Atmos. Chem. Phys. Discuss.,
doi:10.5194/acp-2016-526-RC1, 2016

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Airborne mercury species at the Råö background monitoring site in Sweden: Distribution of mercury as an effect of long range transport" *by* Ingvar Wängberg et al.

Anonymous Referee #1

Received and published: 5 July 2016

Review of acp-2016-526 "Airborne mercury species at the Råö background monitoring site in Sweden: Distribution of mercury as an effect of long range transport"

Overview: The submitted manuscript deals with the measurement and analysis of speciated mercury measurements, performed in two periods between 2012 and 2015 at Råö which is a background site in southern Sweden. For the speciation measurements a Tekran 1130/1135 unit and a Tekran 2537 mercury analyzer was used. The measurements were carried out within the Global Mercury Observation System (GMOS) Project. The analysis of the measurement data focus on the comparison to other European measurements, seasonality, and air mass origin. Within different national and international measurement programs (e.g. AMNet, CAMNet, GMOS,. . .) many mercury

Printer-friendly version

Discussion paper

measurements were made all over the world using equal measurement technique and similar data analysis. Therefore the innovation, new/unique technique or new findings are missing somehow. Nevertheless, the presented dataset is important and should be considered for publication, because it represents the second longest mercury speciation dataset in Europe. This means the dataset will be of high interest for future mercury model studies to validating regional and global atmospheric chemistry transport models. However, there are some substantial limitations of the dataset and some clarification is needed before considering for publication:

General comment:

On Page 3 Line 30 and Page 4 line 11 and 12 the lower detection limits are given to be 0.014 ng m-3 for GEM (sampling time of 5 min with 1 l/min), 0.11 pg m-3 for PBM and 0.23 pg m-3 for GOM (both with sampling time of 180 min with 10 l/min). According to Swatzendruber et al., 2009 (Atmos. Environ., 43, 3648–3651) and Slemr et al., 2016 (ACP, doi: 10.5194/amt-9-1-2016) the Tekran analyzers have significant problems with the internal raw data dump peak integration when the total amount of mercury on the gold traps is below 2 pg. In fact the Tekran internal peak integration underestimates the measured concentration by about 20% when the mercury load is 2 pg and by > 40% when the mercury load is 1 pg (exponential increase; see Fig. 3 in Slemr et al., 2016). The detection limits given in the reviewed manuscript represent mercury loads of 0.07 pg for GEM, 0.2 pg for PBM and 0.4 pg for GOM. Assuming a minimum lower mercury load of 2 pg and the flow rates and sampling times given in the manuscript would result in lower detection limits of 0.4 ng m-3 for GEM and 1.1 pg m-3 for PBM and GOM (all still with an uncertainty of 20%). Considering this, the GOM mean given in Table 1 would be below the detection limit. The good news is that if the raw data dump is available, this error can be corrected/avoided. Did the authors record the Tekran 2537 raw data dump and checked for correct peak integration of the Tekran internal integration algorithm in case of low concentration? If so, did they reanalyzed the data using an external integration algorithm? If not, would it be possible to check the unit

for underestimation of the mercury concentration as a function of mercury load on the traps and to correct the data (like in Slemr et al., 2016)?

Specific comments:

P1 L8 to P2 L2: The statements in the introduction should be underlined with some literature concerning properties of Hg, atmospheric specification, lifetime, deposition, transformation, environmental- and health effects.

P2 L4-6: According to Pirrone et al. 2010 (doi:10.5194/acp-10-5951-2010) and Song et al., 2015 (doi:10.5194/acp-15-7103-2015) coal combustion is the biggest anthropogenic Hg source. It is recommended to change order to importance of source and cite the above mentioned papers, too.

P2 L31: What is the definition of a "real" background site? Dose this imply that the other measurement sites in GMOS, AMNet, CAMNet are no real background sites? This statement is in contrast to a statement in the conclusions (P7 L24).

P2 L31 to P3 L1: Even more important than the wind speed is the main wind direction.

P3 L19-30: The Tekran 1130/1135 setup was already described in many publications and the instrument manual. So this description can be shortened by mention the measurement units, give the setup for the temporal resolution and for the interested reader link to the manual and/or further studies.

P4 L10: Not only the lower detection limit, but also an estimation to the measurement accuracy of GEM, GOM and PBM should be given. As the installation and analysis algorithm is probably similar to those described in Weigelt et al. 2013, the authors could adopt this estimation. However, Gustin et al., 2013 (Do we understand what the mercury speciation instruments are actually measuring? Results of RAMIX, Environ. Sci. Technol., 47, 7295–7306) and Gustin et al., 2015 (Measuring and modeling mercury in the atmosphere: a critical review, Atmos. Chem. Phys., 15, 5697–5713, doi:10.5194/acp-15-5697-2015) should be considered, too.

Printer-friendly version

Discussion paper

P4 L14-20: As trajectory calculations are used in several papers and are a quite common way to check of air mass origin, in my opinion there is no need to motivate and introduce trajectory calculations in general. Just as a suggestion, this section could start with something like “Three day back trajectories were calculated to derive information on transport path and potential sources of the air mases measured at Råö. For the calculation the Hybrid Single-Particle. . .continue line 21” If the time information (three day backward) is shift to the beginning of the section, the sentence on L 20-31 can be skipped.

P5 L1: This section should contain a short statement on the uncertainty of the trajectories, too. For example the authors could give a rough estimation what was the average difference between the trajectories starting at 10, 50, 100, 250, and 500 m (e.g. what was the horizontal difference in the trajectory end points).

P5 L16: It is mentioned Mace Head is a GMOS site, too and according to the GMOS web page the measurements are ongoing. So the authors could also compare the same period.

P5 L16-21: The 1 σ standard deviation given in Tab. 1 is much higher than the difference in the average data. The measurement uncertainty should be somewhat smaller than 1 σ (I guess something between 10 and 20%), but even higher than the difference. Considering the measurement uncertainty, Råö, Mace Head, Aucgencort Moss, and Harwell are equal.

P5 L22-24: Please consider the general comment to the lower detection limit. According to Fig. 3 in Slemr et al., 2015, GOM might be underestimated by more than 30% (average) and 60% (median). If the low GOM concentrations at Råö are real, the authors could additionally discuss why the average GOM is four times the median but for PBM the average is only 60% higher. Furthermore it is interesting the GOM/PBM ratio is more or less similar at Råö, Aucgencort Moss, and Waldhof.

P6 L30-32: Not necessarily influenced by anthropogenic emissions, could be also nat-

ural emissions. Or did the authors measure additional tracers, indicating an anthropogenic origin (e.g. SF6)? The authors should consider also a seasonal changing planetary boundary layer (PBL) height. During summer the height of the PBL and therefore the mixing volume is higher than during summer.

P7 L1: According to the above given general comment during winter GOM might be underestimated.

P7 L6: "proposed earlier" → Where? In 3.2 the authors just mention other regions but not the free troposphere

P7 L9: cloud droplets and aerosol particles

P7 L12-14: Did the trajectory analysis confirmed that air masses with elevated GOM came from the free troposphere, whereas air masses with low GOM traveled inside the PBL all the time? In principle during summer GOM could be formed also in the local PBL around the measurement station. The authors can check this by plotting a daily cycle for the summer month. A three hour sampling interval and six samples a day should roughly resolve a daily cycle when averaging all summer data. If a maximum at noon/early afternoon is visible, it is probably local production because transport from the free troposphere would take several hours and therefore no maximum would be expected at noon/early afternoon.

P7 L24: If all investigated mercury species have direct anthropogenic component, in contrary to the statement on P2 L31 Råö is not a real background station.

P7 L25: "...regarding GEM,..." Looking on Fig. 3b,c and Fig 4a,b the difference is even more pronounced for PBM. The increase is around 10 to 20% for GEM, but 100 to 200% for PBM. So the sentence should be: "This is especially true for PBM,..."

P7 L28: The authors should be more precise what did they mean with small particles (e.g. smaller 10, 100, 1000 nm; or nucleation mode, Aitken mode, accumulation mode coarse mode particles).

P7 L30 to P8 L1: As indicated in a previous comment, it is recommended to test this assumption by analyzing the GOM measurements for the presence of a daily cycle in summer. Are there any tracers available, indicating the air was coming from the free troposphere (low rH, low aerosol concentration,. . .)? If not, at least a statement should be made that the trajectory analysis showed that high GOM concentrations were linked to free tropospheric air origin (was not stated before).

P8 L1-2: The meaning of this sentence is not clear. Do the authors mean that these are the first measurements in Northern Europe giving evidence that GOM is formed in the free troposphere? Did ground based and airborne measurements in other regions observed a similar behavior of GOM (e. g. at other (high elevated) GMOS sites, or studies on vertical distribution of GOM by Lyman and Jaffe 2012, Nature Geosci., 5, 114–117, 2012, and Brooks et al., 2014; Atmosphere, 5, 557–574)?

Table 1: On page 5 Line 30 it is written that 50% of the GOM measurements were below the detection limit. How did the authors consider measurements below the detection limit for the median/average calculation? Please explain in the text. For Waldhof the authors give only the median and for Aucgencort Moss and Harwell only the average concentration. Would it be possible to calculate median and average for all stations?

Technical comments:

P1 L8: “to the” instead of “tot the”

P1 L9: "were" instead of "was"

P2 L13-14: Framework Program (FP7)

P3 L5: were instead of was

P3 L6: please define acronym CVAFS

P3 L12: upstream instead of up streams

P4 L31: “Six such back trajectories were calculated. . .” maybe better “Six back trajec-

tory ensembles were calculated. . .”

P5 L4: acronym VBL needs to be defined

P6 L9: Fig. 3a should be Fig 3b

P6 L17: maybe better write “in air from the south east sector” instead of “in the south east sector”

P6 L18: maybe better write “in the air from south east” instead of “in the south east”

P12 Figure 1a: I’m not sure it is necessary to show the 1130/1135 flow chart, as it is a standard instrument and the flow chart is given in the manual. If the authors want to show the flow chart, at least a link to the source of the graph is needed. HgP should be PBM, because in the text only PBM is used.

P12 Figure 1b: To have a more professional look, the 3d effect with round reflecting edges should be avoided. More space between a) and b) is needed.

P14 Fig 4: It is recommended to avoid the color changeover in the individual columns. Instead two different colors should be used to differ between background air and polluted air. The labeling at the x-axis in a), b), and c) is not correct: Januari and Februari should be January and February. If the y-scale in Fig. a) starts at 1 ng m-3, the seasonality would be better to see.

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-526, 2016.