teledyne API 400A	10 s	±2% of reading	0.6 ppb
SO_2	Thermo: 43C Trace Level	10 s	±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.

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

Figures

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.

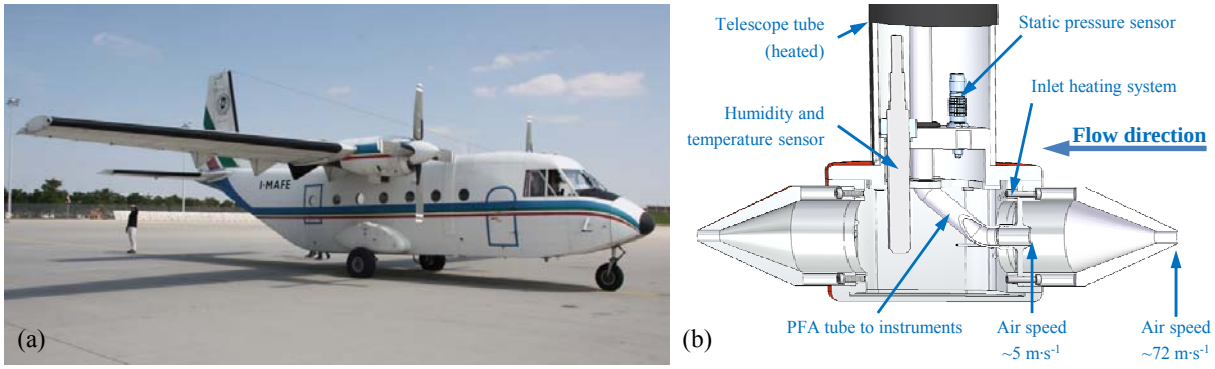

Figure 2: For the ETMEP-2 campaign in August 2013 the CASA 212 (a) from the Italian company Compagnia Generale Ripreseaeree (http://www.terraitaly.it/) was equipped with specially designed and manufactured PTFE coated trace gas inlet (b).

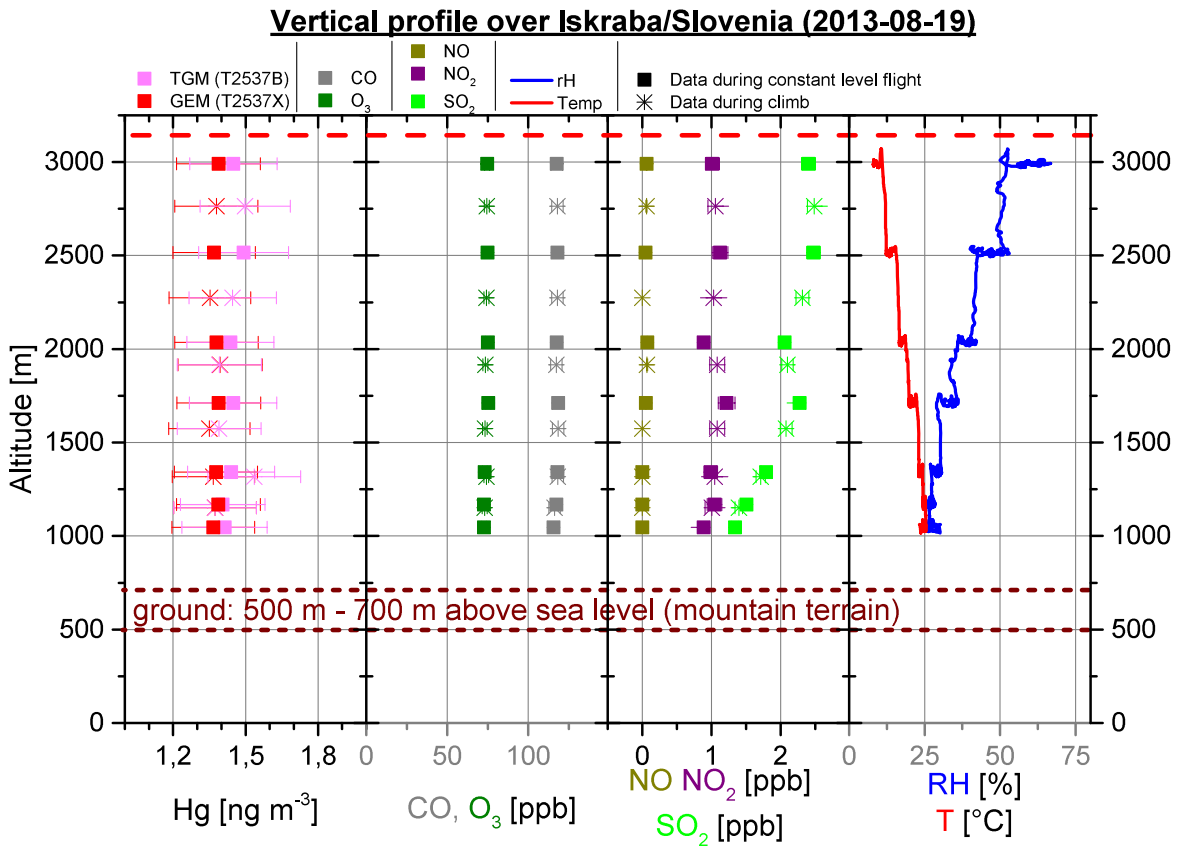

Figure 3: Vertical profile, measured on 19 August 2013 from 13:17:30 to 14:07:30 (local time) over the GMOS master site "Iskraba" (45.561°N, 14.858 °E, elevation: 530 m a.s.l.; mountain terrain). Squares represent 300 s averages with horizontal flight leg; stars indicate 150 s averages during climbing between two neighbouring flight legs. 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).

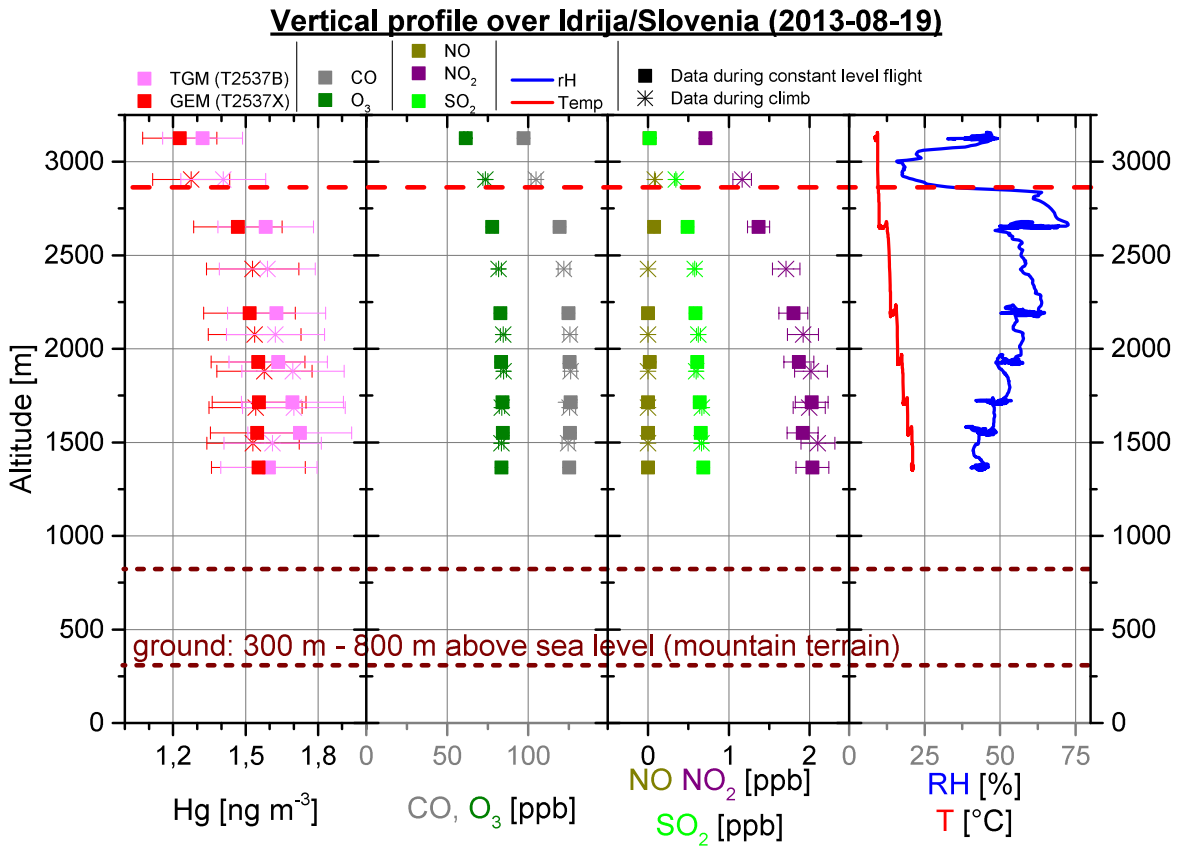

Figure 4: Same as Fig. 3, but for the former mercury mining area "Idrija" (45.000°N, 14.022 °E, elevation: 330 m; mountain terrain up to 800 m). The profile was measured on 19 August 2013 from 14:30:00 to 15:20:00 (local time). The PBL top (red dashed line) was determined to be at 2850 to 2900m a.s.l..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

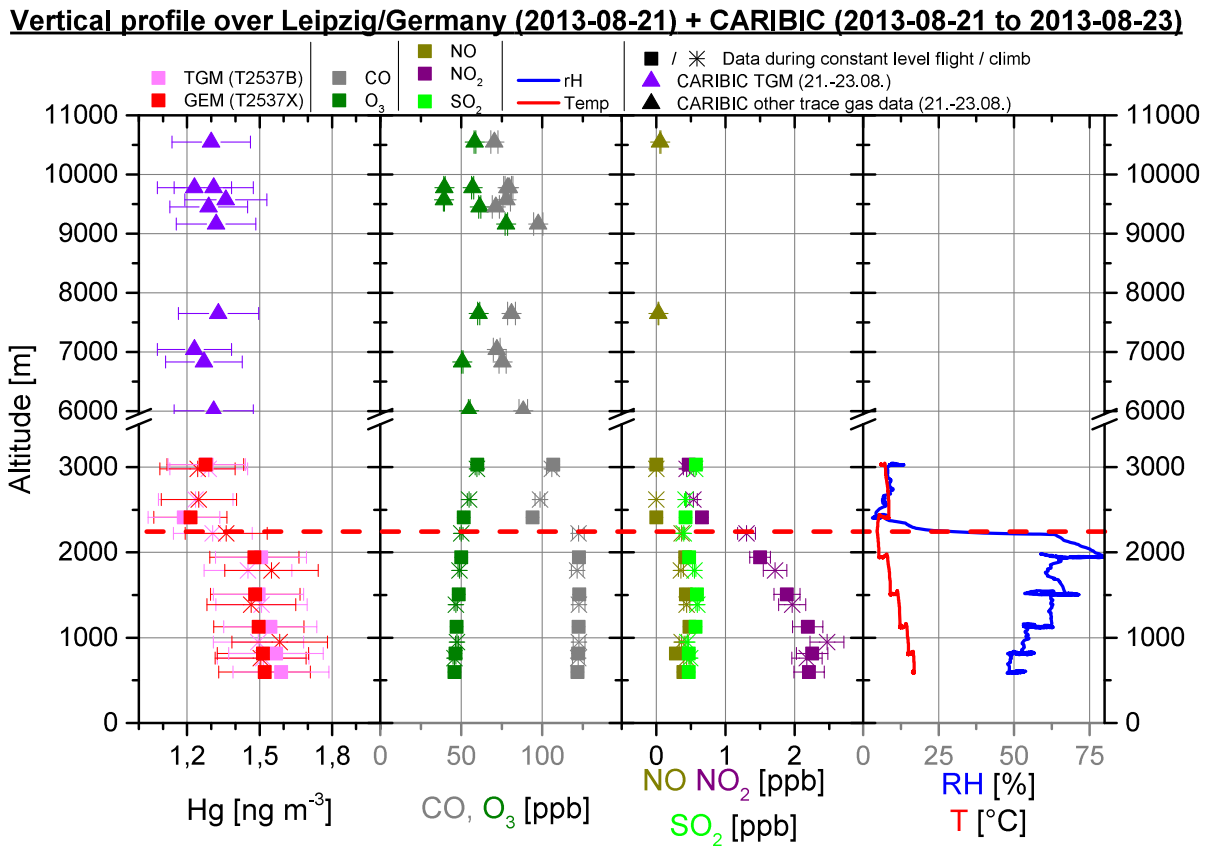

Figure 5: Vertical profile, measured within the ETMEP-2 campaign on 21 August 2013 from 13:15:00 to 14:07:30 (local time) over the city centre of Leipzig/Germany (51.353°N, 12.434 °E, elevation: 125 m, flat terrain) and from 21-23 August 2013 over Western Europe (east of 0 °W; CARIBIC). While the ETMEP-2 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. 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).

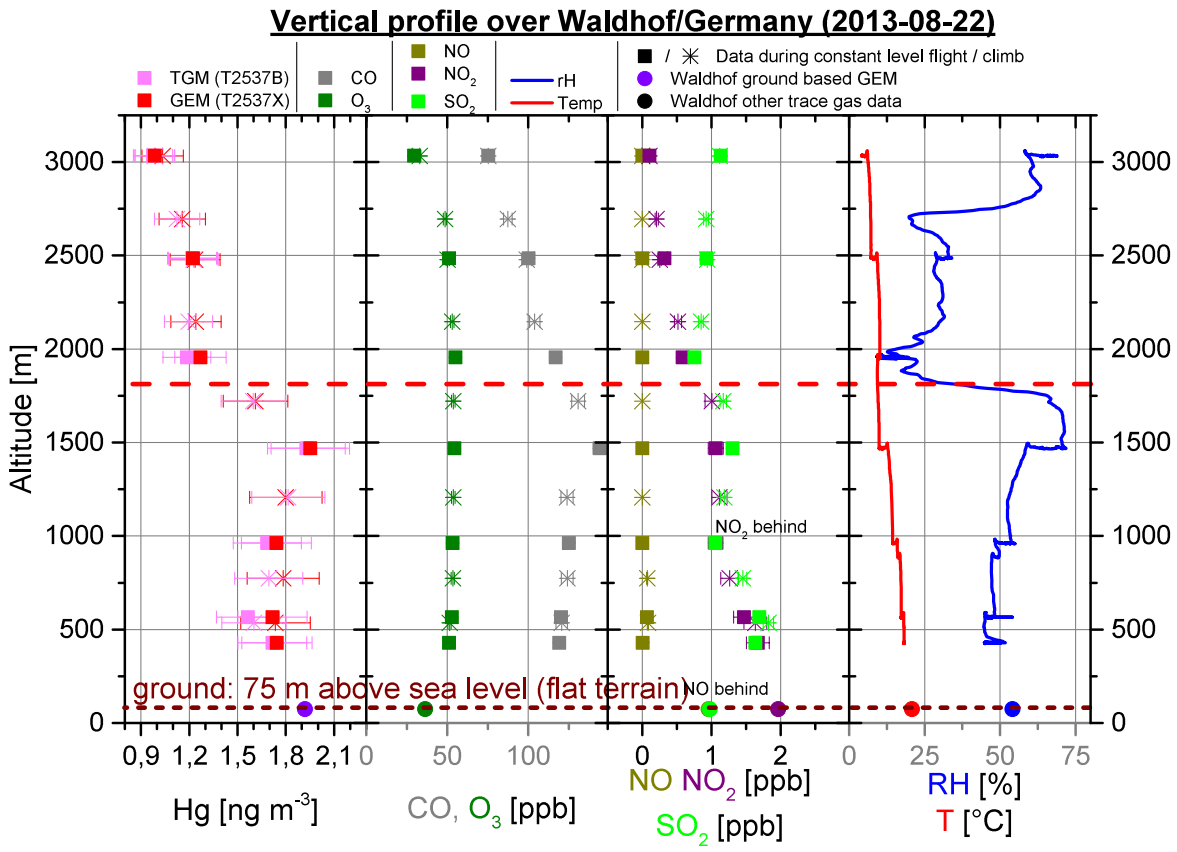

Figure 6: Same as Fig. 3, but over the GMOS master site Waldhof/Germany (52.801°N, 10.756 °E, elevation: 75 m, flat terrain). The profile was measured on 22 August 2013 from 10:22:30 to 11:17:30 (local time). The PBL top (red dashed line) was determined to be at 1750 to 1850 m a.s.l.. Additionally the 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).

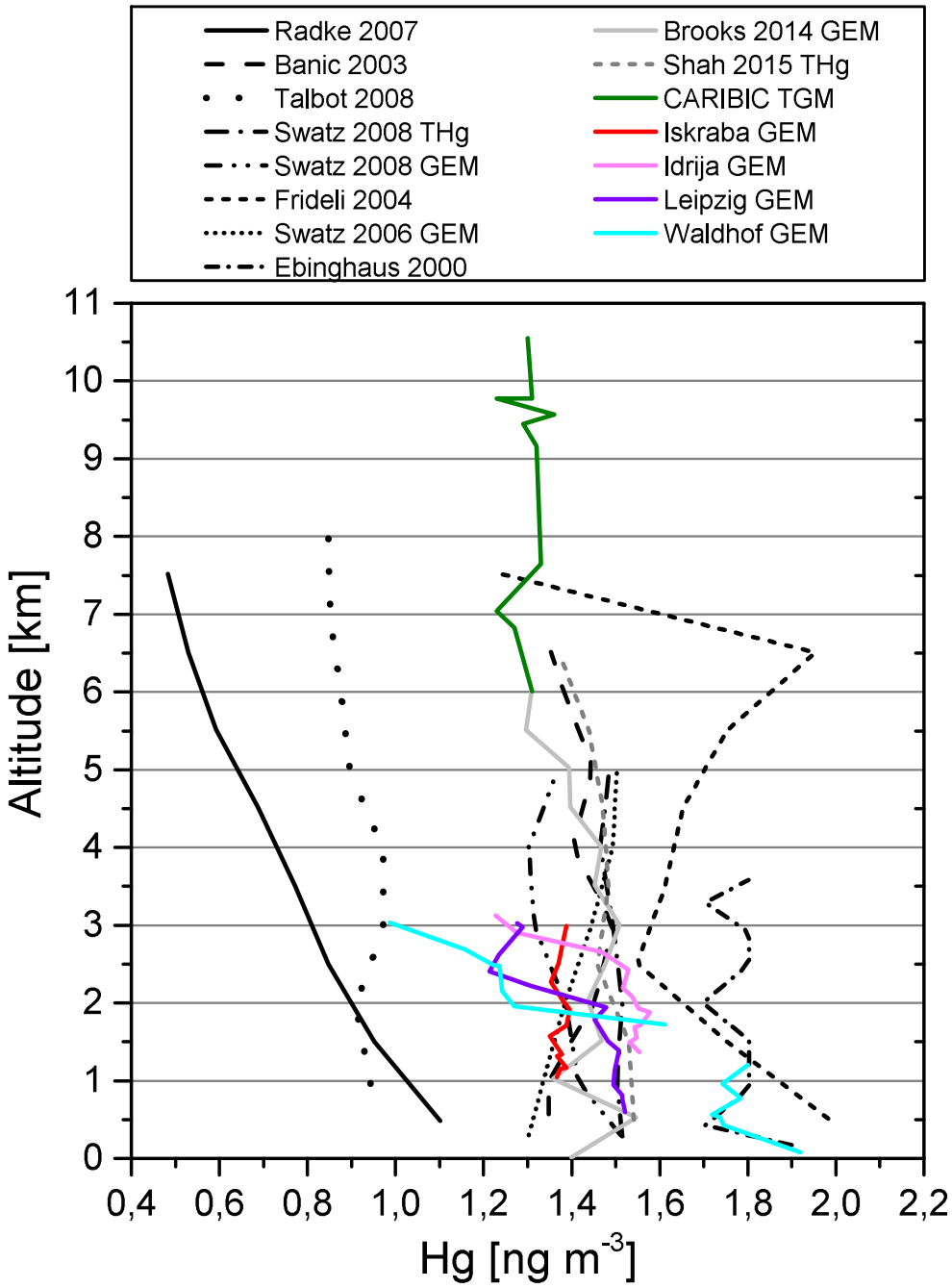

Figure 7: Comparison of known vertical gaseous mercury profiles (THg, TGM and GEM). Data plotted in black were taken from Swartzendruber et al., (2009). Data in grey represent the August measurement from Brooks et al., (2014) and the averaged data from Shah et al., (2015). Coloured data represent ETMEP-2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