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Measurements of atmospheric mercury species at a German rural background site from 2009 to 2011 – methods and results

Andreas Weigelt, Christian Temme, Elke Bieber, Andreas Schwerin, Maik Schuetze, Ralf Ebinghaus, and Hans Herbert Kock

Helmholtz-Zentrum Geesthacht, Institute of Coastal Research, Max-Planck-Strasse 1, D-21502 Geesthacht, Germany.

Eurofins GfA GmbH, Neulaender Kamp 1, D-21079 Hamburg, Germany.


Corresponding author. Email: ralf.ebinghaus@hzg.de

Environmental context. Mercury is a very hazardous substance for human and environmental health. Systematic long-term direct measurements in the atmosphere can provide valuable information about the effect of emission controls on the global budget of atmospheric mercury, and offer insight into source–receptor transboundary transport of mercury. A complete setup for the measurement of the four most relevant atmospheric mercury species (total gaseous mercury, gaseous oxidised mercury, particle-bound mercury, and gaseous elemental mercury) has been operating at the rural background site of Waldhof, Germany, since 2009. We present the dataset for 2009–2011, the first full-speciation time series for atmospheric mercury reported in Central Europe.

Abstract. Measurements of mercury species started in 2009 at the air pollution monitoring site ‘Waldhof’ of the German Federal Environmental Agency. Waldhof (52°48′N, 10°45′E) is a rural background site located in the northern German lowlands in a flat terrain, 100 km south-east of Hamburg. The temporally highly resolved measurements of total gaseous mercury (TGM), gaseous oxidised mercury (GOM), particle-bound mercury (PBM PM2.5, with particulate matter of a diameter of ≤2.5 µm) and gaseous elemental mercury (GEM) cover the period from 2009 to 2011. The complete measurement procedure turned out to be well applicable to detect GOM and PBM PM2.5 levels in the range of 0.4 to 65 pg m⁻³. As the linearity of the analyser was proven to be constant over orders of magnitude, even larger concentrations can be measured accurately. The 3-year median concentration of GEM is found to be 1.61 ng m⁻³, representing typical northern hemispheric background concentrations. With 6.3 pg m⁻³, the 3-year average concentration of PBM PM2.5 is found to be approximately six times higher than the 3-year average GOM concentration. During winter the PBM PM2.5 concentration is on average twice as high as the PBM PM2.5 summer concentration, whereas the GOM concentration shows no clear seasonality. However, on a comparatively low level, a significant diurnal cycle is shown for GOM concentrations. This cycle is most likely related to photochemical oxidation mechanisms. Comparison with selected North American long-term mercury speciation datasets shows that the Waldhof 3-year median speciated mercury data represent typical rural background values.

Introduction
Mercury is a very hazardous substance for human health and the environment. It is present throughout the environment and, in the form of methylmercury, has the capacity to bioaccumulate in organisms. Mercury released into the atmosphere is capable of being transported over long distances.

In the atmosphere, total gaseous mercury (TGM) exists largely as gaseous Hg⁰ (‘gaseous elemental mercury’, GEM) but also includes trace amounts of Hg²⁺ compounds, often designated as Hg²⁺[1–3] Atmospheric Hg²⁺ compounds may be associated with particles or occur as gases, most probably in the form of HgCl₂, Hg(OH)₂ or other mercuric halides. In recent literature, measured species other than GEM are operationally defined as a fraction termed ‘gaseous oxidised mercury’ (GOM) and ‘particle bound mercury’ (PBM). GOM and PBM are found in much lower concentrations, often not more than 1–5 % of the total atmospheric mercury. [4] These fractions are highly water soluble (at least 105 times more than Hg⁰), and this water solubility strongly influences their removal processes and deposition rates from the atmosphere. [5] Their residence times are on the scale of days [4–7].

Systematic long-term direct measurements of mercury in the atmosphere provide valuable information about the effect of emission controls on the global budget of atmospheric mercury.
and offer insight into the source–receptor transboundary transport of mercury. Additional speciated measurements of GOM and PBM can help to improve the understanding of local atmospheric chemistry and short-term oxidation processes regarding the removal of mercury from the atmosphere.

The European Union (EU) air quality directive 2004/107/EC (‘4th Daughter Directive’),[8] relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons (PAHs) in ambient air and deposition, requests indicative measurements of TGM at background sites. Measurements of particulate and gaseous divalent mercury[8] are also recommended. Irrespective of concentration levels, one background sampling point shall be installed every 100,000 km² for the indicative measurement of TGM in ambient air. In Germany these background measurements are performed by the German Federal Environment Agency (Umweltbundesamt, UBA) within its air pollution monitoring network, e.g. at the Waldhof site. The sampling sites for these pollutants are selected in such a way that geographical variation and long-term trends can be identified. The monitoring of mercury is coordinated with the European Monitoring and Evaluation Programme (EMEP) of the United Nations Economic Commission for Europe (UNECE).[9]

TGM has been measured at the German rural background site Waldhof since 2002 and has shown typical northern hemispherical background concentrations of below 2 ng m⁻³.[10] Measurements of mercury species GOM, PBM and GEM at the Waldhof station started in 2008. All speciated mercury measurements have been extended to this day. Because the particle cut-off diameter was 2.5 μm for PBM measurements, it is abbreviated here as PBMPM₂.₅.

Demand for a harmonised protocol
The Group on Earth Observations (GEO) has established the Task 09-02d, ‘Global Monitoring Plan for Atmospheric Mercury’ for the work plan 2009 to 2011. This task supports the achievement of the goals of Global Earth Observation System of Systems (GE OSS) and other on-going international programs such as the UN Environment Programme (UNEP) ‘Mercury Program’ and international conventions dealing with large-scale transboundary transport of mercury (e.g. UNECE, Convention on Long-range Transboundary Air Pollution). Following the lead of these programs, the incorporation of a well-defined mercury monitoring component into the existing network of sites would be the most expeditious and efficient approach to realise a global mercury monitoring network. This has partly been accomplished on a regional scale in Canada and the US (Canadian Atmospheric Mercury Measurement Network, CAMNet, and Atmospheric Mercury Network, AMNet). In November 2010, a European initiative with a global perspective was started (Global Mercury Observation System, GMOS; see www.gmos.eu).

Harmonisation standard operating procedures (SOPs) and quality assurance and quality control (QA/QC) protocols for monitoring ambient concentrations of TGM, GEM, GOM and PBMPM₂.₅ are needed in order to assure a full comparability of site-specific observational datasets with that obtained inside and outside existing monitoring networks.

SOPs and QA/QC protocols should be in accordance with measurement practice adopted in well established monitoring networks in North America and Europe[11] (AMNet, see http://nadp.sws.uiuc.edu/amn/; CAMNet, see http://www.ec.gc.ca/natchem/default.asp?lang=En&n=BFF7F7EE-1, both accessed 14 January 2013) and be based on the most recent standards (M. Olson, AMNet site liaison, pers. comm., December 2012–January 2013).

Methods and QA/QC procedures for speciated mercury measurements optimised for concentrations at background levels in northern Germany as well as the first time series (2009–2011) for speciated atmospheric mercury concentrations in Central Europe are presented in this paper.

Experimental
The measurement of mercury species at the Waldhof station started in 2008 and has been extended to this day. Waldhof (52°48’N, 10°45’E) is a rural background site located in the northern German lowlands in a flat terrain, 100 km south-east of Hamburg and 100 km north-east of Hannover, in a clearing. The immediate vicinity is mostly used for agricultural purposes. The next village is Langenbruegge, ~3 km west, with 300 inhabitants. The nearest small industrial plant is located ~20 km away, however, there are no major industrial facilities within a distance of ~50 km.

The sampling and analysis of TGM are based on the specifications in EN 15852.[11] For the mercury species GOM, PBMPM₂.₅, and GEM a procedure optimised for the respective special requirements (i.e. the expected northern German background concentrations) and local conditions (e.g. personnel and technical facilities like sampling inlet) was defined. Practical details such as the preparation of the denuder and particulate filter, the frequency of maintenance and support or the collection and processing of data were merged into a SOP for the simultaneous determination of the mercury species GEM, GOM and PBMPM₂.₅.

Two mercury vapour analysers (Tekran Model 2537A, Tekran Inc., Toronto, ON, Canada) were operated at the Waldhof site. Both instruments were set up in an air-conditioned laboratory. One instrument measured ambient air concentrations of TGM. The other instrument was equipped with a mercury speciation unit and a particulate mercury unit (Tekran Model 1130 and Model 1135). The analytical species for both instruments was Hg⁰.

The methods are summarised in brief below.

TGM
In principle the analyser collects mercury on gold traps, followed by thermal desorption of mercury which is detected as Hg⁰ by cold vapour atomic fluorescence spectroscopy (CVAFS). The integrated sampling interval for the TGM analyser was 15 min (selected time resolution for long-term measurements of TGM). The sampling inlet was located ~5 m above ground level with directly heated (outside) and unheated (inside) Teflon inlet lines (overall length ~10 m). The complete sample inlet was located above the roof of the laboratory building, allowing an unhindered transport of air masses to the system (Fig. 1).

The air was sampled at a flow rate of 1.0 L min⁻¹ and filtered with a 0.2-μm polytetrafluoroethylene (PTFE) filter in front of the inlet of the inside analyser. There was no soda lime trap applied. The sample inlet was protected against rain and insects.

Quality control checks using zero gas (ambient air filtered by activated carbon) and span gas were carried out twice a day. The span gas was prepared using the built-in permeation source that injects a known quantity of Hg⁰ into a stream of mercury-free air (filtered by activated carbon). The frequent span gas injections allowed for a subsequent adjustment to changing operating
conditions over time. Furthermore, a slow drift of the response of the test gas by an aging lamp, a possible offset, de-activated gold traps or different environmental conditions were considered over time. The subsequent calculations of the concentrations were done with a self developed automated reporting software.

The analytical detection limit (ADL) for Hg\(^0\) in this mode of operation was \(\sim 0.5\) pg. The ADL was calculated as \(3 \times \text{s.d.}\) (standard deviation of blanks or manual injections of low amounts of mercury), whereas the method detection limit (MDL) was calculated to be \(0.033\) ng m\(^{-3}\), with a sample volume of 15 L. At Waldhof station, typical northern hemisphere background concentrations of below \(2\) ng m\(^{-3}\) for TGM\(^{7,10}\) were measured in the years 2002–2011 (see Fig. 2).

**GEM**

A mercury vapour analyser (Tekran Model 2537A, Tekran Inc.) equipped with a mercury speciation unit and a particulate mercury unit (Tekran Model 1130 and Model 1135) was used for the determination of GEM concentrations. The integrated sampling interval for the GEM analyser was 5 min (selected time resolution for atmospheric process studies). The sampling inlet was located \(\sim 5\) m above ground level with directly heated (outside) and unheated (inside) Teflon inlet lines (overall length \(\sim 7.5\) m).

Ambient air was collected at a flow rate of 10.0 L min\(^{-1}\), however, only 10% of the sampled air was used for the determination of GEM. This air passed a soda lime trap and a 0.2-\(\mu\)m PTFE filter in front of the inlet of the inside analyser. Quality control checks using zero gas and span gas as described for TGM were carried out after every sampling cycle.

The ADL for Hg\(^0\) in this mode of operation was \(\sim 0.5\) pg. The ADL was calculated as \(3 \times \text{s.d.}\) The MDL for GEM was calculated to be \(0.1\) ng m\(^{-3}\) with a sample volume of 5 L. Expected GEM concentrations at Waldhof required a measurement range of below \(1\) ng m\(^{-3}\) up to more than \(4\) ng m\(^{-3}\).

**GOM and PBMPM\(_{2.5}\)**

GOM was collected on a KCl-coated and pre-heated (\(\sim 50^\circ\)C) annular denuder, PBMPM\(_{2.5}\), was collected on a regenerable filter assembly (RPF), and GEM passed by and was directly analysed by the mercury analyser. The sampling flow through the denuder and RPF was 10 L min\(^{-1}\), and was frequently checked with a certified flow meter. Only the manually recorded flow rate and the resulting total volume were used to calculate the concentrations of GOM and PBMPM\(_{2.5}\) with a self developed automated reporting software.

GOM and PBMPM\(_{2.5}\) were collected over 3-h intervals. The operationally defined fractions of mercury were sequentially...
thermally desorbed and quantified by CVAFS ($\lambda = 253.7$ nm) in the analyser by successive flushing, desorption and cleaning cycles within a period of 1 h and 5 min. The results of the three respective desorption cycles for PBM$_{PM_{2.5}}$ and GOM were added in the automatic software to calculate the final result for the two species. The final QA/QC cycles (three zero checks and one span gas check) lasted for another 20 min. The complete program sequence for sampling and analysis covered a time period of 4 h and 25 min.

The ADL for Hg$^0$ in this mode of operation was $\sim 0.7$ pg. The ADL was calculated as $3 \times s.d.$ (standard deviation of the first flush cycles over the year 2009, which were normally distributed). The MDL for GOM and PBM$_{PM_{2.5}}$ was calculated to be $0.4 \text{ pg m}^{-3}$ with a sample volume of $\sim 1.800$ L. In addition an automatic blank correction was done in the software by subtraction of three times the average of the second and third flush cycle. This correction was necessary to compensate possible sampling artefacts like memory effects after 3 h of sampling. However, only 3% of the total number of 1930 flush cycles during the measurements in 2009 gave a signal.

These low MDL and blanks could only be achieved by frequent replacement of the denuder and RPF by freshly coated and prepared material (see also Quality assurance and maintenance).

Quality assurance and maintenance

The main sources for systematic and random errors for the detection of Hg$^0$ can be:

- the adsorption efficiency of the gold cartridges,
- the detector signal (e.g. cross sensitivity, unsteady baseline),
- the sample volume,
- the permeation rate.

It is known that volatile organic compounds can deactivate the surface of the gold cartridges in the analyser. This de-activation can reduce the cartridge efficiency significantly. Normally, a monthly exchange of the gold cartridges with the installation of a freshly cleaned and pre-heated pair, as performed in this study, can avoid this artefact. Furthermore, a continuous and frequent quality control by recovery tests can help to check the cartridge efficiency between the exchange interval. This was done by regular low-level span gas checks, using the internal permeation source (see also Development of a SOP).

The accuracy of the analysers’ internal permeation rates was verified twice a year by manual injections of known amounts of Hg$^0$ with a manual calibration source. Usually, 9 $\mu$L of mercury-saturated air was injected in 7.5 L of zero air at 1°C below room temperature, which corresponds to $\sim 115$ to 120 pg of Hg$^0$ and 16 ng m$^{-3}$. No significant deviations ($\geq 5\%$) between the theoretical and measured values were found. Therefore, the permeation source rate was not modified.

The reproducibility of various mercury analysers has been assessed during several field intercomparisons including an urban-industrial site (Windsor, ON), remote marine background locations and during an intercomparison within the EMEP at the Waldhof site. Results from each campaign demonstrated the good comparability of the mercury vapour analyser Tekran Model 2537A with other established instruments and methods.

High data capture and time coverage were achieved by continuous measurements of TGM with a minimum of calibration and service intervals. The frequent span gas checks accounted for 4.3% of the sampling time (15-min zero check, 15-min span check, 675-min measurement). Approximately 1 h per month was needed for monthly maintenance (change of gold cartridges, lamp adjustment, exchange of filter). A manual calibration every 6 months took $\sim 6$ h. Therefore, the complete down time due to QA/QC and maintenance was $< 5\%$ of the total sampling time.

The measurement uncertainty was determined using two different approaches. First, by operating two independent analysers in parallel ($n = 643$), the standard uncertainty for TGM was determined according to ISO 20988, type A6.$^{[16]}$ The expanded ($k = 2$) $95\%$ uncertainty in the range 1.2 to 4.0 ng m$^{-3}$ was found to be 0.24 ng m$^{-3}$. Compared to the respective mean TGM concentration (1.95 ng m$^{-3}$), the relative expanded measurement uncertainty was 12.5%. This uncertainty complies with the quality objective of the EU air quality directive 2004/107/EC$^{[19]}$ of 50%.

A second approach according to ISO 20988, type A2$^{[16]}$ uses a set of input data obtained by daily span gas checks. Here, a possible offset and the drift over time are combined with the uncertainty of the reference material (her, permeation source) by a combination of the standard uncertainties. As a result, the relative expanded ($k = 2$) $95\%$ uncertainty in the range 0.1 to 10 ng m$^{-3}$ amounts to 12%. This is in good agreement with the uncertainty found with the first approach.

Currently there is no direct approach according to ISO 20988 to the uncertainty for the operationally defined mercury species or fractions of GOM and PBM$_{PM_{2.5}}$. To our best knowledge, no reference material is commercially available. Field intercomparisons or parallel measurements over a longer time period have not yet been published. There remains a strong demand for further investigation regarding the uncertainty of the mercury species measurements in ambient air.

The mercury vapour analyser Tekran Model 2537A itself is a complex, but well investigated automatic monitor for TGM and GEM. The most sensitive parts are the gold cartridges and the inert material for the loss-free transport of the analytical species Hg$^0$ to the detector. However, uncertainties, blanks, detection limits, ruggedness and traceability to reference material are well established and have been reported many times.

The measurement of Hg species with an automatic system is more ambitious, including much more sensitive parts like coated and non-coated glassware, heated filters, vials and tubing. Therefore, we turned our attention to the development of a SOP with specific service intervals that will lead to the best performance of the speciation system for the detection of low-level concentrations of GOM and PBM$_{PM_{2.5}}$.

Development of a SOP

During the pre-routine testing of the speciation unit in 2008, the complete measurement procedure, including a 3-h sampling interval, flushing, desorption and cleaning cycles (1 h and 5 min), QA/QC cycles for zero checks and functional tests (20 min) and frequent exchange of glassware (denuder and RPF) were evaluated to be suitable for the application to background levels at Waldhof station. In retrospect, the measurement procedure turned
in the range of 0.4 to 21 pg m$^{-3}$ and the amount of mercury injected into the instrument during frequent span gas checks of 37 pg, i.e. $\sim$21 pg m$^{-3}$ at a sample volume of 1800 L. During manual calibrations of the permeation source, 115 to 120 pg of Hg$^0$ were applied to the analyser. Thus, higher concentrations of up to 65 pg m$^{-3}$ at a sample volume of 1800 L were within the range of quantification. The linearity of the analyser was shown to be constant over orders of magnitude.$^{[17]}$ Therefore, concentrations of GOM and PBMPM2.5 were considered for this calculation showing a right skewed distribution with a mean area of $\sim$2300. This gave us clear evidence of the efficiency of the selected maintenance and cleaning intervals, especially for the preparation and exchange of glassware. No systematic contamination or memory effect can be seen, rather a random signal-to-noise ratio of a baseline, which has a predefined threshold value in order to avoid the integration of low level peaks. The resulting significant number of zero values can also be seen in Fig. 3.

Fig. 3 shows the frequency table (histogram) of the zero gas response of the first flush cycles before starting the thermal desorption and detection of gaseous oxidised mercury (GOM) and particle-bound mercury (PBMPM2.5, with particulate matter of a diameter of $\leq$2.5 $\mu$m). For this histogram all data from the first year of operation (2009) were used.

During the 3-year period 2009–2011 the daily average GEM concentrations vary between 1.4 and 2.1 ng m$^{-3}$ (10th and 90th percentile). The minimum and maximum daily GEM concentrations are found to be 1.1 and 3.1 ng m$^{-3}$. The 3-year median GEM concentration is calculated to be 1.61 ng m$^{-3}$, which is in rather good agreement with the northern hemispheric background concentration of 1.7 ng m$^{-3}$.$^{[7,10]}$ With 6.3 pg m$^{-3}$, the 3-year median PBMPM2.5 concentration is found to be approximately six times higher than the 3-year median GOM concentration of 1.0 pg m$^{-3}$. PBMPM2.5 and GOM show a much stronger variability in daily average concentrations than GEM (Fig. 4). Table 1 summarises the whole dataset. Please note, whereas Fig. 4 shows daily averages, the calculated values in Table 1 are obtained from single measurements (PBMPM2.5, GOM) or hourly averages (GEM). As the hourly variability can be much larger than the daily variability (especially in plumes), the minimum and maximum values given in Table 1 do significantly differ from those displayed in Fig. 4. Although the maximum daily average GEM concentration was 3.05 ng m$^{-3}$ (on 18 February 2010), the maximum hourly concentration was 7.68 ng m$^{-3}$ on 29 January 2009 from 0400 to 0500 hours. With 110 pg m$^{-3}$, the maximum daily average PBMPM2.5 concentration was determined on 24 January 2010, whereas the maximum single PBMPM2.5 concentration of 262 pg m$^{-3}$ was measured on 30 May 2011 from 2100 to 0000 hours. At the same time the highest single GOM concentration (133 pg m$^{-3}$) was detected, whereas the GEM concentration was only slightly increased to 2.0 ng m$^{-3}$. As the PM10 (particulate matter with a diameter of $\leq$10 $\mu$m) mass concentration also showed a significant peak (above 50 $\mu$g m$^{-3}$, not shown here), it is assumed that the high PBMPM2.5 and GOM concentrations are caused by a local combustion plume. The highest daily average GOM concentration (37 pg m$^{-3}$) was observed on 29 June 2011.

To our best knowledge, the data presented here represent the longest Central European time series of atmospheric mercury
species. Fig. 5 compares the Waldhof average GEM, PBM PM2.5, and GOM concentrations (medians) with data from selected sites of the US National Atmospheric Deposition Network (NADP) – AMNet (see http://nadp.sws.uiuc.edu/amn/). Furthermore, Fig. 5 shows data from the European sites Auchencorth Moss (ACM), Scotland (2009–2010) (J. Kentisbeer, S. Leeson, H. Malcolm, I. Leith and J. N. Cape, pers. comm.) and Zabrze, Poland (2011) (H. Pyta, pers. comm.). Supplementary information on all selected sites is given in Table 2.

Fig. 5 shows that the Waldhof (DE02) GEM, PBM PM2.5, and GOM median concentrations are, in general, in rather good agreement with those of most of the other selected sites. The Waldhof median GEM concentration (1.61 ng m\(^{-3}\)) agrees best with the median GEM concentrations measured at the North American sites Birmingham (AL19; 1.67 ng m\(^{-3}\)) and Antelope Island (UT96; 1.57 ng m\(^{-3}\)) (see AMNet). The other North American sites showed somewhat lower median GEM concentrations (up to 15 % lower), especially at the Huntington Wildlife site (NY20; 1.27 ng m\(^{-3}\)) (see AMNet). As the European site Zabrze (IPIS, Institute of Environmental Engineering of the Polish Academy of Sciences) is located in an industrialised area, it is reasonable that the median GEM (2.8 ng m\(^{-3}\)), PBM PM2.5 (24.5 pg m\(^{-3}\)) and GOM (14.9 pg m\(^{-3}\)) (H. Pyta, pers. comm.) concentrations are clearly increased as compared to the rural background concentrations measured at Waldhof. At the other European measurement location, the Scottish rural background site ACM, the median GEM concentration (1.39 ng m\(^{-3}\)) (Kentisbeer et al., pers. comm.) was found to be somewhat lower than at Waldhof. Also, remarkably low median PBM PM2.5 and GOM concentrations are reported for the ACM site (PBM PM2.5 0.6 pg m\(^{-3}\) and zero for GOM) (Kentisbeer et al., pers. comm.). Similarly low values were reported for the TGM concentration at the Irish site Mace Head (1.44 ng m\(^{-3}\), 2009–2011 average, not shown here) (R. Ebinghaus, S. G. Jennings, H. H. Kock, R. G. Derwent, A. J. Manning, T. G. Spain and A. Weigelt, pers. comm.) and for GOM median concentrations at the North American sites Kejimkujik National Park (NS01; 0.2 pg m\(^{-3}\)) and Huntington Wildlife (NY20: 0.6 pg m\(^{-3}\)) (see AMNet). On the contrary, at Birmingham (AL19), Athens Super Site (OH02) and Antelope Island (UT96), median GOM concentrations are significantly higher than at Waldhof (∼3.5 times the Waldhof concentration) (see AMNet). The median PBM PM2.5 concentration at Waldhof (6.3 pg m\(^{-3}\)) agrees best with the median PBM PM2.5 concentration at Athens Super Site (OH02; 5.5 pg m\(^{-3}\)) (see AMNet). Except for the sites Antelope Island (UT96) (see AMNet) and Zabrze (IPIS) (H. Pyta, pers. comm.) all the other selected sites show somewhat lower PBM PM2.5 median concentrations (see AMNet; Kentisbeer et al., pers. comm.) (Fig. 5).

Based on yearly median concentrations, between 2009 and 2011 there is no trend apparent for GEM and PBM PM2.5 at Waldhof (Table 3). The yearly median GOM concentration

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**Table 1. Three-year average percentiles from single measurements (PBM\(_{\text{PM2.5}}\) and GOM) or hourly values (GEM) between 2009 and 2011 at the German rural background site Waldhof**

GEM, gaseous elemental mercury; PBM\(_{\text{PM2.5}}\), particle-bound mercury (with particulate matter of a diameter of ≤2.5 μm); GOM, gaseous oxidised mercury. If the percentile or the minimum concentration is below the calculated method detection limit of 0.4 pg m\(^{-3}\), that value is given.

<table>
<thead>
<tr>
<th>Average percentile</th>
<th>GEM (ng m(^{-3}))</th>
<th>PBM(_{\text{PM2.5}}) (pg m(^{-3}))</th>
<th>GOM (pg m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>0.86</td>
<td>&lt;0.4</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>10th</td>
<td>1.40</td>
<td>1.5</td>
<td>&lt;0.4</td>
</tr>
<tr>
<td>50th</td>
<td>1.61</td>
<td>6.3</td>
<td>1.0</td>
</tr>
<tr>
<td>90th</td>
<td>2.08</td>
<td>20.3</td>
<td>5.8</td>
</tr>
<tr>
<td>Maximum</td>
<td>7.68</td>
<td>262</td>
<td>133</td>
</tr>
</tbody>
</table>

**Fig. 4.** Daily average gaseous elemental mercury (GEM), particle-bound mercury (PBM\(_{\text{PM2.5}}\)) with particulate matter of a diameter of ≤2.5 μm and gaseous oxidised mercury (GOM) concentrations from January 2009 to December 2011 at the German rural background site ‘Waldhof’ (in January 2010 and February 2011 the PBM\(_{\text{PM2.5}}\) daily average concentrations exceeded the given scale – maximum values are shown on top of the graph).
at Waldhof increases in the years 2010 and 2011 by \(\sim 0.5 \text{ pg m}^{-3} \text{ year}^{-1}\). However, these year-to-year variations do not necessarily indicate an increasing trend for GOM. The variations are well in the range of those found at various AMNet sites (see AMNet) (cf. Fig. 5). Prolonged measurements will allow for a statistically sound trend analysis. These will be carried out at the Waldhof site within the GMOS network framework.

Using the 3-year dataset of Waldhof, a first seasonality analysis can be carried out by calculating monthly average concentrations. The most pronounced seasonal variation is found for the \(\text{PBM}_\text{PM}_{2.5}\) concentration (Fig. 6). The squares in Fig. 6 represent the median concentrations, the error bars indicate the 10th and 90th percentiles. Apparently, during winter (December, January and February) the \(\text{PBM}_\text{PM}_{2.5}\) concentration, as well as its variability (range of percentiles), are more than twice as high as during the summer months (June, July and August) (3-year median winter concentration: 10.2\(\text{ pg m}^{-3}\); 3-year median summer concentration: 4.3\(\text{ pg m}^{-3}\)). Besides the \(\text{PBM}_\text{PM}_{2.5}\) concentration, the particles with a cut off diameter of 2.5\(\mu\text{m}\) (PM\(_{2.5}\)) mass concentration is given in Fig. 6 in grey dots. The PM\(_{2.5}\) data are averaged for the same time periods as the \(\text{PBM}_\text{PM}_{2.5}\) data. It is obvious that \(\text{PBM}_\text{PM}_{2.5}\) concentration shows a similar seasonality as the PM\(_{2.5}\) mass concentration.

\(\text{PBM}_\text{PM}_{2.5}\) mass concentrations in winter reflect increased emissions in winter time (e.g. from domestic heating) as well as meteorological effects (e.g. reduced height of the planetary boundary layer). No significant seasonality was found for the GEM and GOM concentration (not shown here).

\(\text{PBM}_\text{PM}_{2.5}\) and GOM concentrations are measured with a temporal resolution of 4 h 25 min (3 h sampling, 1 h and 25 min analysis, cleaning and function check). These data were used for a statistical analysis of the diurnal cycle. All 3-h measurements are binned to 1-h intervals (end of sampling time used for binning). Within three years for each hourly interval at least 195 concentration values (\(\text{PBM}_\text{PM}_{2.5}\), GOM) were available. Neither GEM nor \(\text{PBM}_\text{PM}_{2.5}\) concentrations show a significant diurnal cycle (not shown here). On the contrary, for GOM concentrations, a diurnal cycle becomes apparent (Fig. 7).

Conclusions
Speciated mercury measurements were performed at the German rural background site Waldhof. The high-resolution TGM time series started in 2002 and is ongoing. The dataset for GEM, \(\text{PBM}_\text{PM}_{2.5}\), and GOM, which started in 2009, is the first full-speciation time series reported for Central Europe and will be continued. The long-term monitoring of TGM with internationally accepted quality standards can be described as well established and operational. This is not the case for speciation data. The range of concentrations for the different operationally defined mercury species at different locations, driven by different processes, show the challenges to develop a standard operating procedure which is fit for purpose.

The daily and seasonal variability for GOM and \(\text{PBM}_\text{PM}_{2.5}\) concentrations can be extremely high, making it difficult to choose the best sampling and desorption intervals for the individual application. Furthermore, a sensitive and precise method with high time resolution is needed, in order to measure atmospheric processes and use the automated method for...
long-term monitoring. The reported maintenance procedures and service intervals were the key to achieving this goal. However, more experimental work and knowledge is needed to obtain more information about the reproducibility of the method and to achieve traceability to reference standards. Field intercomparisons should be carried out. Additionally, spike standards should be developed in the near future.

Table 2. Site information for selected sites with long-term monitoring of atmospheric Hg species

<table>
<thead>
<tr>
<th>Site name</th>
<th>Code</th>
<th>Province or state, country</th>
<th>Latitude (deg N)</th>
<th>Longitude (deg E)</th>
<th>Elevation (m)</th>
<th>Period</th>
<th>Reference</th>
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<td>44.43</td>
<td>–84.22</td>
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<td>2009–2011</td>
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<td>2009–2011</td>
<td><a href="http://nadp.sws.uiuc.edu/amn/">http://nadp.sws.uiuc.edu/amn/</a></td>
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Table 3. Yearly average concentrations (medians) of GEM, PBM_{PM2.5}, and GOM measured at the Waldhof site

<table>
<thead>
<tr>
<th>Year</th>
<th>GEM (ng m(^{-3}))</th>
<th>PBM_{PM2.5} (pg m(^{-3}))</th>
<th>GOM (pg m(^{-3}))</th>
</tr>
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<tr>
<td>2009</td>
<td>1.64</td>
<td>6.58</td>
<td>0.55</td>
</tr>
<tr>
<td>2010</td>
<td>1.59</td>
<td>6.36</td>
<td>1.04</td>
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<tr>
<td>2011</td>
<td>1.62</td>
<td>5.91</td>
<td>1.60</td>
</tr>
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</table>

Fig. 6. Monthly median concentrations for particle bound mercury and particles with a cut off diameter of 2.5 \(\mu\)m (PM\(_{2.5}\), with particulate matter of a diameter of \(\leq 2.5 \mu\)m) mass at the Waldhof site (2009 to 2011). Squares and dots represent the median concentrations and error bars indicate the 10th and 90th percentiles. Please note the broken y-axis for both parameters.

Fig. 7. Hourly median concentrations for gaseous oxidised mercury (GOM) at the Waldhof site (2009 to 2011). Squares represent the median concentrations and error bars indicate the 10th and 90th percentiles. Additionally, spike standards should be developed in the near future.
The speciated mercury dataset obtained from 2009 to 2011 at Waldhof showed a satisfactory agreement to speciated mercury datasets obtained at other northern hemispheric measurement sites. At 1.61 ng m\(^{-3}\), the 3-year median GEM concentration at Waldhof is in good agreement with the established northern hemispheric background GEM concentration. The 3-year median PBMPM\(_{2.5}\) concentration (6.3 pg m\(^{-3}\)) is approximately six times higher than the 3-year median GOM concentration (1.0 pg m\(^{-3}\)). Within the three years no trend is apparent for GEM and PBMPM\(_{2.5}\) concentrations. The observed increase in GOM concentrations is within the expected normal year-to-year variation. The observed seasonality for PBMPM\(_{2.5}\) concentrations correlates with the PM\(_{2.5}\) particle mass concentration. Winter concentrations of PBMPM\(_{2.5}\) were found to be more than twice the summer concentrations. It is assumed that the higher PBMPM\(_{2.5}\) concentrations during winter are caused by increased emissions (e.g. domestic heating) into a smaller mixing volume (lower boundary layer height). Statistical analysis further indicates a diurnal cycle for GOM concentrations, but not for GEM and PBMPM\(_{2.5}\) concentrations. As the cycle follows the availability of solar radiation, it is assumed to be a result of local photochemical oxidation and in situ production of GOM.

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References


