Airborne mercury species at the Råö background monitoring site in Sweden: Distribution of mercury as an effect of long range transport

Ingvar Wängberg[1], Michelle G. Nerentorp Mastromonaco[2], John Munthe[1], Katarina Gårdfeldt[2]

[1]IVL Swedish Environmental Research Institute, Gothenburg, 41133, Sweden
[2]Department of Chemistry and Chemical engineering, Chalmers University of Technology, Gothenburg, 41296, Sweden

Correspondence to: Ingvar Wängberg (ingvar.wangberg@ivl.se)

Abstract. Within the EU project, Global Mercury Observation System (GMOS) airborne mercury have been monitored at the background Råö measurement site on the west coast of Sweden from mid May 2012 tot the beginning of July 2013 and from the beginning of February 2014 to the end of May 2015. The mercury concentrations measured at the Råö site was found to be low in comparison to other comparable European measurement sites. A back trajectory analysis to study the origin of air masses reaching the Råö site was performed. Due to the remotely location of the Råö measurement station it receives background air most of the time. However, elevated concentrations with air masses coming from especially the south east are noticeable. Evidence for formation of gaseous oxidised mercury (GOM) in background free tropospheric air is presented.

Keywords: GMOS, Gaseous elemental mercury (GEM), Particulate bound mercury (PBM), Gaseous oxidised mercury (GOM)

1 Introduction

Mercury (Hg) is a poisonous metal which occurs in the Earth's crust at low concentrations, primarily in the form of the mineral cinnabar (HgS, i.e. mercury sulphide). The metal is unique in many ways as it has a lower melting point (-39°C) and a lower boiling point (357°C) than any other metal. This means that mercury is volatile at room temperature and may occur as Gaseous Elemental Mercury (GEM), i.e. as Hg atoms, in the atmosphere. Other than the noble gases, mercury is the only element which occurs as an atomic gas at normal temperatures. Airborne mercury largely consists of GEM (> 98 percent) and small quantities of Gaseous Oxidised Mercury (GOM), i.e. divalent gaseous mercury species, as well as Particulate Bound Mercury (PBM). Mercury atoms are relatively stable, which means that they have a long residence time in the atmosphere (about a year) and can be dispersed globally before they are oxidised and leave the atmosphere via wet or dry deposition. Atmospheric mercury rarely constitutes a direct risk to human health. The principal environmental concern regarding mercury is its ability to be converted to methylmercury which occurs by natural biological processes.

Methylmercury is highly toxic and can bio-concentrate a million-fold in the food chain. This has resulted in regulatory fish consumption guidelines and health advisories in Scandinavia and North America (Schroeder and Munthe, 1998) Atmospheric mercury has both natural and anthropogenic sources and is believed to have increased by a factor of 3 since industrialisation (Lamborg et al., 2002). The principal manmade emission sources of mercury are artisanal and small-scale

5   gold production, coal combustion, non-ferrous and other primary metal production as well as cement production (AMAP/UNEP report 2013). Re-emission of mercury to the atmosphere is caused by reduction of deposited oxidised mercury on sea and land surfaces and enhances distribution and atmospheric exposure of mercury to the environment. Mercury, re-emitted to the atmosphere from sea and land surfaces, is assumed to be equal or even much larger than the total direct anthropogenic emissions (AMAP/UNEP report 2013). The largest natural emission sources of mercury are active

10   volcanoes and weathering of bedrock and the contribution to the atmospheric burden of mercury is estimated to be less than 15 - 30 % of the manmade emissions (AMAP/UNEP report 2013).

As a subtask within the project Global Mercury Observation System (GMOS), funded by the European Union's Seventh Programme for research, technological development and demonstration, the airborne mercury species, GEM, GOM and

15   PBM were measured at the Råö measurement station situated on the west coast of Sweden. The Tekran speciation method was used to obtain values of high temporal resolution. The GOM and PBM measurements are operationally defined, and may depend on the measurement method used. It has been argued that especially GOM is subject to interferences from ozone, water vapour etc. when measured with the Tekran system (Jaffe, et al., 2014). How to accurately measure these mercury fractions still remains an issue since the exact chemical form of GOM or mercury bound to particles is yet not

20   known. The form of mercury bound to particles has also not been identified. At the present the only available automatic method for measuring GOM and PBM is the Tekran system, however.

Here an evaluation of continuous measurements of GEM, GOM and PBM during, 2012-05-15 to 2013-07-03 and 2014-02-01 to 2015-04-30 will be presented and compared to the results from measurements made at other northern European sites

25   using the same measurement method.

2 Experimental Section

2.1 Sampling site

The Råö measurement station is a costal site on the West Coast of Sweden, about 50 km south of Gothenburg (57°23'37.76

30   N, 11°54'50.73 E, 7 m above sea level) and is one of the GMOS, master sites. The site is situated far away from major sources of air pollutants and is considered being a real background site. The annual average temperature, humidity and wind

speed at the site were 8 ^{o}C, 77 % and 6 m s^{-1}, respectively, based on measurements during 2010 to 2015. During 2011 to 2014 the average annual precipitation amount was 720 mm at the Råö site.

2.2 Methods

2.2.1 Fractionation of mercury species in air

5 Mercury species in air was measured using the Tekran mercury speciation system, which constitutes of the Tekran 1130/1135 sampling modules in combination with the Tekran 1130 pump and control module and the Tekran 2537B CVAFS mercury detector (Landis et al. 2002, Lindberg et al., 2002), see Figure 1a and 1b. The Tekran mercury detector measures the amount of elemental mercury vapour trapped on one of two alternating gold traps after thermal desorption and fluorescence detection at 253.7 nm.

10 With the Tekran system GEM, GOM and PBM were simultaneously measured. The sample air is pulled through an inlet impactor separating particles large than 2.5 µm at a flow rate of 10 litres per min. GOM is adsorbed on a KCl coated quartz glass denuder adjacent to the inlet. PBM is collected on a quartz glass fibre filter up streams the denuder, while GEM is passing through the system towards the 1130 pump module. Before the pump module the airflow is divided so that 1 litre per minute is pumped to the Tekran CVAFS detector and the rest goes to the pump module and is not analysed. While GOM and
15 PBM are collected in the 1130/1135 modules GEM values with a time resolution of 5 minutes were constantly obtained. Within the present measurements GOM and PBM were collected during 3 h followed by an analysis cycle of 60 min. During the analysis no GEM measurement is done. Every four hour, three hour average PBM and GOM values are obtained together with 5 min average GEM. Hence, all mercury values are obtained with time coverage of 75 %.

The analysis of GOM and PBM is initiated by flushing purified mercury free air through the system, at a flow rate of 1 litre
20 per min, during 15 minutes. The air is fed to the CVAFS detector and the mercury content is analysed every 5 minutes. Then the combustion oven (Pyrolyzer in Figure 1a) is heated to 800 ^{o}C meanwhile purging with purified air that is fed to the Tekran CVAFS detector for analysis. The combustion oven consists of a quartz glass tube filled with small quartz glass chips and is situated upstream the particulate filter. In the next step the quarts glass fibre filter is heated to 800 ^{o}C. In this process all particulate mercury is reduced to elemental mercury and leaves the filter as GEM and is transported through the
25 combustion oven to the CVAFS detector. Traces of aromatic compounds that may be present on the particulate filter will evaporate during heating and risk to interfere with the mercury detection system. The purpose of the combustion oven is to destroy all aromatics through combustion and to reassure that all oxidised Hg species are reduced to elemental mercury before entering the CVAFS detector. Finally the GOM denuder is heated to 500 ^{o}C while the particulate filter and the combustion oven are kept at 800 ^{o}C. During heating all GOM is reduced to elemental mercury and leaves the denuder to be
30 detected by the Tekran CVAFS detector. The average detection limit of GEM was found to be < 0.014 ng m^{-3} based on calculations of 3 × standard deviation of GEM blanks using zero air values obtained prior to each PBM and GOM analysis cycle. The instrument was set to automatically calibrate every 73 h using the internal permeation source. The accuracy of the

internal permeation source was tested every 6 months against manual Hg vapour injections using an in house built thermostatted mercury vapour source, following the CEN calibration procedure (Brown et al. 2006). Since the two calibration methods agreed within 5 % no adjustments of the internal mercury calibration source was performed during the present measurements. Since the concentrations of GOM and PBM are very low at the Råö site great effort was put to limit blanks in the measurement system. The analysis of PBM and GOM occurred during three, 5 minutes long analysis cycles. When the system is free from blanks PBM and GOM always were detected during their first analysis cycle. In the following 2 cycles the Hg concentration were most of the time equal to zero. For both PBM and GOM the results from the last analysis cycles, when both the PBM trap and the denuder were at high temperature, were considered to represent blank values. Three times the standard deviation of blanks using all data yielded an average detection limit of 0.11 pg m^{-3} for PBM and an average detection limit of 0.23 pg m^{-3} for GOM. The Tekran instruments were maintained according to the standard operational procedure developed within the GMOS project that is harmonised with the operational procedures used in the USA and Canada (Olson and Rhodes, 2011; Steffen et al., 2012).

2.3 Back trajectory evaluation

Trajectory modelling is a Lagrangian alternative to the Eulerian tracer approach. Trajectory modelling allows air parcels to be tracked backwards or forwards in time from a particular place, and so can provide information about the transport paths and potential sources of pollutants transported with the parcel of air. For the past few decades, trajectory models such as the US Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT, Draxler and Rolph, 2003) and FLEXTRA (Stohl et al., 1995) have frequently been used to analyse the transport path of atmospheric constituents such as air pollutants, greenhouse gases or radioactive constituents from the source to the receptor site (eg. Stohl et al., 2003; Tang et al., 2009). The model is usually run backwards in time to determine the source of the species of interest (Stohl, 1995). The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) 4.0 model (Draxler 2003) was used to produce back-trajectories from the Råö site. The HYSPLIT program was run with meteorological analysed fields from the NCEP/NCAR reanalysis project a joint effort between the National Centres for Environmental Prediction (NCEP) and the National Centre for Atmospheric Research (NCAR). The input meteorological data had 2.5 degrees horizontal resolution, with 18 vertical pressure levels extending between 1 hPa and 1000 hPa.

Backwards trajectory modelling is very sensitive to initial conditions, and air parcels released at slightly different times or locations may result in very different trajectories. Thus, trajectory analysis typically involves an ensemble of air parcels released at different locations, and HYSPLIT can calculate multiple back-trajectories simultaneously. For the purpose of this study trajectories were released at 5 different vertical levels (10, 50, 100, 250 and 500 m) every four hours to get a good representation of the transport pathways into the target region. From each of the points a trajectory was started and run backwards in time for 72 h (3 days). Six such back trajectories were calculated for every day to match each of the six daily analysis cycles of GOM and PBM.

To evaluate the mercury concentration as function of origin of air masses the area around Råö was divided into 16, 22.5 degrees wide sectors. There are no known emission sources that are large enough to influence the mercury concentrations at the measurement site within a circle of 150 km. Geographical points on each trajectory associated with the 16 sectors outside the 150 km circle were identified by help of a specially developed Excel VBA software. With this computer program the involved sectors could be joined to each individual mercury measurement. Altogether the origin of air masses associated to 4193 mercury speciation measurements was evaluated.

3 Results and Discussion

3.1 Measured values

Medians and arithmetic means of the mercury concentrations measured at Råö during the period 15/5 2012 to 29/4 2015 are presented in Table 1 and are compared to mercury values obtained at other Northern European sites. The variation of the average data is indicated as ± 1 standard deviation. Mace Head is a Global Atmospheric Watch (GAW) station on the west coast of Ireland. Aucgencort Moss and Harwell are rural background inland sites in Southern Scotland and Oxfordshire, England, respectively, whereas Waldhof is a rural inland background site situated 100 km south east of Hamburg in Germany. The measurements at these sites were performed using the same Tekran instruments as used in the present work, but were made some years earlier and are therefore not directly comparable to the present measurements. As seen in Table 1 the TGM concentration at Mace Head is somewhat higher than at Råö. TGM measurements have been performed on these two stations on a regular basis since 1996 and the tendency of higher values on Mace Head appears to be consistent during the entirely measurement period. The reason for this is not fully understood, but the higher TGM values at Mace Head have been attributed to mercury evasion from the North Atlantic Ocean (Wängberg et al., 2007 and references therein). The TGM/GEM values at Aucgencort Moss and Harwell are somewhat lower and are more similar to the Råö measurements. Regarding GOM and PBM, only data from Aucgencort Moss and Waldhof are available for comparison. The GOM concentration at Aucgencort Moss appears to be lower than at Råö whereas the PBM concentration is about the same. The highest concentrations of mercury species are found at Waldhof in Germany. As is discussed below this is probably a course of that the Waldorf site is close to mercury emission sources in East Europe.

Monthly average GEM, PBM and GOM are presented as whisker and box plots in Figure 2. The GEM data is evenly distributed within a narrow range of 1.4 – 1.5 ng m^{-3} with occasional elevated values reaching above 2.5 ng m^{-3}. The variation in concentration of PBM and GOM is much greater and varies from under the detection limit to 56 pg m^{-3} for PBM and 26 pg m^{-3} regarding GOM. Close to 50 % of the GOM values were under the detection limit, whereas 99 % of all PBM values were higher than the detection limit.

3.2 Origin of air masses reaching the Råö site

In the evaluation of back trajectories no significant difference could be seen between back trajectories starting at 100 m and at 250 m, also the other starting heights gave very similar results. Those at 250 m were chosen in the further evaluation. Results of the back trajectory analysis are shown in Figure 3a, b, c and d. About one third of the air masses entered the Råö site during the investigated period arrived via the sectors 202.5^o to 270° as shown in Figure 3a. The GEM concentration as function of origin of air masses is almost evenly distributed in the sectors 0° to 90° and 247.5^0 to 360^0 with an average value of 1.36 ng m^{-3} as shown in Figure 3a. The highest GEM values are associated with air masses that passed through the sectors 90° to 247.5^o with an average concentration of 1.51 ng m^{-3} and a maximum value of 1.71 ng m^{-3} in the sector $135^o – 157.5^o$. The elevated GEM values within this sector are presumably mainly due to mercury source in Poland, Rumania, Bulgaria, Greece and from some Balkan countries. Coal combustion for production of electricity and heat but also smelters and other industrial activities are the likely sources of mercury. Based on these findings the sectors 0° to 90° and 247.5^0 to 360^0 were classified as mainly associated with background air that is not affected by regional mercury emission sources. This assumption is further supported by the PBM measurements as shown in Figure 3c. Particulate mercury has been proven to be a sensitive marker for polluted air containing mercury (Wängberg et al. 2003). The highest PBM concentrations were found in the south east sector as also is the case with GEM, but the difference in PBM concentration between different sectors is much greater. The GOM values show a similar pattern with elevated concentrations in the south east as shown in Figure 3d. However, in contrast to PBM relatively high GOM concentrations were also received in air masses originating from north and east, indicating an additional source other than direct anthropogenic.

According to the classification of background and polluted air masses given above it was found that the Råö site receives air of background origin 59 % of the time with average concentrations of GEM, GOM and PBM equal to 1.36 ng m^{-3}, 0.76 pg m^{-3} and 2.15 ng m^{-3}, respectively. Average GEM, GOM and PBM concentrations associated with polluted air masses yielded concentrations of 1.51 ng m^{-3}, 0.85 pg m^{-3} and 5,71 ng m^{-3}, respectively.

3.3 Background and polluted air masses

The GEM, PBM and GOM values were divided into monthly averages and into background and polluted air masses according to the classification made in 3.2. The result is shown in Figure 4. Figure 4a show average monthly GEM concentrations. A seasonal variation with high values during the cold season is clearly depicted as well as a difference between air masses associated with background and polluted air. This indicates that both background and polluted air masses are influenced from anthropogenic emissions. A similar result is obtained with PBM as shown in Figure 4b, although the difference between background and polluted air masses is much more pronounced. The GOM data, on the other hand, yields

a quite different pattern with high values mostly occurring during the warm season as shown in Figure 4c. Another difference is that the GOM concentration in background air may be higher than in polluted air, as is shown by the measurements obtained for May June and August. As is indicated by Figure 3d there seem to be a coupling between elevated GOM concentrations and import of polluted air masses to the Råö site. However, the present result strongly suggests an

5 additional source not directly coupled to primary emission sources of mercury, which appears to be important during summer time. As has been proposed earlier, GOM is likely to be formed in the free troposphere by oxidation of GEM. This is a process that is supposed to occur over the oceans and is caused by photolytic bromine driven oxidation mechanisms (Donohoue et al., 2006; Obrist et al., 2011). GOM is probably formed at a slow phase in the marine atmosphere and due to its solubility it is efficiently being scavenged by atmospheric cloud droplets and may also undergo dry deposition and

10 therefore has a short residence time in the atmosphere. However, elevated concentrations may build up during dry atmospheric conditions presumably at high altitudes in the troposphere. Such air masses may occasionally be transferred to the ground (Wängberg et al., 2007). Hence, the observations of GOM at the Råö site can be interpreted as cause of formation of GOM in the free troposphere, by oxidation of GEM, in combination with direct transport of GOM emitted from regional anthropogenic sources.

4 Conclusions

15

Due to the remotely location of the Råö measurement station it receives background air most of the time. However, elevated concentrations with air masses coming from especially the south east are noticeable. About one third of the air entering to the Råö has passed UK and Denmark. Going back some decades earlier a lot of coal was used in the UK for power production and heating. As a result a lot of sulphur, and probably also mercury, was received and deposited in Scandinavia.

20 The present investigation shows that little if any mercury origins from UK or Denmark today as a consequence of shift from coal to cleaner power production techniques. Mercury emissions from other countries, including Sweden, have also dramatically been reduced since 1990. During the period 1985 to 1989 the average TGM concentration at the Råö site was as high as 3.2 ng m^{-3} (Iverfeldt et al., 1995).

The airborne mercury species investigated have all a direct anthropogenic component, i.e. can be attributed to regional

25 mercury sources, as well as of a background atmospheric origin. This is especially true regarding GEM, due to its long atmospherically residence time. The background concentration of GEM in the northern marine hemisphere is likely to resemble that measured at Mace Head. Particulate bound mercury has a much shorter atmospheric residence time, but especially small particles may stay in the atmosphere long enough to contribute to a background level of PBM. Due to the normally sort atmospheric life time of GOM one may not expect to receive air masses of remote origin with substantial

30 concentrations of GOM by the same means as with GEM and PBM. According to the kinetics of the atmospheric oxidation process of GEM to GOM (Donohoue et al., 2006), elevated concentrations of GOM is not likely to be formed locally in the air near background measurement sites. Hence, the elevated GOM concentrations measured in background air at the Råö site

presumably origin from air masses enriched in mercury from the free troposphere. As far as we know, this is for the first time evidence of tropospheric formed GOM has been observed in Northern Europe.

5 Acknowledgment

5   The financial support from The European Commission, FP7 (contract no. 26511) is gratefully acknowledged.

6 References

AMAP/UNEP Technical Background report for the Global Mercury Assessment 2013. www.amap.no

10   Brown, R. J. C., Pirrone N., van Hoek, C., Sprovieri, F., Fernandez, R., Toté, K. Standardisation of a European measurement method for the determination of total gaseous mercury: results of the field trial campaign and determination of a measurement uncertainty and working range. J. Environ. Monit., 12, 689–695, 2010.

Donohoue, D. L., Bauer, D., Cossairt, B., Hynes, A. J. Temperature and Pressure Dependent Rate Coefficients for the
15   Reaction of Hg with Br and the Reaction of Br with Br: A Pulsed Laser Photolysis-Pulsed Laser Induced Fluorescence Study. J. Phys. Chem. A, 110, 6623-6632, 2006.

Draxler, R. R.: Evaluation of an ensemble dispersion calculation, J. Appl. Meterol., 42, 308-317, 2003.

20   Draxler, R. R. and Rolph, G. D.: HYSPLIT (Hybrid Single-Particle Lagragnian Integrated Trajectory), Model access via NOAA ARL READY Website NOAA Air Resources Laboratory, Silver Spring, www.arl.noaa.gov/ready/hysplit4.html, 2003.
Flextra model developed by Andreas Stohl (NILU) in cooperation with Gerhard Wotawa og Petra Seibert (Institute of Meteorology and Geophysics, Wienna)

25

Iverfeldt, Å., Munthe, J., Brosset, C., Pacyna, J. Longterm changes in concentration and deposition of atmospheric mercury over Scandinavia. Water, Air, and Soil Pollution 80, 227–233, 1995.

Jaffe, D. A., Lyman, S. Amos, H. M., Gustin, M. S., Huang, J., Selin, N. E., Levin, L., Schure, A., Mason, R. P., Talbot, R.,
30   Rutter, A., Finely, B., Jaeglé, L., Shah, V., McClure, C., Ambrose, J., Gratz, L., Lindberg, S., Weiss-Penzias, P., Sheu, G-R., Feddersen, D., Horvat, M., Dastoor, A., Hynes, J. H., Mao, H., Sonke, J. E., Slemr, F., Fisher, J. A., Ebinghaus, R., Zhang,

Y., Edwards, G. Progress on Understanding Atmospheric Mercury Hampered by Uncertain Measurements.
dx.doi.org/10.1021/es5026432. Environ. Sci. Technol., 48, 7204−7206, 2014.

Kentisbeer, J, Leeson, S. R., Malcolm, H. M., Leith, I. D., Braban, C. F., Cape J. N. Patterns and source analysis for
5   atmospheric mercury at Auchencorth Moss, Scotland. Environ. Sci.: Processes Impacts, 16, 1112, 2014.

Kentisbeer, J., Leeson, S. R., Clark, T., Malcolm, H. M., Cape J. N. Influences on and patterns in total gaseous mercury
(TGM) at Harwell, England. Environ. Sci.: Processes Impacts, 17, 586, 2015.

10   Lamborg, C. H., Fitzgerald, W. F., O'Donnell, J., Torgersen, T. A non-steady-state compartment model of global-scale
mercury biochemistry with interhemispheric atmospheric gradients. Geochimica et Cosmochimica Acta 66(7), 1105−1118,
2002.

Landis, M. S., Stevens, R. K., Schadelish, F. S., Prestbo E. M. Development and Characterization ofan Annular Denuder
15   Methodology for the Measurement of Divalent Inorganic Reactive Gaseous Mercury in Ambient Air. Environ. Sci. Technol.
36, 3000-3009, 2002.

Lindberg, S. E., Brooks, S., Lin, C. J., Scott, K. J., Landis, M. S., Stevens, R. K., Goodsite, M., and Ritcher, A.: Dynamic
oxidation of gaseous mercury in the Arctic troposphere at polar sunrise, Environ. Sci. Techn., 36, 1245-1256, 2002.

20

Obrist, D., Tas, E., Peleg, M., Matveev, V., Faïn, X., Asaf, D., Luria, M. Bromine-induced oxidation of mercury in the
mid-latitude atmosphere. Nature Geoscience Vol 4, January 2011. (www.nature.com/naturegeoscience)

Olson, M. L., Rhodes, M, F. NADP AMNet Standard Operating Procedures for Field Analysis of Gaseous and Fine
25   Particulate-Bound Mercury. Version 1.1 January 2011. Written and edited by Mark L. Olson and Mark F. Rhodes.

Schroeder W. H., Munthe, J. Atmospheric Mercury–an overwiew. Atmos Environ 32, 809–822, 1998.

Siudek, P., Frankowski, M., Siepak, J. Atmospheric particulate mercury at the urban and forest sites in central Poland
30   Environ Sci. Pollut. Res. 23:2341‑2352, 2016.

Steffen, A., Scherz, T., Ohlson, M., Gay, D., Blanchard P. A comparison of data quality control protocols for atmospheric
mercury speciation measurements. J. Environ. Monit., 14, 752, 2012.

35   Stohl, A., Wotawa, G., Seibert, P. and Kromp-Kolb, H.: Interpolation errors in wind fields as a function of spatial and
temporal resolution and their impact on different types of kinematic trajectories, J. Appl. Meteor., 34, 2149-2165, 1995.

Stohl, A., Forster, C., Eckhardt, S., Spichtinger, N., Huntrieser, H., Heland, J., Schlager, H., Wilhelm, S., Arnold, F. and Cooper, O.: A backward modelling study of intercontinental pollution transport using aircraft measurements, J. Geophys. Res., 108(D12), ACH 8-1–ACH 8-18, 2003.

5   Tang, L., Karlsson, P. E., Gu, Y., Chen, D. and Grennfelt, P. 2009. Synoptic weather types and long-range transport patterns for ozone precursors during high-ozone events in southern Sweden. Ambio 38(8) 459-64

Weigelt, A., Temme, C., Bieber, E., Schwerin, A., Schuetze, M., Ebinghaus, R., Kock, H. K. Measurements of atmospheric mercury species at a German rural background site from 2009 to 2011 – methods and results. Environ. Chem., 10, 102–110,
10   2013. http://dx.doi.org/10.1071/EN12107

Weigelt, A., Ebinghaus, R., Manning, A. J., Derwent, R. G., Simmonds, P. G., Spain, T. G., Jennings, S. G., Slemr, F. Analysis and interpretation of 18 years of mercury observations since 1996 at Mace Head, Ireland. Atmos, Environ., 100, 85-93, 2015.
15
Wängberg, I., Munthe, J., Ebinghaus, R., Gårdfeldt, K., Iverfeldt, Å., Sommar, J. Distribution of TPM in Northern Europe. The Science of the Total Environment 304, 53–59, 2003.

Wängberg, I. Munthe, J., Berg, T., Ebinghaus, R., Kock, H. H., Temme, C., Bieber, E., Spain T. G., Stolk, A. Trends in air
20   concentration and deposition of mercury in the coastal environment of the North Sea Area. Atmospheric Environment 41, 2612–2619, 2007.

Wängberg, I., Munthe, J., Amouroux, D., Andersson, M. E., Fajon, V., Ferrara, R., Gårdfeldt, K., Horvat, M., Mamane , Y., Melamed, E., Monperrus, M., Ogrinc, N.,Yossef , O., Pirrone, N., Sommar, J., Sprovier, F. Atmospheric mercury at
25   mediterranean coastal stations. Environ Fluid Mech 8, 101–116, 2007. DOI 10.1007/s10652-007-9047-2

Tables

Table 1. Median and average mercury concentrations measured at some Northern European sites

Measurement sites	GEM/TGM	GOM	PBM	Period	Reference
	median	median	median		
	ng m^{-3}	pg m^{-3}	pg m^{-3}		
Råö	1.41	0.23	2.21	2012 - 2015	This work
Mace Head*	1.50	-	-	2011 - 2013	Weigelt et al., 2015
Waldhof	1.61	1.0	6.30	2009 - 2011	Weigelt et al., 2013
	Average	Average	Average		
	ng m^{-3}	pg m^{-3}	pg m^{-3}		
Råö	1.42 ± 0.20	0.80 ± 1.6	3.6 ± 4.5	2012 - 2015	This work
Mace Head*	1.49 ± 0.20	-	-	2011 - 2013	Weigelt et al., 2015
Aucgencort Moss	1.40 ± 0.19	0.43 ± 1.7	3.1 ± 5.3	2009 - 2011	Kentisbeer, 2014
Harwell*	1.45 ± 0.24	-	-	2012 - 2013	Kentisbeer, 2015

*Total gaseous mercury measured with Tekran instruments.

Figures
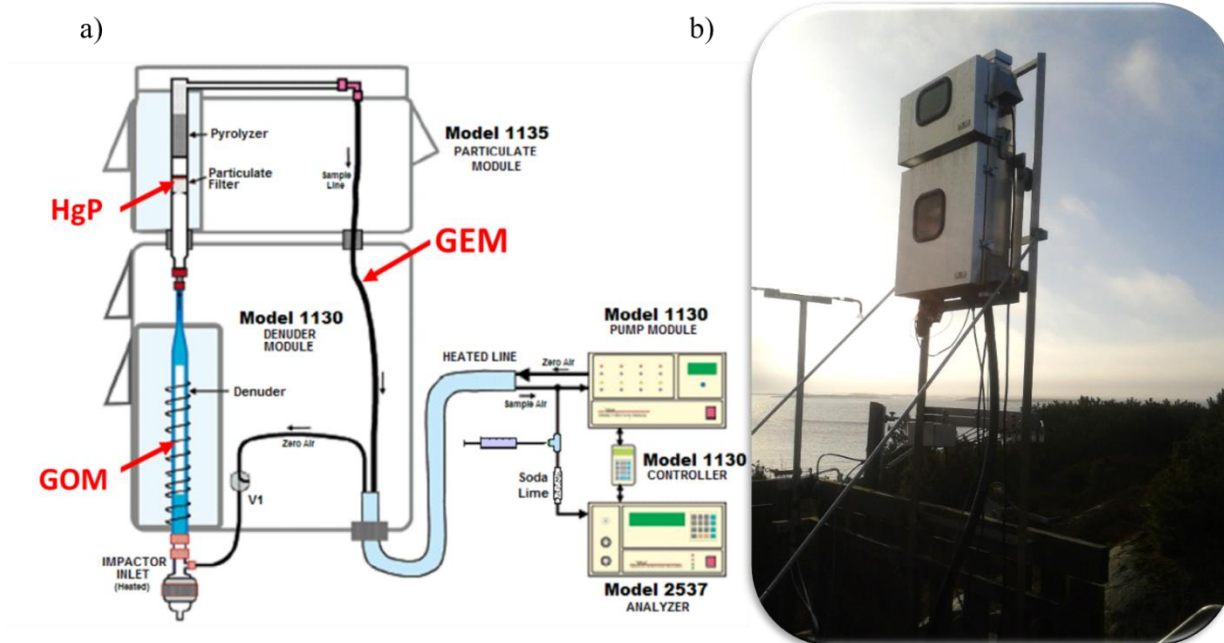
Figure 1. a) a schematic overview of the Tekran mercury speciation system 1130/35 and the 2537 mercury analyser, b) picture of the
5   instrument operating at the Råö station.
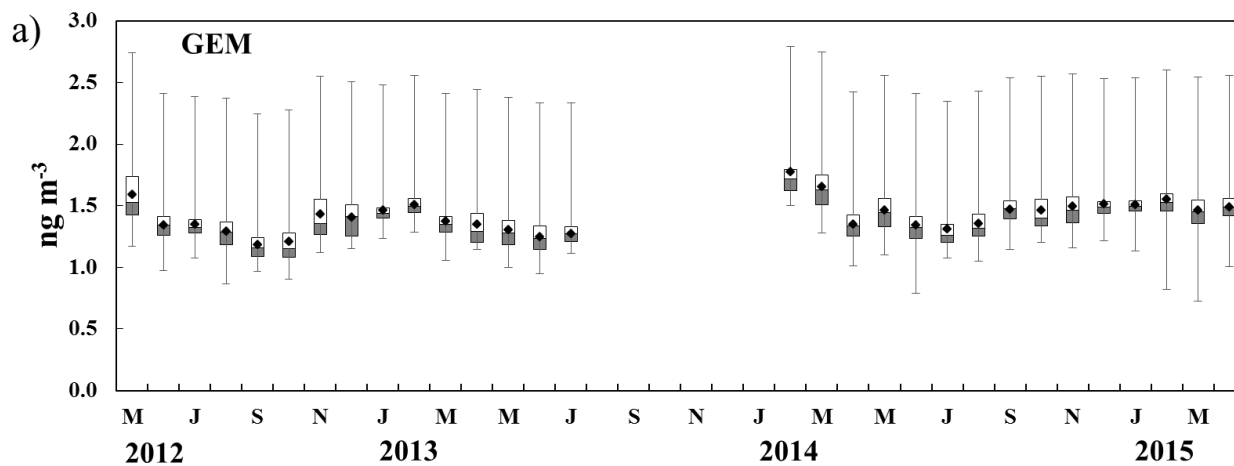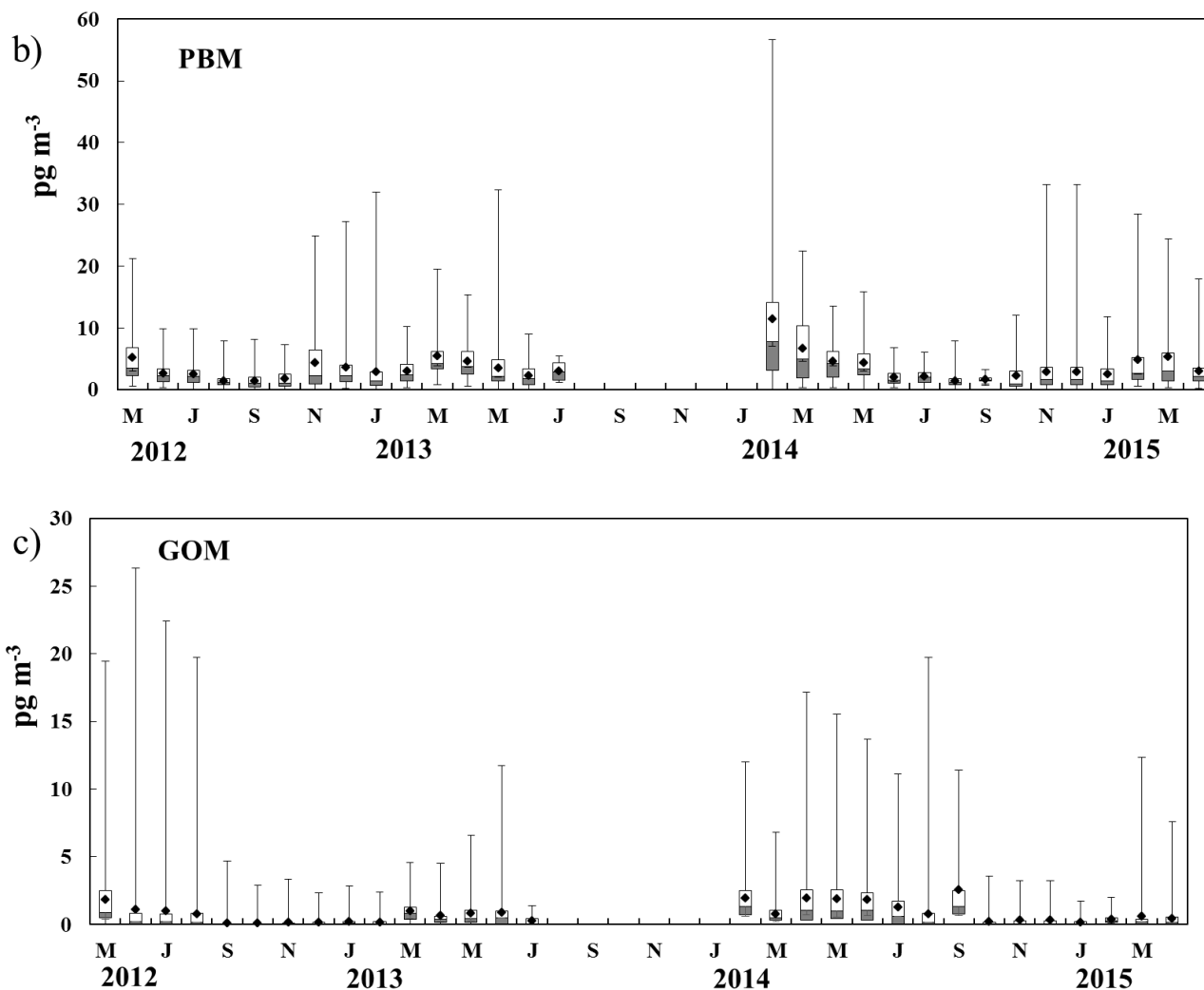
Figure 2. Boxplots of measured a) GEM, b) PBM and c) GOM at Råö/Rörvik from May 2012 to July 2013 and from February 2014 to April 2015. Diamonds show average values. Upper and lower boxes show 75 % and 25 % percentiles, respectively with median values in between. Upper and lower whisker bars shows maximum and minimum values, respectively.
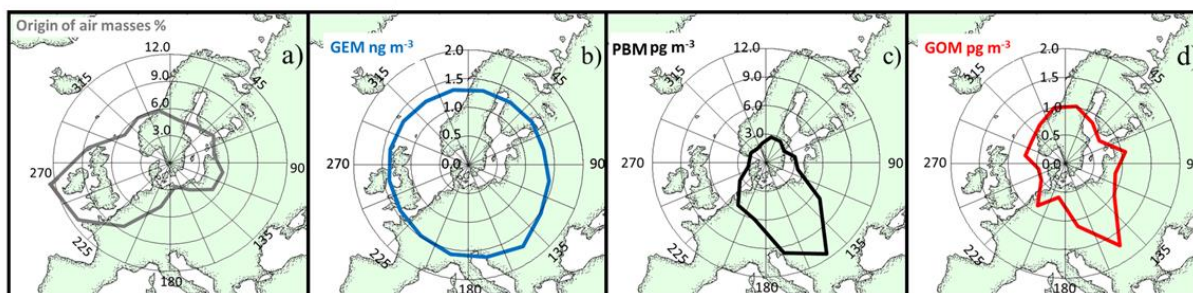
Figure 3. Results of the back trajectory analysis. a) origin of air masses reaching the Råö site presented as relative frequency (%) within each sector. b), c) and d) shows GEM, PBM and GOM concentrations, respectively as function of origin of air masses entering the Råö measurement site.
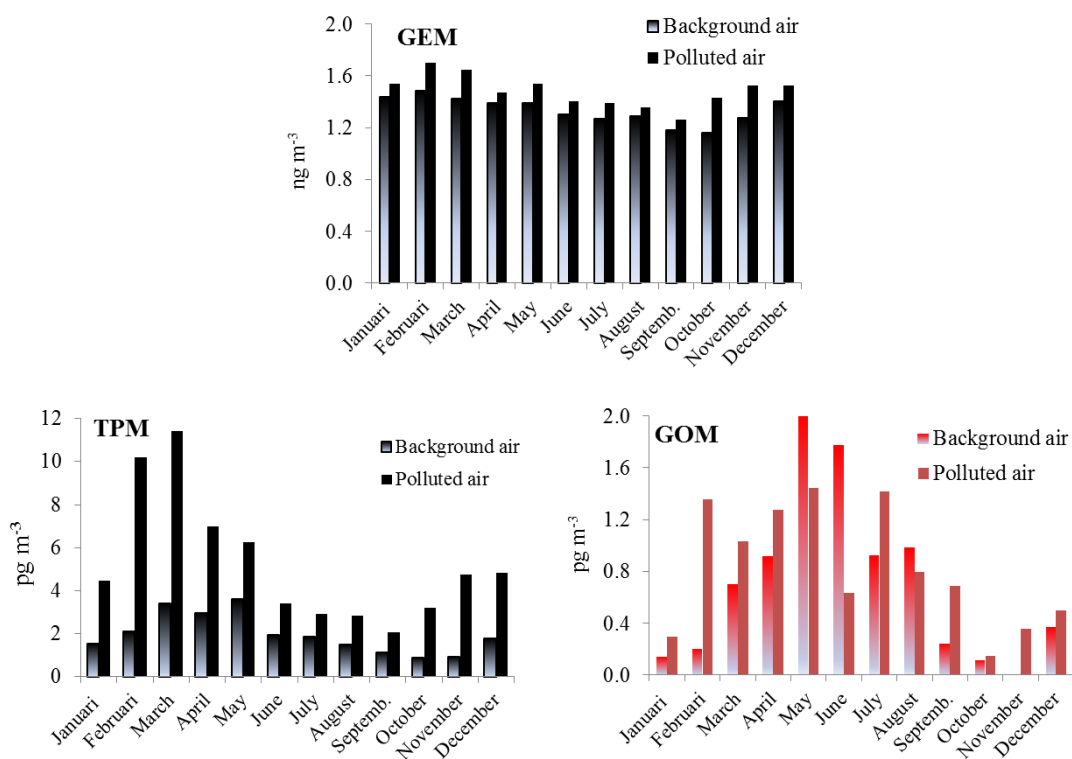
Figure 4. Average mercury air concentrations as function of month and origin of air masses at the Råö measurement site. The values represent monthly averages of all data from the measurements made during 2012-05-15 to 2015-04-29.