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Ten-year trends of atmospheric mercury in the high Arctic compared to Canadian sub-Arctic and mid-latitude sites

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Abstract

Global emissions of mercury continue to change at the same time as the Arctic is experiencing ongoing climatic changes. Continuous monitoring of atmospheric mercury provides important information about long-term trends in the balance between transport, chemistry, and deposition of this pollutant in the Arctic atmosphere. Ten-year records of total gaseous mercury (TGM) were analyzed from two high Arctic sites at Alert (Nunavut, Canada) and Zeppelin Station (Svalbard, Norway); one sub-Arctic site at Kuujjuarapik (Nunavik, Québec, Canada); and three temperate Canadian sites at St. Anicet (Québec), Kejimkujik (Nova Scotia) and Egbert (Ontario). Five of the six sites examined show a decreasing trend over this time period. Overall trend estimates at high latitude sites were: $-0.9\,\%\,yr^{-1}$ (95 % confidence limits: −1.4, 0) at Alert and no trend (−0.5, +0.7) at Zeppelin Station. Faster decreases were observed at the remainder of the sites: $-2.1\,\%\,yr^{-1}$ (−3.1, −1.1) at Kuujjuarapik, $-1.9\,\%\,yr^{-1}$ (−2.1, −1.8) at St. Anicet, $-1.6\,\%\,yr^{-1}$ (−2.4, −1.0) at Kejimkujik and $-2.2\,\%\,yr^{-1}$ (−2.8, −1.7) at Egbert. Trends at the sub-Arctic and mid-latitude sites agree with reported decreases in background TGM concentration since 1996 at Mace Head, Ireland, and Cape Point, South Africa, but conflict with estimates showing an increase in global anthropogenic emissions over a similar period. Trends in TGM at the two high Arctic sites were not only less negative (or neutral) overall but much more variable by season. Possible reasons for differences in seasonal and overall trends at the Arctic sites compared to those at lower latitudes are discussed, as well as implications for the Arctic mercury cycle. The first calculations of multi-year trends in reactive gaseous mercury (RGM) and total particulate mercury (TPM) at Alert were also performed, indicating increases from 2002 to 2009 in both RGM and TPM in the spring when concentrations are highest.

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1 Introduction

Mercury in the atmosphere is transported from natural and anthropogenic emission sources to all parts of the globe. Most of this mercury is in the form of gaseous elemental mercury (GEM) due to its estimated 6–24 month lifetime in the atmosphere. Shorter-lived reactive gaseous mercury (RGM) and total particulate mercury (TPM) in the atmosphere can either be emitted directly or created by oxidation of GEM and deposit within hours to weeks (Schroeder and Munthe, 1998). Following deposition, inorganic forms of mercury can be re-emitted or remain in soil, vegetation, and surface water. A fraction of the inorganic mercury can be methylated by microbial activity in wetlands and sediments as well as in fresh and salt water; toxic methylmercury can then enter the food web, where it bioaccumulates and biomagnifies and poses a health risk to humans and/or wildlife (see Selin, 2009 for review).

In the Arctic, high levels of mercury have been observed in people and wildlife (AMAP, 2005), with historical mercury records indicating a significant anthropogenic source (Dietz et al., 2009; Muir et al., 2009). There are very few local sources of mercury in the Arctic and thus anthropogenic mercury must originate elsewhere. Since the atmosphere is a significant source of mercury to the region (Outridge et al., 2008), long-term monitoring of atmospheric mercury in the Arctic is crucial for assessing the sensitivity of the atmospheric input to changes in global mercury emissions, atmospheric circulation, and deposition (wet and dry). In addition, mercury in the Arctic undergoes large-scale rapid conversion of GEM to RGM and TPM in the springtime in so-called atmospheric mercury depletion events (AMDEs) (Schroeder et al., 1998; Berg et al., 2003; Steffen et al., 2008). These chemical reactions are associated with sea ice and/or snow pack chemistry through surface bromine reactions (Lindberg et al., 2002; Simpson et al., 2007). Therefore, changes in the cryosphere may also impact mercury deposition in the Arctic through atmospheric chemistry and ocean-air exchange, adding to the impetus for ongoing monitoring in this region (AMAP, 2011).

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Recently, GEM concentrations at Alert, in the Canadian high Arctic, were shown to have decreased over 1995–2007 at a rate of 0.6 %yr^{-1} (range 0.1–0.9 %yr^{-1}) (Cole and Steffen, 2010). This was followed by reports of steeper declines of roughly 2.7 %yr^{-1} in total gaseous mercury (TGM, the sum of GEM and RGM) measured at Cape Point, South Africa, from 1996 to 2009 (Slemr et al., 2011) and 1.6–2.0 %yr^{-1} in TGM measured in background air masses at Mace Head, Ireland, over the same period (Ebinghaus et al., 2011). These are the only locations that have reported at least 10 yr of continuous TGM data, highlighting the need for more widely spread monitoring (Sprovieri et al., 2010). Nevertheless, these results from geographically diverse locations suggest a decline in global mercury levels in recent years following relatively stable concentrations in the late 1990s (Slemr et al., 2003). This is not consistent with recent emission estimates of constant or increasing global mercury emissions over much of this period (Pacyna et al., 2006; AMAP/UNEP, 2008; Pirrone et al., 2010; Streets et al., 2011) and the inconsistency has not yet been explained. In addition, the difference in trends between Alert and Mace Head is somewhat unexpected. It is reasonable to expect an interhemispheric gradient in TGM concentrations and their trends (i.e. between Cape Point and Mace Head/Alert), given that the tropospheric lifetime of mercury is approximately equal to the lifetime for mixing Northern and Southern Hemispheric air (Holmes et al., 2010). However, the trend analysis at Mace Head was limited to air masses from background areas (North Atlantic, Arctic Ocean, Greenland) and Alert is far from local sources, so both sites should be dominated by the Northern Hemispheric background concentration of mercury and reflect trends in that background, to a first approximation.

To extend the comparison between Arctic and mid-latitude trends to more than two sites, here we apply a consistent trend analysis to ten years of TGM data from two Arctic sites, one sub-Arctic site, and three Canadian mid-latitude sites. In addition, we investigate the role of AMDEs in this trend by (a) examining the trend on a monthly basis; (b) including a sub-Arctic site that experiences AMDEs; and (c) assessing for the first time eight-year time trends and variability in RGM and TPM at Alert.

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2 Methods

Total gaseous mercury (TGM) has been continuously monitored at Alert since 1995, Zeppelin Station since 2000, Kuujjuarapik since late 1999, Egbert and Kejimkujik since 1996, and St. Anicet since 1994. Site locations are shown in Fig. 1 and described briefly in Table 1. Alert is located on the northern tip of Ellesmere Island on the shore of the Lincoln Sea, on a plateau approximately 6 km from the ocean (Cole and Steffen, 2010). Zeppelin Station is located on a ridge of Zeppelin Mountain accessed by cable car from the coastal settlement of Ny-Alesund, Svalbard, on the western coast of the island of Spitsbergen (Berg et al., 2003). Kuujjuarapik is in a sub-Arctic tundra region on the eastern shore of Hudson Bay (Poissant and Pilote, 2003). The three mid-latitude sites across Eastern Canada are all rural sites affected to varying degrees by regional pollution sources, as described in detail elsewhere (Poissant, 1997; Kellerhals et al., 2003). The Canadian sites were audited in 1999 (Tait et al., 2000) and the results yielded an estimated network intersite uncertainty of ±8.8 % (Temme et al., 2007).

TGM measurements were made using Tekran 2537A instruments. The instruments sample ambient air at 3–6 m a.g.l. through a 0.2 µm Teflon filter (47 mm diameter) at the outside inlet followed by an approximately 10–15 m heated sample line and a second Teflon filter at the back of the instrument. At St. Anicet, the inlet differs in that the Teflon filter inlet is coupled to a sampling manifold (Pyrex). As well, the inlet at Zeppelin includes a soda lime trap placed in line before the instrument filter (Aspmo et al., 2005). Ambient air is then pulled through one of two gold collectors for 5–30 min, providing continuous concentration measurements. Mercury is adsorbed onto the gold trap for a period of time at a specified flow rate. Once the sampling is complete, the trap is then analysed while the second trap collects the next sample. The gold trap is heated to approximately 500 °C and the mercury is thermally desorbed into an argon stream and detected using cold vapor atomic fluorescence spectrometry. This method has been described in detail in Steffen et al. (2008, and references therein). Results from a previous campaign at Alert (Steffen et al., 2002) as well as laboratory tests (Swartzen-

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druber et al., 2008) suggest that the two inlet filters remove some or all of the reactive gaseous mercury (RGM) so that the measured concentrations represent gaseous elemental mercury. However, other field tests suggest that RGM does pass through the filters and is included in the measured TGM concentration (Temme et al., 2003; Slemr et al., 2009), perhaps depending on field conditions. In addition, the soda lime trap at Zeppelin likely removes RGM (Aspmo et al., 2005). In this paper we use the terminology TGM to represent mercury measured by the 2537A instrument, with the caveat that some RGM may be lost and this number therefore represents a lower limit of TGM. However, RGM comprises only a few percent of TGM in most cases and instrumental setup at each site was consistent over the time period studied. The quality control process used for the GEM data sets was the Environment Canada-developed Research Data Management and Quality Assurance System (RDMQ) and follows the protocol for the Canadian Atmospheric Mercury Measurements Network (CAMNet) (Steffen et al., 2012).

Speciated Hg (GEM, RGM and TPM) has been measured at Alert since 2002 using a Tekran® Mercury 1130, 1135 and 2537 speciation unit, as described in detail elsewhere (Landis et al., 2002; Steffen et al., 2008). Briefly, air is pulled into the analyzer through a Teflon® coated elutriator and impactor designed to remove particles $> 2.5\,\mu$m at flow rates of $10.0\,\mathrm{l\,min^{-1}}$ (particle size cut off varies with flow rate). The sample air flows through a KCl coated quartz denuder to trap the RGM in the 1130 unit and then passes through a quartz particulate filter to trap the remainder of the particles in the 1135 unit. GEM passes through both the 1130 and 1135 units during sampling mode and is carried into the 2537 analyzer for analysis. Due to their very low concentration, RGM and TPM are accumulated for 1 to 3 h while the GEM is simultaneously collected and measured every 5 min by the 2537 downstream. After the collection period, RGM and TPM are sequentially thermally desorbed, pyrolized to GEM in zero air and analyzed by the 2537 unit. Exact chemical identification of RGM and TPM fractions are still not known and thus are operationally defined as inorganic gaseous Hg that adsorbs to KCl and Hg associated with $PM_{2.5}$, respectively. In lieu of RGM and TPM standards,

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rigorous procedures during and after sample collection/analysis have been put in place to ensure consistent methods are used (Steffen et al., 2012). The method detection limit for RGM and TPM was calculated as 3 times the standard deviation of the two zero air blanks measured after the RGM measurement cycle and was found to be 3.0 pg m^{-3} over the eight years of measurements.

The seasonal trend analysis used daily averaged TGM values (25 % data completeness required within each day) from 2000 to 2009, inclusive. This time period was chosen as the maximum range for which all six sites had data coverage. Trends in each month were calculated using the seasonal Kendall test for trend and the related Sen's slope calculation (Gilbert, 1987). This method is an extension of the non-parametric Mann-Kendall test for trend, which is a recommended trend test when there are missing values and where the data are not normally distributed – both of which apply to these data sets. In the seasonal Kendall method, data from the 12 months are treated as 12 separate data sets. For each month, the presence of a trend is confirmed or rejected by the Mann-Kendall test and a slope is estimated using Sen's nonparametric estimator of slope. For the purposes of these calculations, each daily average in the month is treated as a replicate measurement. An overall trend can be estimated from the monthly trend statistics; however, this estimate is less reliable if the monthly trends are not sufficiently homogeneous. A test for seasonal homogeneity was therefore performed as well (van Belle and Hughes, 1984). If monthly trends were homogeneous, the results were used to determine an overall trend for the entire period. Otherwise, homogeneous seasonal trends and overall trends were calculated using monthly median TGM (75 % data coverage required within each month). The disadvantage of this technique is that it produces a linear trend over the entire period and can miss complex patterns such as a decrease followed by an increase.

Trends in speciated mercury (GEM, RGM and TPM) over the 8-yr period 2002–2009 were also calculated using the same method, again applied to daily averages. In certain months, concentrations of RGM and TPM were below the method detection limit of the instrument for more than half of the data points over the 8 yr. Therefore, trends in those

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months were discarded and no overall trend for the entire data set was calculated. Monthly trends were also discarded if there were fewer than five years with at least 75 % data coverage in that month.

3 Results and discussion

Monthly trends in TGM based on daily average concentrations are shown in Fig. 2 for all six sites. Each bar represents the median rate of increase (positive) or decrease (negative) over the ten years using data from a single month. At all sites other than St. Anicet, these trend values were significantly different from month to month (i.e. the trend was found to be seasonally heterogeneous) and therefore the calculation was repeated using monthly median values at those sites (not shown). In all cases, the monthly trends calculated using median values were within the uncertainty of the trends calculated using daily averages, but the error bars were larger such that the trends were not seasonally heterogeneous.

Overall trends based on all months, expressed as a percent of the median TGM concentration for the entire data set, are compared in Fig. 3 and Table 1. Figure 3 also includes the reported trend in baseline air masses arriving at Mace Head, Ireland, for 1996–2009 (Ebinghaus et al., 2011). The trend from Cape Point, South Africa (Slemr et al., 2011) is not directly compared here since both the measurement technique (prior to 2007) and the trend calculation method differ from those used for the sites shown. At St. Anicet, monthly trends based on daily averages were homogeneous and therefore an overall trend could be determined with better precision than at the other sites where monthly medians were used to calculate the overall trend.

It is clear from Fig. 3 that the overall trend at Alert is less negative than the trends at Egbert, St. Anicet and Mace Head, but not significantly different from those at Kuujjuarapik and Kejimkujik (at 95 % confidence). However, monthly trends at Alert are the same as or higher than trends at Kuujjuarapik and Kejimkujik in every month (Fig. 2), suggesting that the overall trend at Alert is most likely less negative than

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the trend at those two sites as well. The TGM trend at Zeppelin Station was significantly higher than at all other sites except Alert. Trends at non-Arctic sites agreed well with the reported decrease in background TGM concentration at Mace Head, Ireland of $(-1.8 \pm 0.2)\,\%\,yr^{-1}$, though the time period used for Mace Head was longer. TGM trends at Alert, St. Anicet, Egbert, and Kejimkujik were all more negative than earlier reported trends to the end of 2004 or 2005 (Temme et al., 2007), supporting evidence of an accelerating decline in global mercury air concentrations (Slemr et al., 2003, 2011).

The time series of TGM measurements for all sites are shown in Fig. 4 along with a line showing the time trend for 2000–2009 calculated using Sen's estimator of slope, with the centre of the line fixed to the median measured concentration for the decade. In general, the time trends provide a reasonable fit to the time series, though some non-linearity to the Egbert time series is noted. An abrupt decrease in TGM concentrations at Egbert at the beginning of 2008, which is not seen at St. Anicet or Kejimkujik, suggests a local source discontinuity and may explain why the trend at Egbert is the most negative (though not significantly different) of the three mid-latitude Canadian sites. High variability at Kuujjurapik is likely related to AMDEs during springtime and the impact of Hudson Bay on climate and gas exchange throughout the year. Figure 4 also includes the previously-reported trend for Alert measurements from 1995 to 2007 (Cole and Steffen, 2010) for comparison. The trends are not significantly different. Finally, it is noted that the variability of TGM concentrations at Alert and Kuujjuarapik, occasional outliers at Zeppelin Station and Kejimkujik, and the non-linearity at Egbert result in the larger error bars for trend values at these sites (Fig. 3).

The trend results from the mid-latitude and sub-Arctic sites provide evidence of decreases in the global atmospheric mercury pool. Such a decrease is inconsistent with the most recent estimates of global anthropogenic mercury emissions that show increased emissions since 2000 (AMAP/Wilson et al., 2010; Streets et al., 2011). These inventories have estimated uncertainties on the order of 30 % and end in 2005 or 2008, respectively, and so do not cover the entire measurement period discussed here. These

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emissions also include only anthropogenic releases, which comprise about a third of total mercury emissions to the atmosphere (Pirrone et al., 2010). To our knowledge, trends in natural emissions have not been reported. However, even if total global emissions decreased over 2000–2009, this alone would not explain the differences between Arctic and non-Arctic sites.

Compared to the lower latitude sites, seasonal TGM trends at Alert and Zeppelin Station are more variable from month to month, as shown in Fig. 2. From October through March, trends at Alert are not significantly different from the lower latitude sites. In contrast, trends in April, May and July at Alert are significantly higher than at any other site. At Zeppelin Station, the only significant decreasing trends are seen in January and February, with significant increases in concentration in May, August, September and October. August–October increases in TGM at Zeppelin occur at the time of minimum – and decreasing – Arctic Ocean ice cover, as will be discussed below. Alert and Zeppelin Station show similar seasonal trends from January to July but this agreement breaks down from August to December. Seasonality in the trends is also observed at Kuujjuarapik and Egbert. At Kuujjuarapik, the year-to-year decrease in TGM concentrations using data from November to May was faster than the decrease using data from June to October. This seasonality may be related to the influence of Hudson Bay on that site. During winter, the ice cover limits gas exchange between water and the atmosphere, and the Kuujjurapik site is likely influenced mainly by continental air masses, while in the ice-free season the site is influenced by GEM evasion from the Bay. Water bodies have been shown to be a net source of GEM to the atmosphere on both local and regional scales (Poissant and Casimir, 1998; Soerensen et al., 2010; Durnford et al., 2012). At Egbert, TGM concentrations in February and March declined most rapidly in comparison to the other months. This is likely due to unusually low values of TGM measured in 2008 and 2009 in those months, as seen in Fig. 4. Despite these seasonal variations, the overall trends at both Kuujjuarapik and Egbert are in good agreement with trends at mid-latitude sites.

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The increasing trends at Alert and Zeppelin Station in some months and the more gradual (or no) decline in TGM concentrations overall suggest that mercury in Arctic air is experiencing different long-term changes on a regional basis. This difference is not entirely unexpected, given that the Arctic differs in its mercury chemistry as well as its climatology. In fact, springtime increases in TGM at Alert have previously been attributed to changes in the timing of the AMDE chemistry (Cole and Steffen, 2010). However, Kuujjuarapik also experiences AMDE chemistry and has not experienced the same springtime increases in TGM. The monthly TGM trends at Alert and Zeppelin Station also diverge from those at non-Arctic sites outside of the AMDE season, so this chemistry alone is insufficient to explain the trend differences. The impact on TGM concentration trends of mercury oxidation chemistry and other factors, such as changes in ocean flux and source regions for Arctic TGM compared to elsewhere, are discussed below.

GEM in the Arctic is subject to unique chemistry that leads to fast deposition to the surface in spring and emission from the snowpack and tundra in summer (Steffen et al., 2008). Therefore, changes in this chemistry would influence springtime trends in Arctic GEM levels (and TGM, assuming some RGM is lost to deposition or particulate scavenging). Specifically, decreased oxidation would effectively increase springtime GEM levels over the decade, in agreement with observed April and May TGM trends at Alert and Zeppelin Station. Decreased oxidation would also result in decreases in RGM and/or TPM, the products of GEM oxidation. Speciated mercury has been measured at Alert since 2002, as shown in Fig. 5, to form one of the longest continuous data sets of speciated mercury. These data only cover the last eight years of the decade since automated techniques for measuring speciated mercury were developed quite recently (Landis et al., 2002). The results of a preliminary seasonal trend analysis on RGM, TPM and GEM are shown in Fig. 6. The results show significant increases in RGM in March, May and July, and increases in TPM in March, April and July. The March and April TPM trends and May RGM trend were large, representing 9–17 % yr^{-1} increases (8–16 pg m^{-3} yr^{-1}). Trends in March and July RGM and July TPM were small

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($< 1\,pg\,m^{-3}\,yr^{-1}$) due to low concentrations of those species in those months. In all other months, either no significant trends were found or there were insufficient valid data to determine a trend.

No significant decreases in TPM or RGM were found, suggesting that over this eight-year period GEM oxidation rates are unlikely to have decreased as we might expect from the longer-term TGM trends. In fact, decreases in GEM and increases in TPM and/or RGM in March and May suggest increased oxidation in the atmosphere. However, both GEM and TPM concentrations increased in April. Since TPM is the dominant oxidation product in April, a change in GEM oxidation would result in anti-correlated TPM and GEM trends, all other factors being equal. The importance of oxidation to the year-to-year variability in spring GEM concentrations is seen in Fig. 7, where monthly median GEM and the sum of oxidized mercury (RGM + TPM) are clearly anti-correlated in April. A comparison of GEM and RGM + TPM data in March and May, the two other dominant AMDE months, reveals similar relationships (not shown). However, other factors – such as deposition rates – must also influence the speciated mercury variability given that some years with similar April GEM concentrations (e.g. 2005 and 2007) had very different total oxidized mercury concentrations, leading to the observed positive trends in both GEM and TPM for 2002–2009. Note that monthly median values are shown in Fig. 7 for clarity; the trends shown in Fig. 6 were calculated using daily mean concentrations. The use of daily means reduces uncertainty (because of the larger sample size) and intrinsically weights years according to their relative data coverage.

The uncertainty in speciated mercury trends should not be understated even though the data has been subjected to rigorous QC procedures. The large interannual variability shown in Fig. 7 illustrates that longer data sets are needed in order to establish a robust long-term trend. This is also shown by the difference in the seasonal trend patterns for eight years of GEM measurements (Fig. 6) and ten years of TGM measurements at Alert (Fig. 2). In addition, TPM trends are sensitive to any changes in particle size, e.g. due to changes in humidity or temperature, since only $PM_{2.5}$ is collected. And the operational definition of the speciation measurements assumes there

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is no breakthrough of RGM, which cannot be tested until the exact chemical species that comprise RGM are identified. Therefore, these speciation trends should be considered preliminary and not definitive proof that oxidation rates have increased at Alert. It is still possible that oxidation rates at Alert, Zeppelin Station, and/or Kuujjuarapik decreased over 2000–2009, contributing to the observed springtime TGM trends at those locations.

The seasonal trend differences between Arctic and lower-latitude sites persist intermittently into the summer at Alert and the fall/winter at Zeppelin Station, indicating that spring AMDE chemistry cannot be the only reason for the latitudinal trend differences. Transport of mercury-laden air from source regions could increase mercury in Arctic air relative to mid-latitude regions in two ways. First, increased exchange of air between the Arctic and more polluted lower latitudes could be a positive driver of GEM trends (Macdonald et al., 2005). A recent dispersion modelling study found that from 1985 to 2008, the frequency of air arriving at Alert from the Arctic Ocean had decreased, and the frequency of transport from North America to Alert had increased (Hirdman et al., 2010). However, there was no significant transport trend at Zeppelin Station due to a slightly shorter time period (1990–2009). The interannual variability of this transport suggests that the 10-yr period discussed here for Alert would also be insufficient to discover this type of trend. In addition, their analysis of concentration trends in black carbon and sulphate found that transport changes accounted for only 0.3–7.2 % of the observed pollutant trends at three Arctic stations, with emission changes being the dominant factor (Hirdman et al., 2010).

The second mechanism for a transport-driven difference between the Arctic and non-Arctic trends is a difference in source regions for the two areas. If the Arctic is more strongly impacted by emissions from Asia than the other sites, this could explain an increase or slower decrease in GEM concentrations given increasing Asian emissions over the decade (Streets et al., 2011). However, a source attribution study using Environment Canada's Global/Regional Atmospheric Heavy Metals (GRAHM) model found that Asia uniformly contributed about 30–35 % of surface GEM at Arctic, sub-Arctic

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and mid-latitude sites, with relative contributions varying by site and season (Durnford et al., 2010). North American emissions have a relatively greater impact at mid-latitude sites, as evidenced by a potential source contribution function (PSCF) study done at St. Anicet (Poissant, 1999), but according to the global model they contributed only 10–20 % of the total mercury observed at all sites: about 0.15 ng m^{-3} at the two Arctic sites and about 0.3–0.4 ng m^{-3} at the non-Arctic sites (Durnford et al., 2010). Based on the observed trends (Table 1), if emissions from all other regions stayed constant, a decrease of about 8–10 % yr^{-1} in North American emissions (anthropogenic and natural) would be needed to account for the trends at Alert and mid-latitude sites over the ten years, and would be inconsistent with the observed Zeppelin Station trend. However, anthropogenic emissions from North America did not dramatically decrease after 2000, and particularly not enough to offset increased Asian emissions (AMAP/Wilson et al., 2010; Streets et al., 2011). For example, Canadian emissions estimates (not including natural sources or biomass burning) show a decrease of only about 2 % yr^{-1} over the decade (NPRI, 2012). It is possible that natural emissions have decreased, but at this point we have no basis for invoking a large decrease in natural emissions that does not extend to the Arctic. Therefore we conclude that North American emission trends may close some of the gap between mid-latitude and Arctic TGM trends but are unlikely to account for all of the decrease in TGM at these sites.

Another factor influencing GEM trends in the Arctic could be evasion of GEM from the ocean to the atmosphere. Since sea ice may form a physical barrier to evasion (Andersson et al., 2008), decreases in Northern Hemisphere sea ice cover that occurred over the decade (Fetterer et al., 2002, updated 2009) could result in enhanced evasion and help explain the more positive TGM trends in the Arctic compared to regions without sea ice. Analogously, decreased ice cover and warmer temperatures in the Arctic since 1993 have been found to be positive forcers of air concentrations of organic pollutants (Ma et al., 2011). In support of this hypothesis for mercury, the Arctic Ocean was identified as a likely source of mercury to the Arctic atmosphere in summer (Hirdman et al., 2009; Durnford et al., 2012), and the bulk of air arriving at both Alert and Zeppelin

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stations arrives from the Arctic Ocean (Hirdman et al., 2010). In addition, some of the mercury in surface ocean water may come from riverine input as melt water flushes terrestrial mercury out to sea (Andersson et al., 2008; Fisher et al., 2012). It has been postulated that a warming climate could increase the amount of mercury released to Arctic rivers as mercury locked in permafrost is released (Schuster et al., 2011). This would make more mercury available in the surface Arctic Ocean for subsequent reduction and emission to the atmosphere. A positive trend in Arctic Ocean emissions by either mechanism would help explain the TGM trends in the Arctic in the summer but also throughout much of the year, since sea ice is declining in all months (Fetterer et al., 2002, updated 2009) and simulations predict some evasion from the ocean as a whole in all months other than January and December (Fisher et al., 2012). Sea ice cover, and changes in that cover, are also spatially variable and may therefore explain differences in the TGM trends between Alert and Zeppelin Station. For example, Alert is usually surrounded by multi-year ice throughout year, often including the summer, while Svalbard is normally surrounded by open water in the summer and fall and occasionally the western coast is free of ice year-round. Therefore, oceanic emissions may act as a significant local source to Zeppelin Station but a more regional, diffuse source at Alert.

4 Conclusions

This trend analysis provides the first evidence that mercury in the high Arctic atmosphere behaves differently than at mid-latitudes not only on short time scales (e.g. AMDE chemistry) but also in long-term trends. We have postulated several mechanisms to explain this difference (AMDE chemistry, sea ice behavior, transport patterns) and provided a first look at trends in speciated mercury compounds at Alert. It is important to determine the mechanism responsible for the more positive TGM trends at Arctic sites, because the effect on the deposition of mercury to the Arctic ecosystem could be very different. For example, decreased oxidation chemistry would lead to

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increased spring TGM concentrations but decreased deposition to the surface, while increased transport of mercury from lower latitudes would have a positive effect on both Arctic TGM concentrations and total mercury deposition. Detailed modeling studies and better knowledge of natural emission trends would help resolve the reason(s) for latitude-dependent trends and also extrapolate the impact on mercury deposition in the Arctic. Also, continued observations in the Antarctic (Pfaffhuber et al., 2012), where AMDEs occur but emission sources are more distant, and at other remote Northern Hemisphere locations that do not experience AMDEs, may help separate the effects of chemistry, emissions, and transport. Finally, we note that the high variability of atmospheric mercury concentrations in the Arctic – particularly in the spring and summer – indicates that continued monitoring is required in order to be confident in the long-term trends at these locations.

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Table 1. Site details and trends in TGM for 2000–2009, with 95 % confidence range.

Site	Latitude	Longitude	Elevation, m	Site description	TGM trend, $pg\,m^{-3}\,yr^{-1}$	TGM trend, $\%\,yr^{-1}$
Alert	82.5° N	62.3° W	210	Remote Arctic; tundra	−13 (−21, 0)	−0.9 (−1.4, 0)
Zeppelin Stn	78.9° N	11.9° E	474	Remote Arctic mountain ridge; tundra	+2 (−7, +12)	+0.1 (−0.5, +0.7)
Kuujjuarapik	55.3° N	77.7° W	14.3	Forest/tundra; sub-Arctic	−33 (−50, −18)	−2.1 (−3.1, −1.1)
St. Anicet	45.1° N	74.3° W	49	Flat, grassy, rural; urban/industrial within 100 km	−29 (−31, −27)	−1.9 (−2.1, −1.8)
Kejimkujik	44.4° N	65.2° W	127	Forested rural/remote	−23 (−33, −13)	−1.6 (−2.4, −1.0)
Egbert	44.2° N	79.8° W	251	Forest/agricultural; urban within 100 km	−35 (−44, −27)	−2.2 (−2.8, −1.7)

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Fig. 1. Site map.

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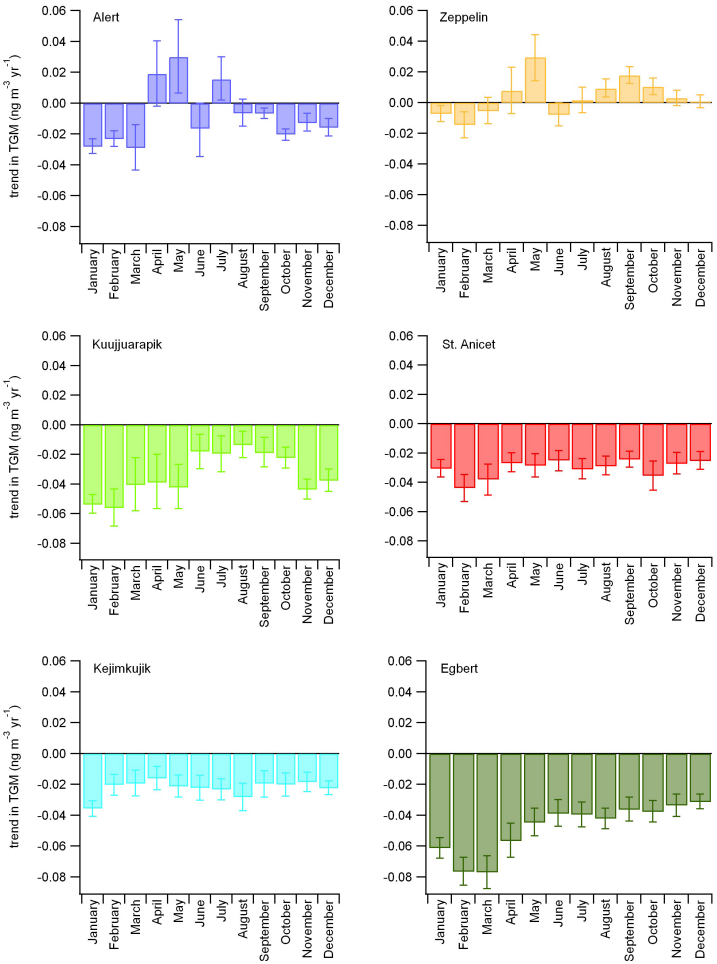

Fig. 2. Seasonal (monthly) trends in TGM based on daily average measurements 2000–2009. Error bars represent 95 % confidence limits.

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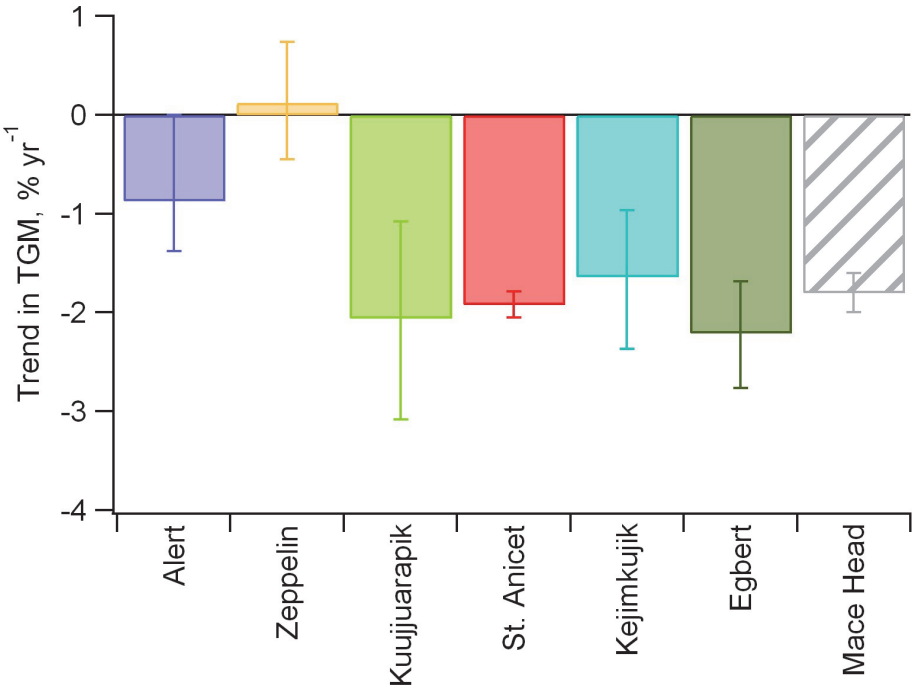

Fig. 3. Trends in TGM at all sites for 2000–2009 and Mace Head, Ireland for 1996–2009. Error bars represent 95 % confidence limits.

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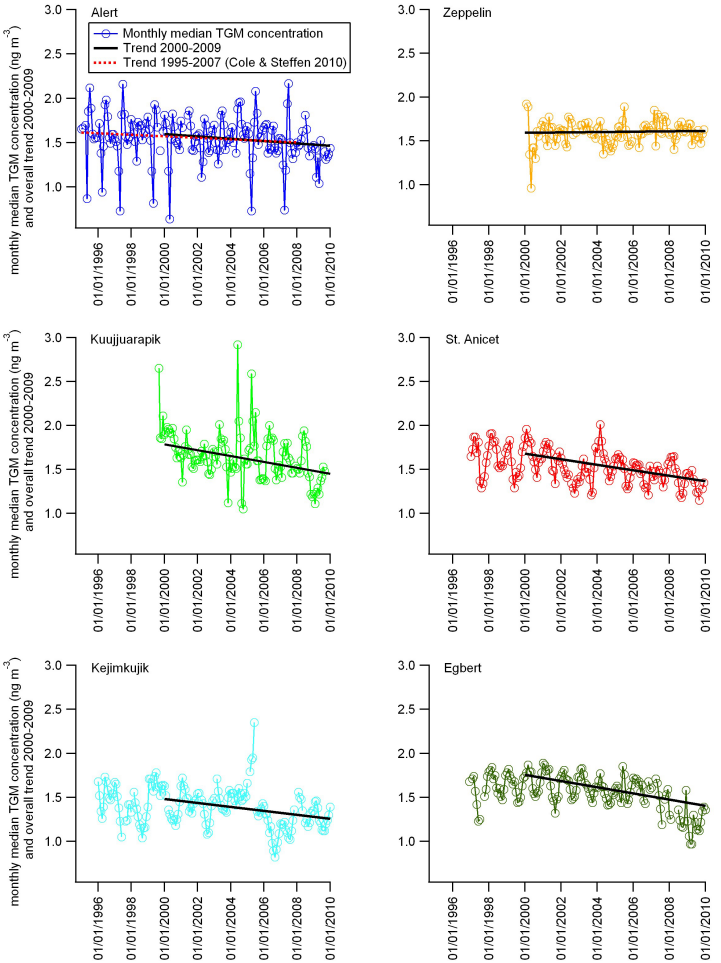

Fig. 4. Time series of monthly median TGM concentrations compared to time trends for 2000–2009 calculated from Sen's estimator of slope.

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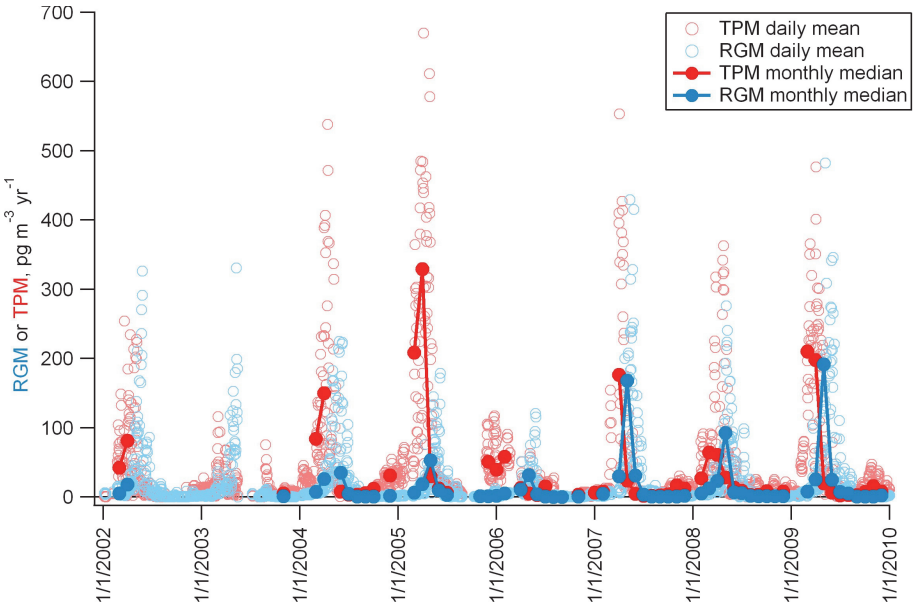

Fig. 5. Time series of reactive gaseous mercury (RGM) and particulate mercury (TPM) at Alert.

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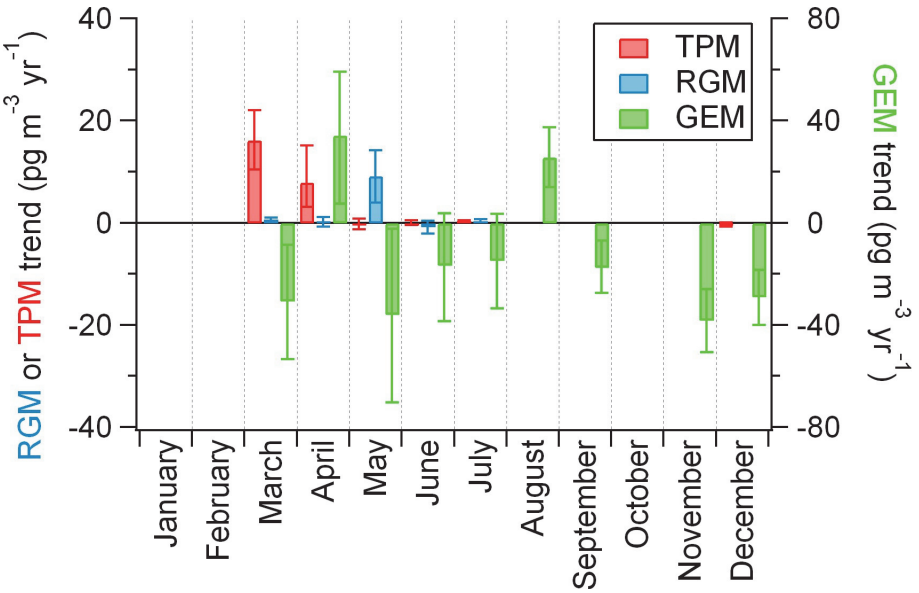

Fig. 6. Seasonal (monthly) trends in GEM, TPM and RGM from Alert based on daily average measurements, 2002–2009. Error bars represent 95 % confidence limits.

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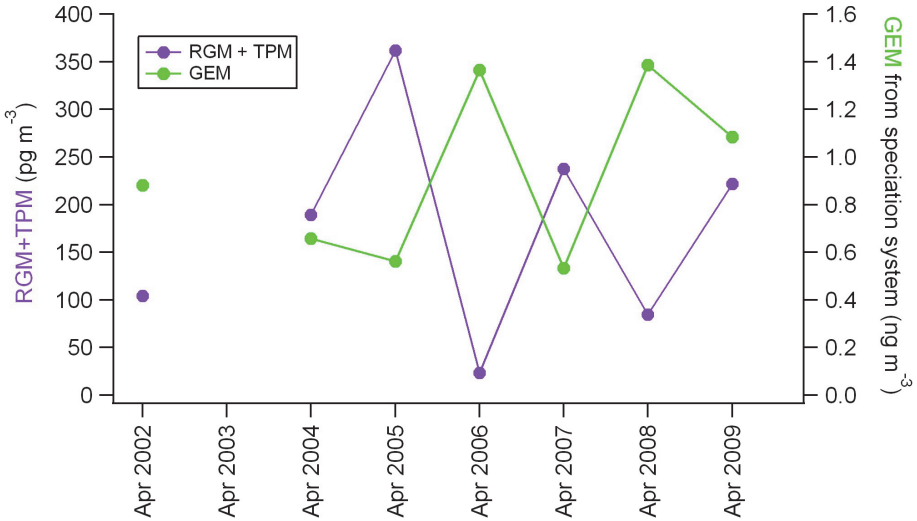

Fig. 7. Monthly median concentrations of GEM and the sum of RGM and TPM at Alert in the month of April. Only months with > 75 % data coverage are included.

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