

Hg⁰ trends in the North and South Atlantic

A. L. Soerensen^{1,2*}, D. J. Jacob², D. Streets³, M. Witt⁴, R. Ebinghaus⁵, R. P. Mason⁶, M. Andersson^{6,7}, E. M. Sunderland^{1,2}

¹ Harvard School of Public Health, Department of Environmental Health, Boston MA 02215, USA,

*alsoeren@hsph.harvard.edu

² Harvard University, School of Engineering and Applied Sciences, Cambridge MA, 02138, USA

³ Decision and Information Sciences Division, Argonne National Laboratory, Argonne, Illinois, USA

⁴ University of Oxford, Department of Earth Sciences, South Park Road, Oxford, OX1 3AN, UK

⁵ Helmholtz-Zentrum Geesthacht, Institute of Coastal Research, Max-Planck-Strasse, 21502 Geesthacht, Germany

⁶ University of Connecticut, Department of Marine Sciences, 1080 Sennecossett Road,

Groton, CT, 0634, USA

⁷ ESSIQ AB, Gothenburg, Sweden

Abstract. It was recently found that atmospheric Hg had decreased with 20-38% worldwide since the mid 1990s. However, the decrease is not supported by emission inventories that show rising global anthropogenic emissions over the past decades. We analyzed atmospheric data from 22 ship cruises in the North Atlantic (defined as 2°N-65°N), and 15 in the South Atlantic (defined as 70°S-8°N) between 1977 and 2010, as well as surface water Hg⁰ from 10 cruises in the West Atlantic Ocean between 1998 and 2010. Linear regression analysis based on these cruise ensembles for each hemisphere will be discussed. We use the GEOS-Chem biogeochemical model to explore possible drivers of the Hg⁰ trends found in this study and at previous studies at land based stations. These findings will also be discussed.

Key words: Mercury, atmosphere, ocean, Atlantic, trend, decline, Hg⁰

Introduction

Total gaseous mercury (TGM) has been measured on ship cruises since the 1970s (Temme et al., 2003) and at long term monitoring sites on land since the 1990s (Temme et al., 2007; Slemr et al., 2011; Toersth et al., 2012). Wet deposition fluxes have also been measured in Europe and North America since the 1990s (Prestbo and Gay, 2009; Toersth et al., 2012).

Long-term trends over these periods have previously been weak or inconsistent (Wangberg et al., 2007; Kock et al., 2005; Prestbo and Gay, 2009), but recently Slemr et al. (2011) found that atmospheric Hg had decreased worldwide with 20-38% since the mid 1990s. Their trend was based on analysis of data from Mace Head, Ireland, and Cape Point, South Africa, as well as 5 cruises from the Atlantic Ocean. Independently, Ebinghaus et al. (2011) have applied inverse modelling to identify baseline air masses arriving at Mace Head, Ireland, which confirmed the decrease. A worldwide decrease of 20-38% is large compared to that seen in other trace gases.

Additionally, the observed decrease is contradicting emission inventories that show 30-40% increase in global

anthropogenic emissions over the past decade (Streets et al., 2011).

Here we present cruise trends of gaseous elemental mercury (Hg⁰) in the Atlantic marine boundary layer (MBL) and North Atlantic surface ocean including data from 31 cruises over the period 1977 to the present. We show that surface air Hg⁰ has not decreased worldwide. We furthermore show that changes in subsurface aqueous Hg in the North Atlantic Ocean can help explain observed Hg⁰ trends in the Northern Hemisphere (NH).

Materials and Methods

We used linear regression to analyze atmospheric data from 21 ship cruises in the North Atlantic (defined as 2°N-65°N), and 15 in the South Atlantic (defined as 70°S-8°N) between 1977 and 2010 (Temme et al., 2003, Mason et al., 1998, Lamborg et al., 1999, Mason et al., 2001, Laurier and Mason, 2007, Aspomo et al., 2006, Sommar et al., 2010, Soerensen et al., 2010a, Kuss et al., 2011, Andersson et al., 2008, Mason et al., 2009, M. Witt (unpublished data, 2010), R. Ebinghaus (unpublished data, 2010)). During cruise campaigns atmospheric

gaseous Hg was measured as either Total Gaseous Mercury (TGM = $\text{Hg}^0 + \text{Hg}^{\text{II}}$), where Hg^{II} is gaseous oxidized mercury, or as Hg^0 . Hg^{II} comprises only a few percent of TGM in the remote MBL (Gustin and Jaffe, 2010); thus we do not distinguish between TGM and Hg^0 in the rest of our discussion.

We also analyzed surface ocean data of aquatic Hg^0 collected by Mason et al. (2001) during five cruises between 1998 and 2000 and by Andersson et al., (2008), Mason et al., (2009), and R.P. Mason, (unpublished data, 2010) during another five cruises between 2008 and 2010. All ten cruises were from the NH West Atlantic. We used a t-test to test if surface water Hg^0 measured between 1998-2000 were statistically different from the observations between 2008-2010.

Results and Discussion

Atmospheric cruise observations from the North Atlantic surface air support the reported decrease of Hg^0 at terrestrial sites since the mid 1990s. We note some different spatial patterns that will be discussed in this presentation. In addition, we will discuss trends in Hg^0 data from the North Atlantic surface ocean.

We use the GEOS-Chem biogeochemical mercury model to test possible drivers of the Hg^0 trend seen in North Atlantic surface air and water. The model is described thoroughly in Soerensen et al. (2010b) and Holmes et al. (2010).

To test the implication of Hg^0 and Hg^{II} emissions changes we run the model with historic anthropogenic emissions estimates from Streets et al. (2011) from the years 1990 (1435 Mg/a) and 2008 (1968 Mg/a). To test the implications of a decline in subsurface seawater Hg in the North Atlantic Ocean we also run the model with different subsurface Hg concentrations.

The results from these model simulations will be discussed further at the conference.

Acknowledgements

This work was supported by the U.S. NSF Atmospheric Chemistry and Chemical Oceanography Divisions as well as the Electric Power Research Institute.

References

Andersson, M.E., W.F. Fitzgerald, and R.P. Mason (2008), Mercury air-sea exchange on the New England shelf, paper presented at AGU fall meeting 2008, American Geophysical Union, San Francisco, USA.

Aspmo, K., C. Temme, T. Berg, C. Ferrari, P. A. Gauchard, X. Fain and G. Wibetoe (2006), Mercury in the atmosphere, snow and melt water ponds in the North Atlantic Ocean during Arctic summer, *Environ. Sci. Technol.*, 40(13), 4083-4089.

Ebinghaus, R., S.G. Jennings, H.H. Kock, R.G. Derwent, A.J. Manning, T.G. Spain (2011), Decreasing trends in total gaseous mercury observations in baseline air at Mace Head, Ireland from 1996 to 2009. *Atmos. Environ.* 45, 3475-3480.

Gustin, M. and D. Jaffe (2010), Reducing the Uncertainty in Measurement and Understanding of Mercury in the Atmosphere, *Environ. Sci. Technol.*, 44(7), 2222-2227.

Holmes, C. D., D. J. Jacob, E. S. Corbitt, J. Mao, X. Yang, R. Talbot and F. Slemr (2010), Global atmospheric model for mercury including oxidation by bromine atoms, *Atmos. Chem. Phys.*, 10(24), 12037-12057.

Kock, H. H., E. Bieber, R. Ebinghaus, T. G. Spain and B. Thees (2005), Comparison of long-term trends and seasonal variations of atmospheric mercury concentrations at the two European coastal monitoring stations Mace Head, Ireland, and Zingst, Germany, *Atmos. Environ.*, 39(39), 7549-7556.

Kuss, J., C. Zulicke, C. Pohl, and B. Schneider (2011), Atlantic mercury emission determined from continuous analysis of the elemental mercury sea-air concentration difference within transects between 50°N and 50°S, *Global Biogeochem. cycles*, 25, GB3021, doi:10.1029/2010GB003998.

Lamborg, C. H., K. R. Rolfhus, W. F. Fitzgerald and G. Kim (1999), The atmospheric cycling and air-sea exchange of mercury species in the South and equatorial Atlantic Ocean, *Deep-Sea Res.*, 46(5), 957-977.

Laurier, F. and R. Mason (2007), Mercury concentration and speciation in the coastal and open ocean boundary layer, *Journal of Geophysical Research-Atmospheres*, 112(D6).

Mason, R. P., K. R. Rolfhus and W. F. Fitzgerald (1998), Mercury in the North Atlantic, *Mar. Chem.*, 61(1-2), 37-53.

Mason, R. P., N. M. Lawson and G. R. Sheu (2001), Mercury in the Atlantic Ocean: factors controlling air-sea exchange of mercury and its distribution in the upper waters, *Deep-Sea Res.*, 48(13), 2829-2853.

Mason, R.P., M.E. Andersson, A.L. Soerensen, and E.M. Sunderland (2009), Measurements and modeling of the air-sea exchange of mercury, paper presented at AGU fall meeting 2009, American Geophysical Union, San Francisco, USA.

Prestbo, E.M., and D.A. Gay (2009), Wet deposition of mercury in the U.S. and Canada, 1996-2005: Results and analysis of the NADP mercury deposition network (MDN), *Atmos. Environ.* 43, 4223-4233.

Streets, D.G., M.K. Devane, Z. Lu, T.C. Bond, E.M. Sunderland, and D.J. Jacob (2011), All-Time Release of Mercury to the Atmosphere from Human Activities, *Environ. Sci. Technol.*, 45(24), 10485-10491.

Slemr, F., E.-G. Brunke, R. Ebinghaus, and J. Kuss (2011), Worldwide trend of atmospheric mercury since 1995, *Atmos. Chem. Phys.*, 11, 4779-4787.

Soerensen, A.L., H. Skov, D.J. Jacob, B.T. Soerensen, and M.S. Johnson (2010a), Global concentrations of gaseous elemental mercury and reactive gaseous mercury in the marine boundary layer, *Environ. Sci. Technol.*, 44, 7425-7430.

Soerensen, A.L., E.M. Sunderland, C.D. Holmes, D.J. Jacob, R.M. Yantosca, H. Skov, J.H. Christensen, S.H. Strode, and R.P. Mason (2010b), An improved

- global model for air-sea exchange of mercury: High concentrations over the North Atlantic, *Environ. Sci. Technol.*, *44*, 8574-8580.
- Sommar, J., M. E. Andersson and H. W. Jacobi (2010), Circumpolar measurements of speciated mercury, ozone and carbon monoxide in the boundary layer of the Arctic Ocean, *Atmos. Chem. Phys.*, *10*(11), 5031-5045.
- Temme, C., F. Slemr, R. Ebinghaus and J. W. Einax (2003), Distribution of mercury over the Atlantic Ocean in 1996 and 1999-2001, *Atmos. Environ.*, *37*(14), 1889-1897.
- Temme, C., P. Blanchard, A. Steffen, C. Banic, S. Beauchamp, L. Poissant, R. Tordon and B. Wiens (2007), Trend, seasonal and multivariate analysis study of total gaseous mercury data from the Canadian atmospheric mercury measurement network (CAMNet), *Atmos. Environ.*, *41*(26), 5423-5441.
- Toerseth, K., W. Aas, K. Breivik, A.M. Fjaeraa, M. Fiebig, A.G. Hjellbrekke, C. Lund Myhre, S. Solberg, and K.E. Yttri (2012), Introduction to the European Monitoring and Evaluation Programme (EMEP) and observed atmospheric composition change during 1972-2009, *Atmos. Chem. Phys. Disc.*, *12*, 1733-1820.
- Wangberg, I., J. Munthe, T. Berg, R. Ebinghaus, H. H. Kock, C. Temme, E. Bieber, T. G. Spain and A. Stolk (2007), Trends in air concentration and deposition of mercury in the coastal environment of the North Sea Area, *Atmos. Environ.*, *41*(12), 2612-2619.