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Multi-decadal decline of mercury in the North Atlantic atmosphere explained by changing subsurface seawater concentrations

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Abstract

We analyze 1977-2010 trends in atmospheric mercury (Hg) from 21 ship cruises in the North Atlantic (NA) and 15 in the South Atlantic (SA). We find a steep1990-2010 decline of -0.046±0.010 ng m^{-3} a^{-1}(-2.4% a^{-1}) in NAsurface air (steeper than at NH land sites) but no significant declinein the SA. Surface water Hg^0 measurements in the NAshow a decline of -5.7 % a^{-1}since 1999, while the few subsurface ocean data available show ~85% decline from 1980 to

present. We use a coupled global atmosphere-ocean modelto show that the decline in the NA atmosphere can be explained by decreasing evasion from the ocean driven by declining subsurface water Hg concentrations. Wepropose that past historical enrichment of the NA ocean was caused by enhanced riverine and wastewater discharges of Hg.

1. Introduction

Mercury (Hg) is emitted to the atmosphere by natural processes (crustal degassing, volcanoes) and also by human activities (fuel combustion, industry, mining). This atmospheric Hg deposits to the surface, cycles through ecosystems, may be re-emitted to the atmosphere, and is eventually incorporated into more stable reservoirs in the soil and the deep ocean. Accumulation of mercury in ecosystems and subsequent human exposure through fish consumptionis a major environmental concern[*Mergler et al.,*2007;*Mahaffey et al.,* 2009].

Total gaseous mercury (TGM) has been measured on ship cruises since the 1970s [*Temme et al.,*2003] and at long-term land monitoring sites since the 1990s [*Temme et al.,*2007*; Slemr et al.,*2011*; Toerseth et al.,* 2012]. Several recent studies have reported a declining Hg trend. *Slemr et al.* [2011] found that atmospheric Hg decreased worldwide by 20-38% over the 1996-2009 period, based on long-term data from Mace Head (Ireland) and Cape Point (South Africa), as well as five cruises over the Atlantic Ocean. Statistically significant declinesfor the 1995-2009 period have also been reported for Mace Head [*Ebinghaus et al.,* 2011], Alertin Arctic Canada [*Cole and Steffen,* 2010], and St. Anicet and Kuujjuarapik in eastern Canada [*Cole et al.,*2011].These decreases are inconsistent with the Hgemission inventory from *Streets et al.* [2011], which finds a global increaseof 30% over the past decadedriven by rising Asian emissions. Atmospheric Hg^0 is sufficiently long-lived that emission trends should be reflected in atmospheric observations at least on a hemispheric scale [*Corbitt et al.,* 2011].

The observed decline in atmospheric Hg couldreflect a decrease in Hg re-emission from geochemical reservoirs to the atmosphere [*Slemr et al.,*2011]. In particular, high Hg in subsurface seawater of the North Atlantic (NA) [*Laurier et al*., 2004]has been attributed to a historical legacy of 20th-century anthropogenic emissions [*Sunderland and Mason,*2007] and canexplain the high surface air concentrations observed in NA cruises[*Soerensen et al.,* 2010b].A decline in this subsurface loading would cause atmospheric concentrations to decrease.

Here wepresentan analysis of 1977-2010Hg trends in the atmosphere and surface ocean using the full ensemble of cruise data available for the NA and South Atlantic (SA). We finda steep decline in the NA since 1990 but no significant trend in theSA. We show that the NA decline can be explained by historical enrichment of the subsurface ocean and propose that past wastewater discharges could be a major factor in this enrichment.

2. North and South Atlantic trends

We analyzedatmospheric data from 21ship cruisesin the NA (5°N-65°N), and 15in the SA(70°S-11°N)(Figure 1) between 1977 and 2010. We know of no cruise data between 1981 and 1989. We separate NA fromSAby the location of the Intertropical Convergence Zone (ITCZ) at the time of the cruise. Atmospheric Hg is measured as either TGM ≡Hg^0 + Hg^{II} or as Hg^0. Hg^{II}accounts for only a few percent of TGM in the remote MBL[*Gustin and Jaffe,*2010], thus we do not distinguish between the two in our discussion.

Figure 1 shows the 1977-2010 surface air concentrations for the ensemble of cruises, separately for the NA and the SA. Also shown are the 1996-2009 data for Mace Head and Cape Point. There are no significant trends between the late 1970s and the early 1990s for eitherthe

NAor SA. For 1990-2009,we find a significant decrease in the NA of-0.046±0.010 ng m^{-3} a^{-1}(±standard error)or -2.4% a^{-1} (p<0.001, n=18), steeper than the 1996-2009decrease reported by *Slemr et al.* [2011] and *Ebinghaus et al.* [2011] for Mace Head (-0.024±0.005 ng m^{-3} a^{-1} and -0.028±0.01 ng m^{-3} a^{-1}, respectively).Accounting for the seasonal variation of Hg over the NA [*Soerensen et al.,* 2010a] does not change this result. We find no significant trend in the SA cruise data, in contrast to Cape Point where *Slemr et al.* [2011] reported a 1996-2010 decreasing trend of -0.034±0.005ng m^{-3} a^{-1}, corroborated by their fiveSA ship cruises. However, Figure 1shows that these five cruises (filled squares) may not be representative of the ensemble of cruise data in the SA. In particular, thelow 2008-2009 concentrations from *Kuss et al.* [2011] that anchor the *Slemr et al.* [2011] decreasing trend are not consistent with three other 2006-2010 cruises that show higher values.

We do not have a good explanation for the inconsistency in 1996-2010 trends between the SA cruises and Cape Point. However, atmospheric Hg at Cape Point exhibits anomalous behavior. Frequent Hg depletion events have been recorded at that site since the introduction of high-resolution measurements in 2007 and appear to be of local origin (indicated bylow wind speed) but are otherwise not understood[*Brunke et al.,*2010]. Of the eight SA cruises that used high-resolution Tekran measurements, only the *Kuss et al.*[2011]cruise reported evidence of sporadic depletion events [*Brunke et al.,*2010]. Interpretation of the Cape Point trend may require better understanding of factors determining local Hg depletion events.

Slemr et al.[2011] argued that the 1996-2009 decrease in Hg was worldwide, mainly on the basis of the similarity between Mace Head, Cape Point, and their selected cruises. We find otherwise from the ensemble of cruise data, with a sharp contrast between the strong decreasing trend in the NA and the lack of trend in the SA. Such a hemispheric contrast is not inconsistent with theatmospheric lifetime of ~6 months for Hg that allows it to mix efficiently on a hemispheric scale but less so between hemispheres [*Corbitt et al.*,2011]. It appears furthermore that the decrease over the NA is stronger than observed elsewhere in the Northern hemisphere (NH) over the past 20 years, including atthe nearby continental sites of Mace Head, Kuujjuarapik, and St. Anicet(-0.024 to -0.033 ng m^3 a^{-1}[*Ebinghaus et al.*,2011; *Slemr et al.*,2011; *Cole et al.*,2011]) and at Artic sites (-0.009 ng m^{-3} a^{-1} at Alert and no trend at Svalbard) [*Cole and Steffen,* 2010; *Cole et al.*, 2011]).

Concentrations of Hg in the MBL reach steady state with the surface ocean mixed layer on a time scale of less than a year [*Soerensen et al.,* 2010b]. Surface seawater Hg^0data were collected during five cruises in the Northwest Atlantic in 1998-2000 [*Mason et al.,* 2001] and five cruises in the same area in 2008- 2010 [*Andersson et al.*,2008; *Mason et al.*,2009; R.P. Mason, unpublished data]. The data are given in Auxillary Table A2. Observed mean concentrations were 244±100fM in 1998-2000 and 136±33fM in 2008-2010. This representsa significant decrease of -5.7% a^{-1}during the period(t-test paired means difference, $p<0.05$).Thus, surface water Hg^0 data support the decline found in the NA surface air and are even steeper than in surface air over the same 1999-2009 period (-0.066 ng m^3 a^{-1}, -4.0% a^{-1}, $n=14$).As we will see below, this is consistent with oceanic forcing of the atmospheric trend.

3. Causeof the North Atlantic Hg decline

We use the GEOS-Chem global biogeochmicalmercury model (v 9-01-02; http://www.geos-chem.org) toinvestigatepossible causes of the Hg trend in the NA. The model is describedby*Soerensen et al.*[2010b],*Holmes et al.*[2010], and Zhang *et al.* [2012] and has been extensively evaluated against observed concentrations and wet deposition from surface sites and ship cruises.The model couples a 3-D atmosphere with 2-D (horizontal) surface ocean and land reservoirs. Subsurface ocean concentrations are specified as constant values from mean observed concentrations in different ocean basins (Soerensen et al., 2010b). Here 'surface ocean' denotes the ocean mixed layer (annual global mean depth ~50 m), and 'subsurface ocean' denotes the water column from the bottom of the mixed layer to the depth of the permanent thermocline (~1000-1500 m)[*Mason et al., 2012*]. We updated the standard simulation of aqueous-particle partitioning of Hg^{II} in the surface ocean [*Soerensen et al.,* 2010b] with a specificK_D(affinity of aqueous Hg^{II} for the solid phase) of $1x10^5$ L kg^{-1} for the NA based onobserved values from*Mason et al.*[1998]. All simulations presented here use $4^o x 5^o$ horizontal resolution, are initializedfor two years (2006-2007) and use the same meteorological year (2008).

Global anthropogenic Hg emissions increased by 30% between 1990 and 2008 according to *Streets et al.*[2011] but Hg^{II} emissions in the USA and Europedecreased by -20% and -40%, respectively. Hg^{II} is removed regionally by deposition, in contrast to Hg^0, which mixes on a hemispheric scale.Thus, decreases in locally emitted Hg^{II}could haveselectively impacted the North Atlantic seawater Hg levels and associated evasion rates.We conducted GEOS-Chemsimulations using 1990, 2000, and 2008 anthropogenic emissions from*Streets et al.* [2011] withall else kept constant. As shown in Figure 2, regional decrease of Hg^{II} emissions is insufficient to compensate for the global rise of Hg emissions except over western Eurasia. GEOS-Chem includes fast in-plume reduction of Hg^{II} from power plant emissions [*Zang et al., 2012*], but a sensitivity simulation without this in-plume reduction still does not show a 1990-2008 decline over the NA.

In the 1980s and 1990sNA subsurface waterswere found to be enriched in total Hg compared to the North Pacific [*Gill and Fitzgerald,*1988*; Laurier et al.,* 2004]. Howeverthere is evidencethat North Atlantic subsurface seawater concentrations havedeclinedsharply over the pastseveral decades.Profile measurements near the Bermuda Atlantic Time-Series Study (BATS) station(32N, 64W) showed values of 5-9 pM in July 1979 and September 1983 [*Gill and Fitzgerald,*1988],1.0-2.5 pM in different seasons in 1999-2000 [*Mason et al.*, 2001], and 0.6-0.8 pM in June 2008 [*Mason et al.,*2012]. Similarly, Scotian Shelf inflow water measured by *Dalziel* [1992] in the mid-1980s showed more than a two-fold enrichment compared to concentrations measured in 2002 [*Sunderland et al.,* 2012]. Clean measurement techniques were established in the1980s [*Gill and Fitzgerald,* 1987] and allow confidence in thesetrends.

We conducted GEOS-Chem simulations imposing different subsurface ocean concentrations inthe NA (0-70°N)for 1990, 2000 and 2008, with all else constant including anthropogenic emissions at 2008 levels(*Streets et al.* 2011).Since the surface air data show no significant trend for 1977-1990 (Figure 1), we assume a subsurface ocean concentration of 5 pM (lower range from *Gill and Fitzgerald* [1988]) in 1990, 1.8 pM in 2000, and 0.7 pM in 2008. Modeled Hg concentrations in the surface ocean and atmosphere respond to changes in subsurface ocean Hg within 5-6months [*Corbitt et al.,* 2011], so that individual simulations for each decade can adequately capture the 1990-2008 trend.

Figure 2 shows that changes in NAsubsurface seawater concentrations results in a -0.042 ng m^{-3} a^{-1}(-2.4%) 1990-2008 model decline in surface air concentrationsacross the NA, closely reproducing the observed trend of -0.046±0.010 ng m^{-3} a^{-1}(Figure 1).The simulated surface ocean Hg^0 concentration in the NAdeclinesby -7.0 % a^{-1} between 2000 and 2008, close to the observed -5.7% a^{-1} decline. The steeper decline in the NA surface ocean relative to the atmosphere is thus reproduced by the model, providing further support for a subsurface ocean driver of the atmospheric trend.

Simulations show that declining Hg concentrations in subsurface seawater have a spatially variable impact on surface air Hg^0 concentrations, with more pronounced effects on the NA MBL and Coastal Europeansurface air Hg^0compared to elsewhere in the NH (Figure 2). Using the 1990-2008 model estimateswe capture the yearly percentage decline of Hg^0 at mid latitudeterrestrial sites within an average of ±28% [*Ebinghaus et al.,* 2011; *Cole et al.,* 2011]. Thus, declines in subsurface seawater Hg concentrations help to explain variablerates of declinesin the surface atmosphere observed across sites in the NH. The simulated trend in South Atlantic surface air is -0.8% a^{-1} for the period 1990 to 2008 (Figure 1). This is much weaker than in the Northern Hemisphere as would be expected from the atmospheric lifetime of Hg^0 [*Corbitt et al.,* 2011].A simple bootstrapping procedure shows that given the variability in cruise observations the weak modeled trend over the South Atlantic would be undetectable in observations (Figure 2).

4. Drivers of the North Atlantic subsurface waterdecline

Vertical seawater profiles from the West Atlantic [*Gill and Fitzgerald,* 1988; *Mason et al.,* 2001, 2012]suggest an 80% decline in NA subsurface watersin the last 30years. A parallel can be drawn withPbconcentrations, which declined by 85% in the subsurface NAbetween 1979 and 2008after leaded gasoline was phasedoutin the 1970s and1980s [*Wu and Boyle,*1997; *Lee et al.,* 2011].Tracer data for NA subsurface waters indicate a mean age of 10-30 years since last contact with the atmosphere [*Fine et al.,* 2010]. Thus a 30-year trend in the Hg content of this reservoir would be sensitive to trends in inputs going back to the 1960s.We consider different possibilities below.

Parrella et al. [2012] suggested that decreased Hg input to NA subsurface waters over the past decades could have been caused by a decrease in Hg^0 oxidation in the MBL, which appears to be the principal supplier for Hg deposition to the NA [*Selin et al.,* 2008; *Holmes et al.,* 2009]. If Br atoms are the main oxidant for Hg^0 in the MBL [*Hedgecock and Pirrone,* 2004; *Holmes et al.,* 2009], then a large decrease in Hg^0 oxidation would be expected because of the observed two to three times increase of surface ozone over the NAover the past fivedecades [*Lelieveld et al.,* 2004; *Parrish et al.,2009*]. Increasing surface ozone causes a proportional decrease in Br concentrations by shifting the Br/BrO radical equilibrium toward BrO.

Large declines in Hg inputs from rivers and wastewater to the NA Ocean concurrent with regulation of industry and other point sources are another possible driver of the temporal trend in subsurface NAseawater between the 1970s and present. Rivers are presently estimated to provide up to 220 Mg a^{-1} to the NA Ocean compared to ~860 Mg a^{-1} from atmospheric deposition [*Sunderland and Mason*, 2007]. However, a decline of ~50% in this source relative to peak discharges in the 1970s is observed in multiple sedimentaryarchives collected at the mouths of rivers from estuaries in North America and Europe [e.g., *Sunderland et al.* 2010; *Varekamp et al.*, 2000; *Boutier et al.,* 2011; *Elbaz-Poulichet et al.,* 2012] suggesting a much larger historical supply of Hg to the NA.

Chlor-alkali plants were a particularly large (losses > 875 Mg a^{-1})Hg source in the 1970s in the US and Europe [*D'Itri and D'Itri,*1977,*Euro Chlor,* 2005]. The European chlor- alkali industry reported that Hg discharged in effluents almost equaled atmospheric Hg losses in the 1970s [*Euro Chlor,* 2005]. Manychlor-alkali factorieswere located in coastal areas with effluents containing Hg discharged directly into estuaries [*D'Itri and D'Itri,* 1977].The Hg source from the chlor-alkali industry is now only a few percent of what it was in the 1970s [*D'Itri and D'Itri,*1977,*Euro Chlor,* 2005; *Chlorine Institute,* 2009].

Municipal wastewater discharged directly into marine ecosystems is another Hg source that has declined dramatically over the past several decades. For example, measured Hg in wastewater from the largest facility serving the city of Bostonindicates that Hg concentrations declined by >95% between 1991 and 2009 due to implementation of secondary wastewater treatment [*NOAA*, 1994; *Wu*, 2011]. Phase-out of Hg from consumer products and widespread introduction of secondary municipal wastewater treatment both likely caused large declines in Hg inputs to ocean margins.

We thus hypothesize that wastewater and riverine Hg were major historical sources of Hg to the NA ocean and subsequently to the atmosphere. We suggest thatphasing outofHg in wastewater and many industriesin North America and Europe over the past decades is at least partly responsible for the rapid decline ofatmospheric concentrations over the NA and nearby continents. Timescales of Hg cycling in subsurface waters of the NA means that presently much of the historic Hg has accumulated in the deep ocean or dispersed globally through evasion. Thus, we expect the declineof NH atmospheric Hg concentrations to slow down, or possibly reverse if global emissions continue to rise. Our work highlights the need for better understanding the contribution ofeffluent Hg releases to global anthropogenic Hg both in the past and in the present.

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Figure Captions

Figure 1. Ship cruises used in the surface air Hg trend analysis (left). Cruise data are from *Temme et al.* [2003] *(1, 2, 3, 4, 5, 7, 9, 12, 13);Mason et al.* [1998] *(6); Lamborg et al.* [1999] *(8); Mason et al.* [2001] *(10,11,14); Laurier and Mason* [2007] *(15); Aspmo et al.* [2006] *(16); Sommar et al.* [2010] *(17); Soerensen et al.* [2010a] *(18, 19, 20); Kuss et al.* [2011] *(21, 24), Andersson et al.* [2008] *(22), Mason et al.* [2009] *(23, 25),* M. Witt (manuscript in preparation,

2012) *(26),* R. Ebinghaus (unpublished data, 2010) *(27).* Hg concentration trends in surface air of the NA(upper right) and SA (lower right), 1977-2009, reported as total gaseous mercury (TGM) or elemental mercury (Hg^0) which we view here as equivalent (see text). Squares representmean concentrations measured on ship cruises, with vertical bars indicating standard deviations. The regression line for the observed 1990-2009 trend inNA is shown (0.046±0.010 ng m^{-3} a^{-1},p<0.001, n=18). Model trends forNA including changes in anthropogenic emissions or in subsurface NA are also shown. Red circles are yearly medians for Mace Head (Ireland) and Cape Point (South Africa) taken from *Slemr et al.* [2011]. Filled squares represent the cruise observations used by *Slemr et al.* [2011] in their trend analysis.Further information on cruises is found in the Auxiliary Table A1.

Figure 2. Simulated differences of Hg surface air concentrations in GEOS-Chem between 1990 and 2008 as driven by changes in anthropogenic emissions (left) and subsurface ocean concentrations of the NA for 0°-70°N (right). The results are expressed as an annual trend (a^{-1}).