

Interactive comment on “Bimodal variation in mercury wet deposition to the coastal zone of the southern Baltic” by P. Siudek et al.

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We would like to thank the reviewer for valuable comments.

General comments Comments on the part Materials and Methods has been taken into account in the corrected paper. We hope that the correction is sufficient.

1. Quality control/quality assurances

Calibration curves have been done by determining Hg in solutions of known concentrations (5, 10, 25, 50 i 100 ng Hg L⁻¹) and in blanks (milliQ 18.2 MΩ resistance) with single and double amount of reagents. Standard solutions and reagents were prepared from top quality products (Suprapur Merck). Analyses were carried out in a laboratory meeting the standards specified for trace metals analyses, where Hg concentration in

the air was relatively low. Repeatability of the results for standards (triplicates) was lower than 10%. The detection limit of the method was 1.0 ng L⁻¹ (triple standard deviation of the blank). Over 80% of the environmental samples were analyzed twice or three times. The average standard deviation for Hg compounds easily reducible in SnCl₂ solution measured in precipitation samples was <10% (for 74% of samples) and the precision of THg analyses in precipitation was 8.0%. The average blank value obtained by measuring Hg concentration in milliQ water, which was used to wash the Teflon reception surface, was <0.5 ng L⁻¹. The relative error of Hg concentration in precipitation was 4.8% (for the range of concentrations 5-20 ng L⁻¹) and 7.9% (for the range >50 ng L⁻¹). 2. 22781-22782: The average THg concentration in rain is very high in this study, which is even higher than the measurement in China. Clarify the reason (such as the site description).

High values of mercury concentrations in precipitation over the southern Baltic were due to specific character of the study area, which was added to the manuscript. It has been emphasized several times that Hg wet deposition values can be elevated in areas close to the important sources of Hg (Dvonch et al., 1998, Munthe et al., 2001, Zielonka et al., 2005). The results presented in the Paper come from the first long series of studies on Hg deposition in the urbanized and industrialized coastal zone of the Gulf of Gdansk. Previous studies by Ebinghaus (1995), Boszke (2005) and the HELCOM reports suggested high concentrations of Hg in precipitation over the southern Baltic (58 ng L⁻¹). The city of Gdynia is a part of the Tricity Agglomeration (population of about 1 million) where anthropogenic emission sources of mercury are constantly active. Location of the measurement site in the center of the city, about 1 km from the coastline, caused that it was under the influence of different emission sources among which regional and local, situated on the land as well as marine sources were the most important. Important sources of Hg in the city and nearby area are: coal-burning heat and power plants of over 336 MW power, several hundreds of individual power and heat generating stations and domestic furnaces, where coal is the main fossil fuel. Moreover, stockyards, dumping grounds for municipal wastes, hospital and domestic

sewage, sewage treatment plants as well as different industrial units producing metals and paints, chemical industry, the refinery, harbours and shipyards can be also regarded as sources of Hg emission. Domestic furnaces are usually not equipped with combustion gases treatment units and also different types of wastes are burnt in such furnaces apart from coal (Ćwiklak, 2006). During heating seasons, heat-generating plants in Gdansk and Gdynia use about 3000 tons of coal per day (EC Wybrzeze Report, 2006). On the basis of previous data ($n=7$) on average concentrations of Hg in wet precipitation over the southern Baltic (58 ng L⁻¹, Ebinghause et al., 1995), the average atmospheric Hg inflow with dry and wet precipitation (depth of precipitation: 570 mm) in that area, was calculated to be 100 ng m⁻² day⁻¹ (35-190 ng m⁻² day⁻¹). Zielonka (2005) gives the value of 3.980 $\mu\text{g m}^{-2} \text{d}^{-1}$ in the heating season for the southern Poland, where the average consumption of coal in individual domestic furnaces is 2.5 Mg. The results of THg concentrations in precipitation over the southern Baltic are high but comparable to data from the other region of the southern Baltic - Zingst, Germany (Ebinghause et al., 1995). Concentrations of Hg in precipitation over the northern Poland (Baltic) are two orders of magnitude lower than those measured over the southern Poland or observed at some measurement sites located in the cities of Central and Eastern Europe. For example, in Vilnius (Lithuania) concentrations of Hg in precipitation collected in bulk collectors were within the range of 70-180 ng L⁻¹ and the average value of monthly and yearly Hg deposition was over 3.0 $\mu\text{g Hg m}^{-2}$ and 60 $\mu\text{g Hg m}^{-2}$, respectively (Milukaite i in., 2008).

3. The word "purify" has been used incorrectly, we meant "mercury scavenging processes" which wash mercury out of the air. It has been corrected.

4. By the term "labile Hg" we meant easily reducible in SnCl₂ solution ionic mercury which did not need to be oxidized by BrCl and reduced by NH₂OH HCl.

Specific comments:

1. The introduction is way too long and not focused on wet deposition. The introduction

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has been shortened and is now mainly focused on wet deposition.

2. Page 22780 Line 5: What are the “both forms of Hg”? By the term “both forms” we meant Hg(II) (ionic, dissolved) and THg in precipitation.

3. Page 22780 Line 10-14: The dissolved fraction was separated by filtration only during from spring to late autumn. How are the authors convinced that there was no contamination from filtration process? Contamination by filtration could cause the seasonal variability of Hg conc. in precipitation. Also did the authors use “dissolved Hg” concentration as Hg(II) in the result? In that case, THg in this article is sum of “dissolved Hg” and “particulate Hg”? What does Hg(II) mean in this article? Terms are very confusing.

By the term “THg” we meant the sum of dissolved and non-dissolved fractions in the filtrated samples. The process of filtration was carried out in clean bench (laminar flow chamber). Contamination of environmental samples was excluded by carrying out the tests for filtration. The series of filtrated blanks (milliQ water) was tested for Hg and we obtained the results similar to non-filtrated blanks. The results did not show statistically significant differences. The filtration was also used in the works of Poissant and Pilote, 1998, Zielonka et al., 2005.

4. The following terms were used for Hg in precipitation: a. total mercury – THg (after oxidation by BrCl and pre-reduction by NH₂OH HCl and then after reduction by SnCl₂) b. ionic mercury, dissolved – operationally defined (Hg(II)), measured by direct reduction in SnCl₂. Methods after Ebinghause et al. (1995). In this Paper the term “Hg(II)” indicates Hg compounds conventionally defined as ionic, dissolved forms of Hg measured by direct reduction of Hg(II) to elemental Hg in SnCl₂ solution.

5. Page 22781 Line 20: How did you measure “the concentration of reactive mercury forms”? What does the reactive mercury form mean?

RGM was not measured. By the term “reactive Hg forms” used in the manuscript we

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meant the ionic fraction of Hg, dissolved and easily reducible in SnCl_2 , measured according to the procedure by Ebinghaus et al. (1995).

6. 22783, Line 5-9: The authors explained that the elevated THg concentration (in precipitation) in summer was derived by the reemission of Hg from natural surfaces. However, re-emitted form is almost entirely Hg_0 , which is very insoluble. On the other hand, the Hg forms that are easily deposited are gaseous divalent Hg and particulate Hg. Therefore reemission is hardly the reason of an increase in THg in rain.

In the conditions described by us, Hg is emitted from water to the atmosphere. Elemental mercury emitted from seawater to the atmosphere can be oxidized to the ionic forms by reactive chloride radicals and by components of marine aerosol. Very reactive mercury compounds formed during transformations mentioned above can be transported inland if marine breeze or strong wind from the sea occurs, and then deposited on land. In the coastal areas these processes are intensified by hydrodynamical and meteorological conditions and by availability and high concentration of Cl_2 . Similar dependences were also observed and described by Steding and Flegal, 2002, Laurier et al., 2003, Sheu and Mason, 2004, Hedgecock et al., 2005, Lai et al., 2007. Additionally, high concentrations of Hg in precipitation during summer can be the result of elevated concentrations of oxidants as hydrogen peroxide, hydroxyl radicals, halogens, which stimulate GEM transformation into reactive Hg forms included in rains (Engle et al., 2008).

7. 22787 Line 14-17. What does the sentence “The lower they were flowing, the higher were the concentration of Hg in wet precipitation” mean? How did you identify the height at which the air masses were flowing?

The height at which the air mass was flowing over the study area was determined using the HYSPLIT model (NOAA/ARL), the heights were as follows: 20, 100 and 250 m.

8. Fig. 5: What does the legend (>40 , <24 , <4) mean?

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In Fig. 5 the legend means THg concentrations in precipitation occurring at the given wind speed and with reference to the prevailing wind direction (eight major wind directions).

9. 22783, Line 20-26: I cannot understand the logic here. The authors said that it was found that a 1000-fold lower volume contains a 14-fold higher amount of mercury, which proves: : ... effectively. What does this sentence mean? Most of TGM in ambient air is Hg⁰, and most of THg in rain is Hg(II). Hg⁰ should have very little contribution to THg concentration in rain.

We agree with this suggestion. We only wanted to show that wet precipitation reduces the atmospheric mercury pool. TGM contains 90%-95% of Hg⁰ insoluble in water, so Hg⁰ amount in precipitation is generally less than 0.5%. Elemental mercury can be wash out from the atmosphere by wet or dry deposition only when it is previously oxidized to easily soluble gaseous mercury Hg(II) or particulate Hg.

10. Figure 2: THg concentration is volume-weighted? It should be volume-weighted, because concentration in rain is generally dependent on precipitation depth. Both fluxes and concentrations need to show 95% confidence interval or one standard deviation. Also precipitation depth should be inserted because it is a major factor influencing deposition amount.

In Fig. 2 there were presented the arithmetic averages of Hg concentrations in precipitation and deposition (for 2008). According to the suggestion, it has been corrected (now it is Hg volume-weighted concentration) and precipitation depth has been inserted. We also included in the description of the figure information on the significance level obtained from trend analysis for individual measurement months.

11. 22784, Line 20-25, and Figure 4: This figure (this result) does not necessarily indicate that pH in rain can control the forms of Hg. I suggest the authors to create this figure using THg as well, and see whether the result would be same or not. If same, pH is not a factor on determining the forms of Hg. I suspect that SO_x and NO_x, the

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major pollutant emitting from fossil-fuel combustion caused the low pH during heating seasons, and THg in rain increased as well. Therefore low pH and high Hg might happen to be observed together, but one does not affect to another. Also since the both pH and Hg concentration in rain are likely to be affected by precipitation depth, the effect of precipitation depth should be excluded in interpretation. Maybe one can use volume-weighted concentration and volume-weighted pH.

THg/pH dependences has been checked and compared with Hg(II)/pH. For the non-heating season we have obtained different results: Hg(II) depends on pH in direct proportion and, on the other hand, THg depends on pH in indirect proportion ($p < 0.05$). For the heating season we have got no differences: both Hg(II) and THg correlated negatively with pH. These results might indicate that pH in precipitation can be regarded as an additional parameter giving information on Hg transformations in a liquid phase. The discussion has been extended to precipitation depth in the part about pH and Hg concentration.

12. Figure 1: Much more details should be included, such as adjacent countries.

A more detailed map has been attached.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/9/C10098/2010/acpd-9-C10098-2010-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 22773, 2009.

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