



Contents lists available at ScienceDirect

Science of the Total Environment

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## Trends in mercury wet deposition and mercury air concentrations across the U.S. and Canada

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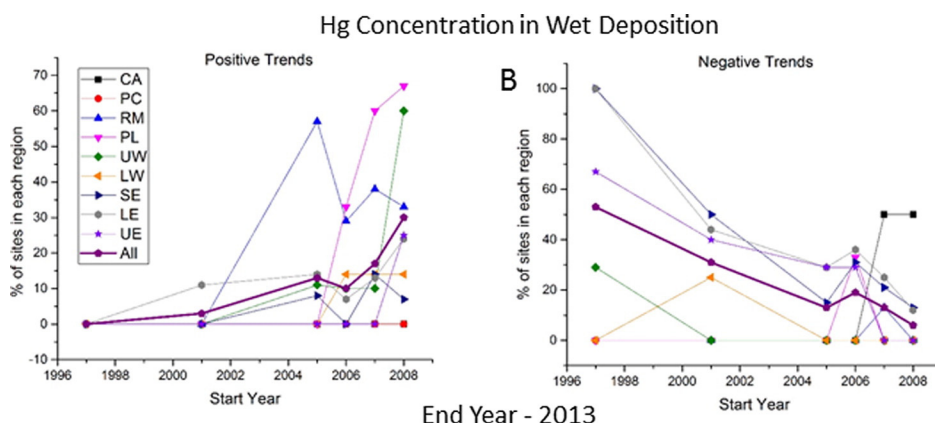
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### HIGHLIGHTS

- 53%/0% of sites had negative/positive trends in mercury wet deposition for 1997–2013.
- 6%/30% of sites had negative/positive trends in mercury wet deposition for 2008–2013.
- Positive trends in mercury wet deposition in middle of continent
- Mercury air concentrations followed similar pattern.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 12 September 2015

Received in revised form 12 December 2015

Accepted 11 January 2016

Available online xxx

#### Keywords:

Mercury

Wet deposition

Trends

Mercury deposition network

Gaseous elemental mercury

North America

Sulfate

Precipitation

### ABSTRACT

This study examined the spatial and temporal trends of mercury (Hg) in wet deposition and air concentrations in the United States (U.S.) and Canada between 1997 and 2013. Data were obtained from the National Atmospheric Deposition Program (NADP) and Environment Canada monitoring networks, and other sources. Of the 19 sites with data records from 1997–2013, 53% had significant negative trends in Hg concentration in wet deposition, while no sites had significant positive trends, which is in general agreement with earlier studies that considered NADP data up until about 2010. However, for the time period 2007–2013 (71 sites), 17% and 13% of the sites had significant positive and negative trends, respectively, and for the time period 2008–2013 (81 sites) 30% and 6% of the sites had significant positive and negative trends, respectively. Non-significant positive tendencies were also widespread. Regional trend analyses revealed significant positive trends in Hg concentration in the Rocky Mountains, Plains, and Upper Midwest regions for the recent time periods in addition to significant positive trends in Hg deposition for the continent as a whole. Sulfate concentration trends in wet deposition were negative in all regions, suggesting a lower importance of local Hg sources. The trend in gaseous elemental Hg from short-term datasets merged as one continuous record was broadly consistent with trends in Hg concentration in wet deposition, with the early time period (1998–2007) producing a significantly negative trend

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( $-1.5 \pm 0.2\% \text{ year}^{-1}$ ) and the recent time period (2008–2013) displaying a flat slope ( $-0.3 \pm 0.1\% \text{ year}^{-1}$ , not significant). The observed shift to more positive or less negative trends in Hg wet deposition primarily seen in the Central-Western regions is consistent with the effects of rising Hg emissions from regions outside the U.S. and Canada and the influence of long-range transport in the free troposphere.

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## 1. Introduction

Mercury (Hg) is a pollutant of global concern due to its persistence in the environment and ability to biomagnify and bioaccumulate as monomethylmercury ( $\text{CH}_3\text{Hg}^+$ ), a neurotoxin for humans (especially in utero) and wildlife (Mergler et al., 2007; Scheuhammer et al., 2007; Buchanan et al., 2015). Marine seafood in the diet is the primary route of exposure for most residents of North America (Li et al., 2014), however, eating fish caught from rivers and lakes is also a concern (Stahl et al., 2009; Wathen et al., 2015). Exposure pathways and impacts of  $\text{CH}_3\text{Hg}^+$  on terrestrial food webs have also been highlighted (Cristol et al., 2008; Evers et al., 2011). Mercury is a naturally occurring element that has been mobilized into the environment by human activity for thousands of years due to its use in precious metal extraction (e.g. gold), its presence as an impurity in many materials (coal, metal ores), its use in products (e.g. electronic devices, fungicides, paint) and subsequent disposal (waste incineration), and by industry (chlor-alkali plants) (AMAP, 2013). Concern regarding Hg releases to the environment were initially focused on large industrial sources that discharged wastes directly to rivers and lakes such as the Great Lakes in the United States (U.S.) and Canada, but since the 1970s these sources have largely been controlled (Evers et al., 2011). Atmospheric deposition of Hg is now seen as the major source to most environments (Evers et al., 2011; Schmeltz et al., 2011) because the major species of Hg is gaseous elemental Hg (GEM or  $\text{Hg}^0$ ), which has an atmospheric lifetime of 6 months to 1 year allowing for global dispersion (Selin, 2009).  $\text{Hg}^0$  becomes oxidized in the atmosphere to gaseous and particle bound  $\text{Hg}^{\text{II}}$  compounds, which can undergo wet and dry deposition resulting in a much shorter atmospheric lifetime than  $\text{Hg}^0$ , of several hours to days (Pirrone et al., 2013). Hg deposition to water and land surfaces provides Hg for iron and sulfate-reducing, and other bacteria in water, sediment, and soils, that methylate Hg (Gilmour et al., 2013) and begin the process of movement and accumulation of  $\text{CH}_3\text{Hg}^+$  in aquatic and terrestrial biota (Harris et al., 2007; Risch et al., 2012; Blackwell and Driscoll, 2015).

Mercury control policies, both legally binding and voluntary actions, have been adopted on regional, national, and global scales in order to decrease the exposure of humans and wildlife to Hg in fish and other biota (Driscoll et al., 2013). Hg anthropogenic emissions in the U.S. have declined substantially from 223 megagrams (Mg) in 1990 to 92 Mg in 2005 to 51 Mg in 2011 (Fig. 1). Substantial reductions from waste incineration (95–99% reduction) and chlor-alkali plants (97% decrease) occurred before 2002 (Butler et al., 2008) with coal-fired power plant (CFPP) reductions occurring more gradually throughout the period (Schmeltz et al., 2011). Since 2007, CFPP emissions have fallen more substantially, and contribute approximately 50% of the 51 Mg of Hg emissions in 2011 from all anthropogenic sources (Fig. 1). Several factors are likely responsible for decreasing Hg emissions from U.S. CFPPs, including some plants have closed or switched to natural gas, compliance with State rules, voluntary reductions by CFPP operators, and the co-benefits from controls installed for the reduction of other pollutants, such as sulfur dioxide ( $\text{SO}_2$ ) and particulate matter (Zhang and Jaeglé, 2013). Additionally, the chemistry of Hg emitted by CFPPs is likely shifting toward a greater proportion of  $\text{Hg}^0$  (57% in 2010 vs. 50% in 2007) and smaller proportions of the reactive and short-lived gaseous  $\text{Hg}^{\text{II}}$  compounds (41% in 2010 vs. 47% in 2007) and particulate Hg (2% in 2010 vs. 3% in 2007) (Electric Power Research Institute (EPRI), 2009 and unpublished data). These data have large uncertainties since they are calculations based on the chlorine content of the coal

burned at an individual power plant, which in most cases was near the detection limit. In spite of the uncertainty, a shift in speciation was expected since scrubbers for  $\text{SO}_2$  removal preferentially capture divalent mercury.

Mercury emissions in North America comprised about 7% of worldwide anthropogenic Hg emissions to the atmosphere in 2005 (Pirrone et al., 2010). The largest Hg emitter is currently China estimated at 643 Mg in 2007 (Wang et al., 2014), although this number has been recently revised downward to 538 Mg emitted in 2010 (Zhang et al., 2015). In contrast to these “bottom-up” calculations, a recent attempt to estimate Chinese emissions using atmospheric observations and a global model (the “top-down” approach) indicates that these emissions range between 650–1770  $\text{Mg year}^{-1}$  (Song et al., 2015). Total anthropogenic Hg emissions globally were estimated to have risen from 1400  $\text{Mg year}^{-1}$  in 2000 to 2000  $\text{Mg year}^{-1}$  in 2008 (Streets et al., 2011) primarily driven by coal combustion in East Asia and changes in emissions factors. Smaller absolute emissions, but a similar growth rate of 1.3% annually from 1970 to 2008, and a total emission estimate of 1287  $\text{Mg year}^{-1}$  were reported by Muntean et al. (2014). However, other reports indicate that global Hg emissions have remained essentially constant since 2000 largely the result of improved energy production efficiency and control technologies that have compensated for increases in the amount of coal combusted (Wilson et al., 2010; AMAP, 2013). The inclusion of Hg emissions from commercial products, a previously unquantified source, resulted in a revised global inventory that peaked at nearly 3000  $\text{Mg year}^{-1}$  in 1970 and due to the phase out of these products, led to a reduction to 2100  $\text{Mg year}^{-1}$  in the year 2000 (Horowitz et al., 2014). Thus, there is no current consensus on the trend of global Hg emissions during the 1997 to 2013 period, although U.S. emissions have declined.

The relative contribution of Hg emissions originating in the U.S. to Hg wet depositional fluxes over the U.S. has been the focus of many studies. Seigneur et al. (2004) and Selin and Jacob (2008) found this contribution to be 24% in 1998 and 27% in 2004 and 2005, respectively,

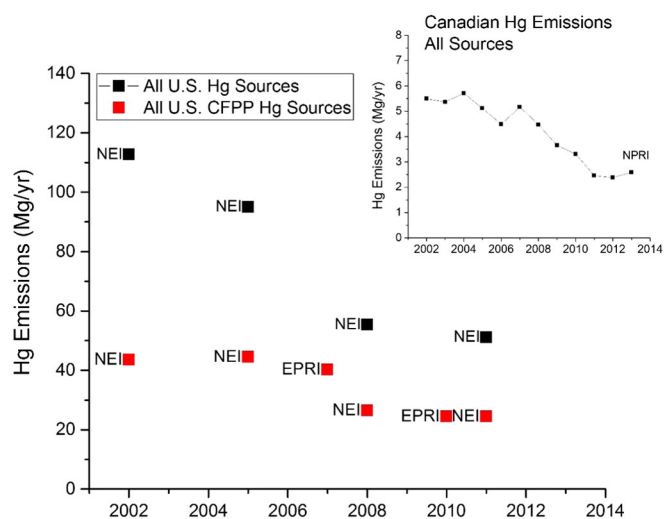


Fig. 1. Mercury point-source emissions in the U.S. and Canada. U.S. data comes from the U.S. EPA National Emissions Inventory (NEI) (US EPA, 2015) and the Electric Power Research Institute (EPRI) (Electric Power Research Institute, 2009). Canadian data comes from the National Pollutant Release Inventory (NPRI; Environment Canada, 2015b) [CFPP, coal-fired power plant].

whereas Zhang et al. (2012) used a modified source profile to account for in-plume reduction and found the contribution to be only 10%. However, in certain regions such as the Ohio River Valley, where many CFPPs are located, the relative contribution of U.S. Hg emissions to Hg in wet deposition was found to be much higher (40–60%, Zhang et al., 2012; and 72%, White et al., 2009).

Monitoring networks for atmospheric Hg in North America have produced continuous multi-year datasets that, along with investigations of temporal trends in Hg air concentrations and concentrations in wet deposition, are used to determine the possible influence of changing anthropogenic emissions. Negative trends of Hg concentration in wet deposition have been reported in Canada (1996–2010) with a 6-site mean trend of  $-2.1 \pm 0.6\% \text{ year}^{-1}$  (Cole et al., 2014) (note that a change  $\pm$  a percent represents percent change with one standard deviation). Likewise, ambient total gaseous Hg (TGM) concentrations displayed a median trend of  $-0.34\% \text{ year}^{-1}$  across 11 sites in Canada from 1995–2005 (Temme et al., 2007). Cole et al. (2013) found significant TGM trends ranging from  $-2.2$  to  $-1.6\% \text{ year}^{-1}$  at 4 sites in eastern Canada (2000–2009) but no significant trends at 2 Canadian Arctic sites. Butler et al. (2008) observed significant trends in Hg concentration in wet deposition (1998–2005) of  $-1.70 \pm 0.51\% \text{ year}^{-1}$  and  $-3.52 \pm 0.74\% \text{ year}^{-1}$  for sites grouped in the Northeast and Midwest U.S., respectively, but no significant trend in the Southeast U.S. region. Prestbo and Gay (2009) also found significant negative trends in Hg concentration in wet deposition mostly in Northeast U.S. and South-eastern Canada (1996–2005) ranging from  $-4.4$  to  $-1.0\% \text{ year}^{-1}$ . A similar pattern was observed by Zhang and Jaeglé (2013) of predominantly negative trends in Hg concentration in wet deposition (2004–2010) for the Northeast U.S. ( $-4.1 \pm 0.5\% \text{ year}^{-1}$ ) and the Midwest U.S. ( $-2.7 \pm 0.7\% \text{ year}^{-1}$ ), and of no significant trends over the Southeast U.S. These patterns in North America are consistent with TGM trends from Europe at Mace Head, Ireland (Weigelt et al., 2015); Cape Point, South Africa; and ship cruises in the Atlantic Ocean (Slemr et al., 2011) which point to a systematic decline in Hg air concentrations and Hg in wet deposition since the mid-1990s.

In this work, we perform trend analysis of Hg concentrations in wet deposition for the time period 1997–2013 and for five additional shorter time periods with starting years of 2001, 2005, 2006, 2007, and 2008 for sites in the National Atmospheric Deposition Program (NADP) Mercury Deposition Network (MDN) in the U.S. and Canada. With successively shorter time periods the confidence in the temporal trends becomes weaker, however, the number of sites included in the network increased from 19 in 1997 to 81 in 2008, thus improving the spatial resolution of Hg wet deposition data especially in the western region of the continent. Our central hypothesis was that because anthropogenic Hg emissions in the U.S. and Canada have decreased by at least a factor of 2 from 2002 to 2011 (Fig. 1), these changes could be detectable as temporal trends in Hg concentrations in wet deposition and Hg air concentrations at sites in our domain. We also compared two trend analysis methods for Hg concentrations in wet deposition, examined trends in wet Hg deposition, precipitation, as well as GEM concentrations in air, and wet sulfate ( $\text{SO}_4^-$ ) concentrations, in order to postulate the reasons for any observed trends in Hg wet deposition.

## 2. Methods

### 2.1. Data sources

Mercury concentrations in weekly integrated wet deposition samples, precipitation depth, and calculation of Hg depositional flux were obtained from the NADP/MDN (NADP, 2015) (Table S-1). Sulfate concentrations in weekly integrated wet deposition samples from co-located NADP National Trends Network (NTN) sites were also obtained (NADP, 2015). Details on the data quality assurance protocols for the MDN are presented in the Supplemental Information (Wetherbee,

personal communication, 2015). Only samples qualified as valid by NADP quality assurance methods were used for all analyses.

Air concentrations of GEM were obtained from the NADP Atmospheric Hg Network (AMNet) (NADP, 2015), Environment Canada (EC) networks (CAMNet and NatChem) (Environment Canada, 2015a), and various other sites in western North America (Table S-2). Data from each site were of various term lengths and collectively covered the time period between 1998 and 2013. GEM data from each site were taken from hourly means and converted into monthly medians. Details on data management and quality assurance for AMNet are available (NADP, 2012; Gay et al., 2013).

### 2.2. MDN site selection, data handling, and region definitions

As of 2014, there were 181 active and inactive MDN sites in the U.S., Canada, and Mexico with weekly Hg wet deposition data expressed in both concentration ( $\text{ng L}^{-1}$ ) and annual deposition ( $\text{ng m}^{-2}$ ), and 81 sites in the U.S. (77) and Canada (4) were used in this study. For analysis of temporal trends it was important to only compare data between sites with data spanning equivalent time periods. In this study varying time periods were considered for trend analysis: the longest was January 1997–December 2013 with 19 sites with continuous (>90% completeness) data. Shorter time periods were also considered that allowed for inclusion of data from more sites in the network for better spatial coverage, but at the expense of shorter time spans from which to calculate temporal trends. The shortest time period considered was 2008–2013 (6 years); details of the 81 sites selected are shown in Table S-1.

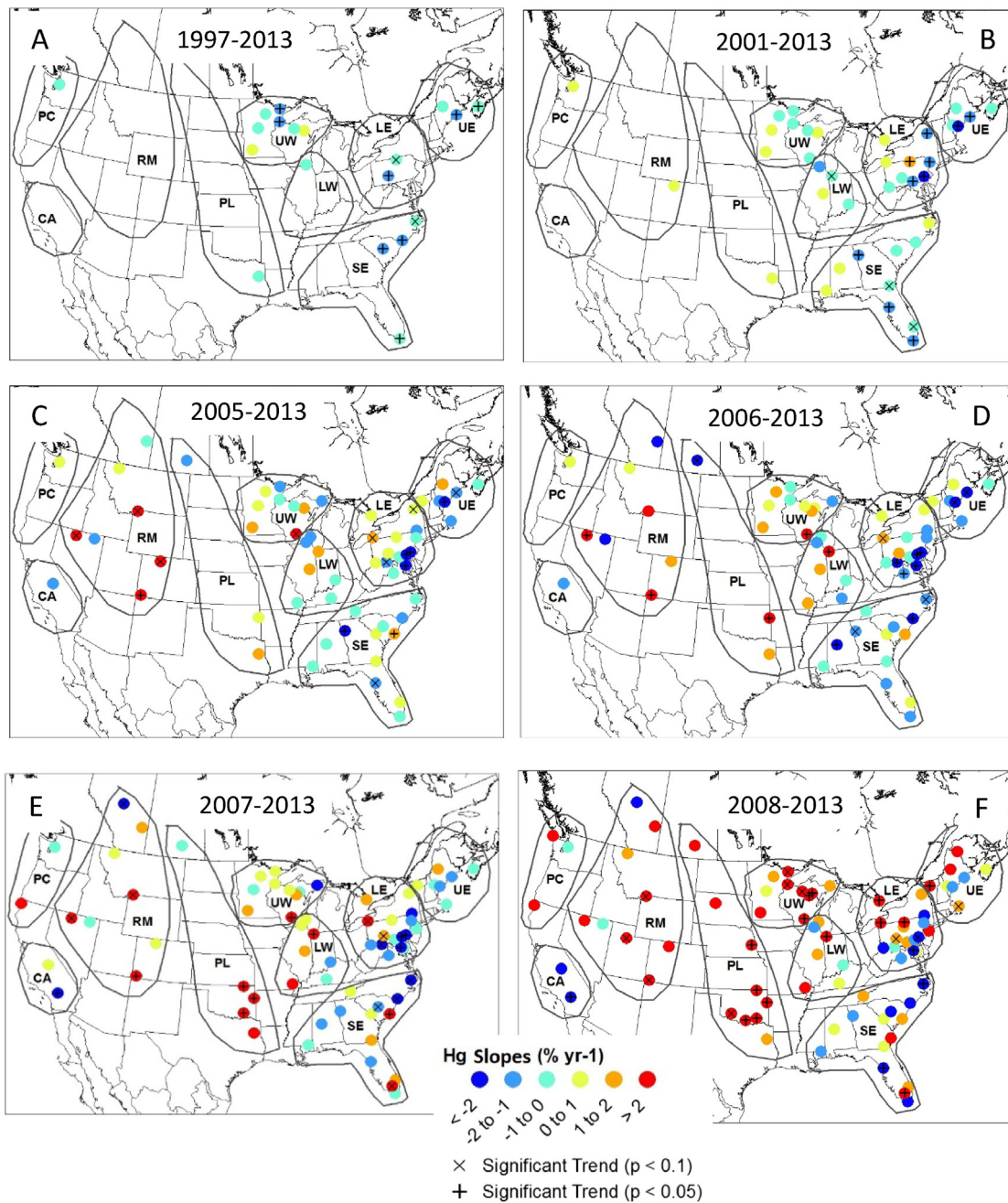
Regional boundaries defined in this work were determined based on a review of the previous trend analysis work of Butler et al. (2008) and Prestbo and Gay (2009), and with a knowledge of CFPP distribution and general climate characteristics. No distinction was made between urban and rural sites. Refer to Table S-1 for regional designations for each site and Fig. 2 shows the distribution of sites within each region. For simplicity, the “western” regions include coastal locations Alaska (AK) (not shown on maps), California (CA), and Pacific Coast (PC). The Rocky Mountain (RM) region includes 2 rural sites in Nevada (NV), 1 urban location in Utah (UT), 2 rural sites in Colorado (CO), and 1 rural site each in Montana (MT) and Wyoming (WY). The Great Plains (PL) sites are concentrated in Oklahoma (OK). The “eastern” regions have much better coverage, and include Upper Midwest (UW), Lower Midwest (LW), Southeast (SE), Lower Northeast (LE), and Upper Northeast (UE).

### 2.3. Trend calculation procedures

In this work, two methods for determining trends in Hg concentration in wet deposition were compared: non-parametric seasonal Mann–Kendall (SMK) and linear parametric (LP). For the SMK method, weekly residual Hg concentration was determined from a regression of weekly  $\log[\text{Hg}]$  vs.  $\log(\text{precip depth})$  according to the following equation:

$$\log[\text{Hg}] = \beta_0 + \beta_1 \log(\text{precip depth}) + \varepsilon, \quad (1)$$

where  $\beta_0$  is the intercept,  $\beta_1$  is the slope, precip depth is the precipitation depth, and  $\varepsilon$  is the weekly residual Hg concentration, i.e., the precipitation-depth adjusted  $\log[\text{Hg}]$ . Precipitation-weighted monthly mean (PWM) residuals were then calculated and used as input to the SMK method. The SMK is a non-parametric ranking procedure that is appropriate to run for environmental data containing seasonal cycles (Gilbert, 1987). The tests were run for each season (where month = “season”) over all years independently. Monthly time steps were chosen over weekly observations to reduce high variability due to dry weeks and highly variable Hg concentrations in low precipitation observations. Monthly steps were chosen over true meteorological seasonal medians/averages to preserve cycles (if present) that occur over less than three month periods. For all SMK runs, observations from a particular season



**Fig. 2.** Annual slopes (% year<sup>-1</sup>) in PWM residual Hg concentration from MDN sites with data from the periods: (A) 1997–2013, (B) 2001–13, (C) 2005–13, (D) 2006–13 (E) 2007–13, and (F) 2008–13, with statistical significance shown with × (p < 0.1) and + (p < 0.05) symbols.

are only compared against later observations within the same season; i.e., January observations are compared only against other January observations, with all months combined to derive annual summaries. After the SMK trends determination on PWM residuals, the annualized trend rate was determined with Sen’s Test of trends (Gilbert, 1987).

The LP method used the following equation:

$$\log[\text{Hg}] = \beta_0 + \beta_1 \log(\text{precip}) + \beta_2 \sin(2\pi t) + \beta_3 \cos(2\pi t) + \beta_4 \sin(4\pi t) + \beta_5 \cos(4\pi t) + \beta_6 t, \quad (2)$$

where  $\beta_0$  is the intercept,  $\beta_1$ – $\beta_6$  are regression coefficients, and  $t$  is time in years (using the sample start date). For all sites and time periods,  $\beta_1$  values were significant (p < 0.05) and in nearly every case, highly significant (p < 0.0001) indicating the importance of accounting for precipitation volume when assessing trends in [Hg]. Fourier terms are generally

added to regression models in pairs to model sinusoidal patterns in the data with phase shifts determined by the data. For this study, the first pair of Fourier terms were significant for all sites and time periods, i.e. either or both  $\beta_2$  and  $\beta_3$  were significant. The second pair of Fourier terms ( $\beta_4$  and  $\beta_5$ ) were significant at a subset of sites and, for consistency, were retained in all regression models. The regression coefficient for time ( $\beta_6$ ) is the linear trend in [Hg], accounting for the exogenous effects of precipitation depth and seasonality. This approach removes the heteroscedasticity from the data (Helsel and Hirsch, 2002) and has been used previously for Hg wet deposition trend studies (Brigham et al., 2014). Time coefficients are converted to an annual percentage change by Eq. (3) (after Helsel and Hirsch, 2002).

$$(e^{\beta_6} - 1) \cdot 100. \quad (3)$$

At each site, mercury concentrations in precipitation show a washout effect of generally decreasing concentrations with increasing precipitation. Therefore, accurate trend calculation methods must take into account the exogenous effect of precipitation depth. The relationship between concentrations and precipitation depth is heteroscedastic, i.e. variance of the error term in Hg concentration is not constant as a function of precipitation depth (Huang and Gustin, 2012; Gratz et al., 2013; Brigham et al., 2014). Log transformation of the concentration and precipitation depth data removed much of the heterogeneity in the error term. Trends in Hg deposition and precipitation were determined with the SMK method using non-adjusted monthly sums to accurately account for weeks with zero precipitation. Trends in GEM in air concentrations were determined with the SMK method using non-adjusted monthly medians.

Sites were grouped into regions and regional trends were determined with the regional Mann Kendall method (RMK). This variation of the generalized Mann-Kendall test uses chi-square  $\chi^2$  statistics based on seasonal and site variation, and interaction terms to determine if records from multiple sites can be appropriately grouped into a single pre-defined region, and then to determine statistical significance and direction of the trend, but not the magnitude (Van Belle and Hughes, 1984). For Hg concentration, the RMK used PWM residuals, for Hg deposition and precipitation, monthly sums were used as input to the RMK.

#### 2.4. Data presentation, statistics, and analysis

For the trends determination, MATLAB (Mathworks) and SAS/STAT (V 9.3) (SAS Institute) were used. Maps were generated using ArcGIS 10.3 with a Lambert Conformal Conic projection, and graphs were made in Origin 9.0. Statistical significance was determined using  $p < 0.1$  for individual site trends in wet Hg concentration and Hg deposition, and  $p < 0.05$  for regional trend analysis and GEM air concentration trends. A criteria of  $p < 0.1$  for significance was chosen for Hg concentration and deposition so that more sites satisfied the criteria and general spatial patterns in the temporal trends could be revealed. In this paper, the term “trend” is reserved for annual rates of change that are statistically significant, whereas annual rates of change that were not significant are called “slopes”.

### 3. Results and discussion

#### 3.1. Comparison of trend calculation methods

Annual rates of change in Hg concentration were calculated with the SMK and the LP methods over the longest (1997–2013) and shortest (2008–2013) time periods and a good comparison was found (Fig. S-1A, B). Out of the 19 MDN sites with data from 1997–2013, the SMK method found 10 sites with significant negative trends and no sites with significant positive trends (distribution of sites across domain shown in Fig. 2A). The LP method found 11 sites with significant negative trends and one site with a significant positive trend. Eight sites were found to have significant negative trends using both methods and no sites were found to have opposite significant trends using both methods. Out of the 81 MDN sites with data from 2008–2013, 19 sites displayed significant positive trends and two sites displayed significant negative trends using both methods (distribution of sites across domain shown in Fig. 2F). Only one site had a significant trend with one method and the opposite direction with the other method. A linear regression of all annual rates of change, whether significant or not, obtained from the SMK versus the LP methods produced a slope of 0.80, an  $r^2$  of 0.74 and a  $p$ -value of  $< 0.001$ . This indicates that the two methods produced annual rates of change that were very similar, but with a slight bias for SMK to be about 20% higher. Again, only rarely did one method predict a trend of different sign compared to the other method. Thus, both methods were deemed adequate for trend analysis on Hg concentrations in wet deposition and for the remainder of this paper, results from the SMK method

will be presented. For the following discussion, when the term Hg concentration is used, it represents the PWM residual Hg concentration and when the term Hg deposition is used it means the monthly sum of Hg deposition.

#### 3.2. Trends of Hg in wet deposition

Annual rates of change in Hg concentrations and Hg deposition were determined using the SMK method for each site over six time periods (Fig. 2A–F, Fig. S-2, Tables S-3, S-4, S-5). For the 1997–2013 period, 10 of 19 (53%) sites had significant negative trends in Hg concentration (Fig. 2A, Table S-4), and no sites had significant positive trends. Specifically, only two sites had positive slopes. For Hg deposition one site had a significant negative trend and one site had a significant positive trend (Fig. S-2, Table S-5). The spatial coverage across the continent was not uniform for this time period with only the UW, SE, and UE regions containing more than 2 sites.

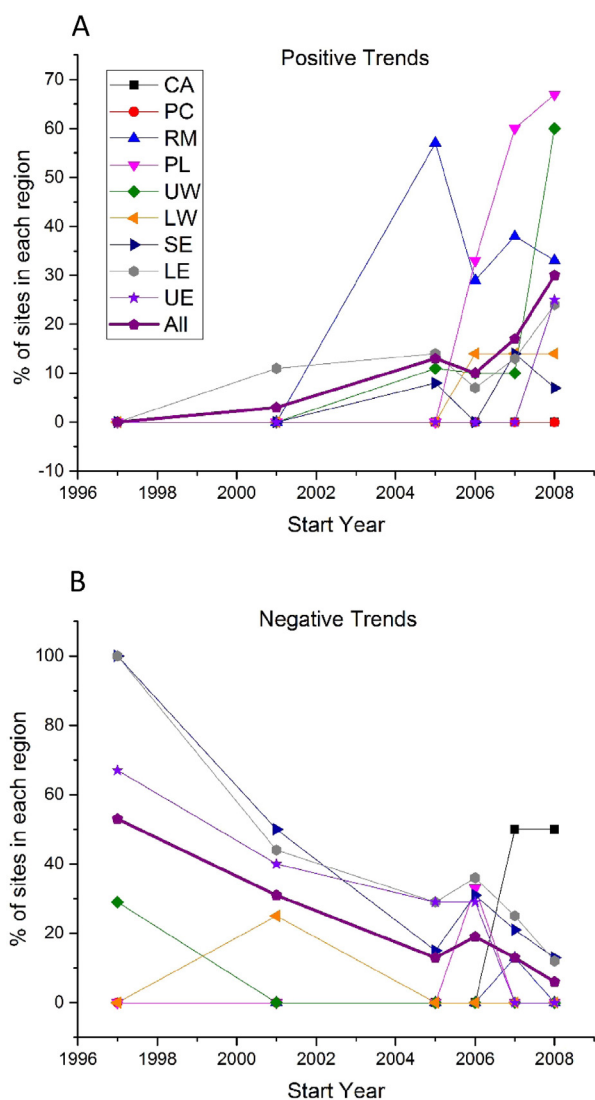
For the 2001–2013 period, the number of sites in the network nearly doubled resulting in good coverage in the eastern regions (UW, LW, SE, LE, and UE), but still no western regions had more than one site. Similar to the 1997–2013 period, there were many sites in the eastern regions with significant negative trends in Hg concentration (12 of 39, 31%) (Fig. 2B, Table S-4), but now locations in all regions of the country except the UE were beginning to show non-significant positive tendencies. Only one site displayed a significant positive trend in Hg concentration and this was located in Pennsylvania (PA90) in close proximity to other sites with significant negative trends. For Hg deposition there were two sites with significant negative trends and nine sites with significant positive trends (Fig. S-2, Table S-5). The sites with significant positive trends in Hg deposition were distributed across all five eastern regions and none were in the western regions.

For the 2005–2013 period, there was a noticeable increase in the number of sites in the western regions ( $N = 12$ ). There were also the same number of sites with significant positive trends in Hg concentrations compared to the number of sites with negative trends (8 of 62, 13% for each) (Fig. 2C, Table S-4). All sites with significant negative trends in Hg concentration were confined to the SE, LE, and UE regions, whereas four of seven sites in the RM region displayed significant positive trends. There are also now sites tending positive in every region except CA (27 of 62, 44%). For Hg deposition there were 11 sites with significant negative trends and 5 sites with significant positive trends (Fig. S-2, Table S-5). The LE region had six sites with significant negative trends in Hg deposition. In contrast, the RM region had four sites with significant positive trends in Hg deposition.

For the 2006–2013 time period, there were more sites with significant negative trends ( $N = 12$ ) in Hg concentration than sites with significant positive trends ( $N = 6$ ) (Table S-4). The negative trends were once again primarily at sites in the SE, LE, and UE regions, while the positive trends were spread across many regions (Fig. 2D). For Hg deposition there were 9 sites with significant negative trends, mostly clustered in the LE and UE regions, and 6 sites with significant positive trends mostly spread throughout the domain (Fig. S-2, Table S-5).

For the 2007–2013 time period, there was a shift toward more significant positive trends in Hg concentration and deposition (Fig. 2E, Fig. S-2, Tables S-4, S-5). Twelve sites were found to have significant positive trends in Hg concentration and 12 sites had significant positive trends in Hg deposition. This is in contrast with only 9 and 3 sites with significant negative trends in Hg concentration and deposition, respectively.

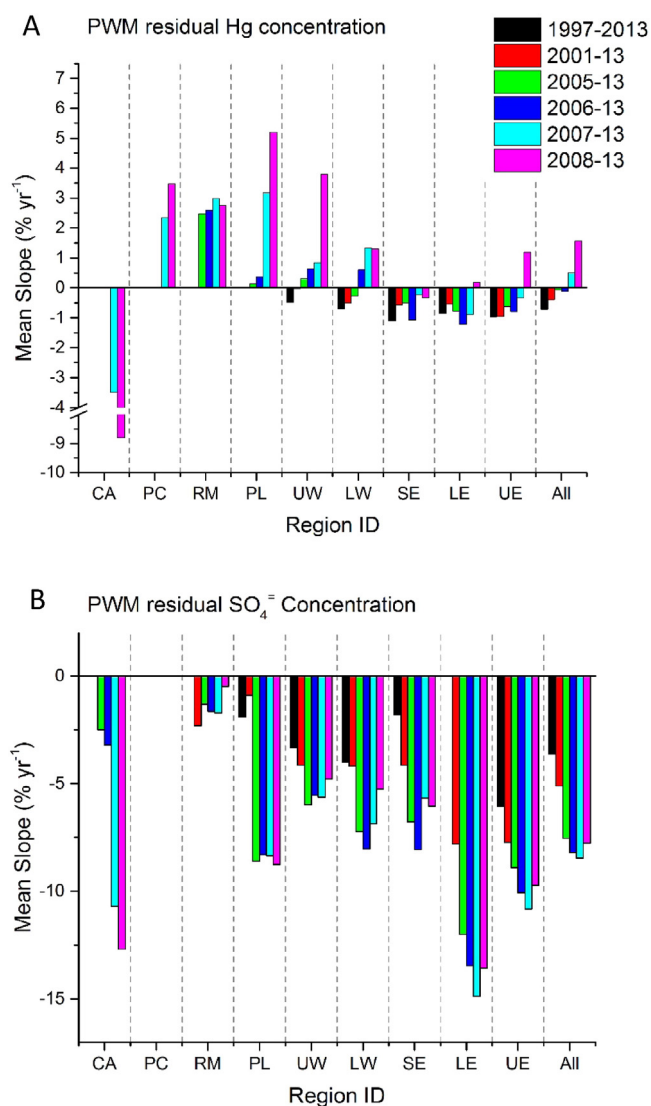
For the shortest time period considered (2008–2013), analysis showed trends that were positive at more sites compared with any other time period considered. Caution must be used when considering annual rates of change from 6 years of data, however, the pattern that emerged from these data is noteworthy and extended what was seen in earlier time periods. For Hg concentration, 24 out of 81 (30%) sites had significant positive trends and only 5 sites had negative trends



**Fig. 3.** Percentage of MDN sites in each region that displayed (A) significant positive or (B) significant negative ( $p < 0.1$ ) trends in PWM residual Hg concentration over the multiple time periods with the starting year shown and each with an ending year of 2013. The number of sites in each region for each time period is given in Table S-4.

(Table S-4). Overall, there were more sites having positive slopes than with negative slopes, and are now occurring in all regions. Most of the sites with positive trends were clustered in the RM, PL, and UW regions, whereas all but one of the sites with negative trends were located in the SE and LE regions (Fig. 2F). For Hg deposition the pattern was similar with 19 of 81 (23%) sites displaying significant positive trends and only one site displaying a significant negative trend (Table S-5).

Fig. 3 provides a quantitative summary of the number of sites (expressed as percentage of total sites in a region) with significant negative and significant positive trends in Hg concentration for each time period considered. Most sites that displayed negative trends for the time periods with data starting in 1997 or 2001 were no longer displaying negative trends when the data started in 2007 or 2008. Conversely, there were very few sites displaying positive trends when the data started in 1997 or 2001, but for data starting in 2007 or 2008, there are many sites with positive trends. The regions with greatest proportion of sites with positive trends for the 2008–2013 time period are  $PL > UW > RM > UE > LE > LW > SE$ . Note the two sites in the CA region are the exception as one site



**Fig. 4.** Mean slopes by region of PWM residual Hg and PWM residual  $SO_4^{2-}$  concentrations from the Mercury Deposition Network and National Trends Network datasets for the time periods shown. "All" refers to the means across all sites.

had a negative annual rate of change (not significant) and the other site had a significant negative trend for 2008–2013.

### 3.3. Regional analysis

#### 3.3.1. Mean trends by region

Mean slopes for all sites grouped together in each region from trend analysis for the six time periods considered are shown for Hg concentration, and  $SO_4^{2-}$  concentration (Fig. 4A, B). Although statistical significance was not considered here, and thus, magnitudes of a regional trend cannot be stated, there was a noteworthy pattern in the slopes as the time periods became more recent across almost all regions for Hg concentrations. For the 2007–2013 and 2008–2013 time periods there was a noticeable uptick in the regional mean slopes relative to earlier time periods for the PL, UW, LW, and UE regions, and for all sites combined. The same tendency is present, but less strong, in the SE and LE regions. The PC and RM regions are consistently strong for the time periods available.

Precipitation trends (not shown) show that the 2008–2013 period produced more negative slopes in precipitation for the LW, LE, and UE

regions compared to earlier periods, which is the opposite pattern that is shown for Hg concentration and deposition. This indicates that precipitation was not the primary cause of more positive trends in Hg deposition for the 2008–2013 period in these regions. Following the concentration trends, trends in Hg deposition were the most positive for the 2008–2013 period compared to earlier periods, although the pattern was not as well defined as that seen for Hg concentration.

Patterns in  $\text{SO}_4^-$  concentration regional mean slopes, on the other hand, were very different from those for Hg concentration (note there were no co-located MDN-NTN sites in the AK and PC regions). All regions had negative mean slopes for all time periods, which is consistent with decreasing  $\text{SO}_2$  emissions in the U.S. over the past two decades (Fig. S-3). The most negative regional mean slopes occurred for the periods beginning in 2005, 2006, 2007, or 2008, in other words the most recent time periods, which was when the major reductions in  $\text{SO}_2$  emissions occurred from CFPPs starting in 2005 (Fig. S-3). The LE region, which includes Pennsylvania and the upper Ohio River Valley, and the down-wind UE region displayed the most negative  $\text{SO}_4^-$  concentration mean regional slopes, which is consistent with the locations of many major CFPPs in the U.S. and reflects the emissions inventory. Thus, this does not support a hypothesis that CFPP emissions in the U.S. and Canada might be responsible for the observed upward trends in Hg concentration at many sites across the domain over the most recent time periods (2007 and 2008 through 2013).

### 3.3.2. Mann–Kendall modeled trends by region

Table 1 shows the results of the regional Mann–Kendall (RMK) analysis for the nine regions (not including AK) and for all sites combined (All) using data from three time periods: 2001–2013, 2007–2013, and 2008–2013. The time period beginning in 2001 represents the maximum length of time when there was reasonable distribution of sites in the eastern regions (see Fig. 2B). For the RMK analysis, a criteria of significance was set at  $p < 0.05$ . Trends were determined for PWM residual Hg concentration, and the monthly sums of precipitation and Hg deposition as described in the methods section. For the 2001–2013 time period, there were significant negative trends in Hg concentration for the SE and UE regions, significant positive trends in precipitation in most regions, and a significant positive trend for All in Hg deposition. For the more recent time periods, there were a total of four regions in which significant positive trends in Hg concentration were observed: RM, PL, UW, and LW. Only the CA region had a significant negative trend for Hg concentration for the 2008–2013 time period.

For precipitation, only the UW and All regions had significant positive trends for the 2007–2013 time period, and no regions had significant trends for the 2008–2013 time period. For Hg deposition, there were positive trends observed in the RM, UW, and All regions for data sets starting in 2007 and 2008. In the case of the RM region, positive trends in Hg concentration were also observed but none observed for

precipitation. Thus, we can conclude the trends in Hg deposition in this region were driven by trends in Hg concentration. For the UW region, the results were mixed with trends in Hg deposition likely driven by trends in precipitation for the 2007–2013 time period and driven by trends in Hg concentration for the 2008–2013 time period. Positive trends in Hg deposition for the All region were likely driven by positive trends in precipitation for the 2001–2013 and 2007–2013 time periods. For the 2008–2013 time period, the positive trend in Hg deposition for the All region (Fig. S-4A) was probably driven by an observed positive tendency in Hg concentration for the All region (Fig. S-4B), although the RMK test assumptions were violated for Hg concentration and thus a result of “NA” was obtained. Trends were not sensitive to outlier concentrations or depositions as the same results were obtained when the highest 1% of the values were removed. As a regional test summary, we can conclude that (a) negative concentrations were clearly decreasing with time and that positive trends were appearing in many regions in the later years (b) that some compounding precipitation trends were present in the longer periods but were not significant in the shortest periods, and (c) that mixed spatial and temporal concentration trends were present when treating all sites together which precludes our ability to conclude a continent-wide concentration increase, but increasing concentration trends were present in a number of regions.

### 3.3.3. Interpretation of spatial patterns in Hg concentration in wet deposition

Most significant positive trends in Hg concentration and deposition were observed at sites in the central and western part of the continent (regions RM, PL, and UW). We suggest that this was a result of general air flow patterns identified for U.S. Great Basin (Huang and Gustin, 2012) and Colorado Rockies (Fain et al., 2009) that indicate that free tropospheric air contributes to enhanced levels of gaseous oxidized mercury (GOM) due to complex terrain and high elevations. Free tropospheric air also can contain elevated concentrations of other pollutants from upwind areas, notably Asia (VanCuren and Gustin, 2015; Christensen et al., 2015). Once descended from the free troposphere, these air masses move eastward and it is plausible that the impacts of elevated pollutants from long-range transport may be seen in the PL and UW regions, and that this effect would become diluted as the air mass moved further to the east. Note that the SE region, which is dominated, particularly in the summer, by the Bermuda High and flow from the Gulf of Mexico, shows no dominant increasing trend in Hg concentration in wet deposition, and therefore consistent with it receiving relatively little input from long-range transported emissions (Gustin et al., 2012) that are more commonly seen over the Great Basin (Huang and Gustin, 2012).

The sites in southern California (CA75 and CA94) have pronounced negative trends in Hg concentration in wet deposition, and this region is less impacted by air from the free troposphere (Wright et al., 2014) and more impacted by pollution emissions within California that have

**Table 1**

Trend analysis on PWM-residual Hg concentration, monthly sums of Hg deposition, and monthly sums of precipitation for the time periods shown by region and for all sites together using the regional Mann–Kendall (RMK) method. NT stands for “no trend” meaning statistical significance ( $p < 0.05$ ) was not met. NA stands for “not appropriate,” meaning that there were significant and dissimilar site and season trends so that a Mann–Kendall regional test was not valid. **Pos** and **Neg** indicate statistical significance and direction of the trend.

Region	2001–2013			2007–2013			2008–2013		
	Hg Conc	Precip	Hg Dep	Hg Conc	Precip	Hg Dep	Hg Conc	Precip	Hg Dep
California (CA)	–	–	–	NT	NT	NT	<b>Neg</b>	NT	NT
Pacific Coast (PC)	–	–	–	NT	NT	NT	NT	NT	NT
Rocky Mountain (RM)	–	–	–	<b>Pos</b>	NT	<b>Pos</b>	<b>Pos</b>	NT	<b>Pos</b>
Plains (PL)	–	–	–	<b>Pos</b>	NT	NT	<b>Pos</b>	NT	NT
Upper Midwest (UW)	NT	<b>Pos</b>	NT	NT	<b>Pos</b>	<b>Pos</b>	<b>Pos</b>	NT	<b>Pos</b>
Lower Midwest (LW)	NT	<b>Pos</b>	NT	<b>Pos</b>	NT	NT	NT	NT	NT
Southeast (SE)	<b>Neg</b>	NT	NT	NT	NT	NT	NT	NT	NT
Lower Northeast (LE)	NA	<b>Pos</b>	NT	NT	NT	NT	NT	NT	NT
Upper Northeast (UE)	<b>Neg</b>	<b>Pos</b>	NT	NT	NT	NT	NT	NT	NT
<b>All</b>	NA	<b>Pos</b>	<b>Pos</b>	NA	<b>Pos</b>	<b>Pos</b>	NA	NT	<b>Pos</b>

declined since the mid-1990s, as demonstrated by a decreasing number of ozone exceedance days measured across the South Coast Air Basin in the Los Angeles metropolitan area (AQMD, 2015). Such a decline in locally and regionally produced oxidants could have the potential to drive downward atmospheric GOM concentrations and subsequently lower Hg concentration in wet deposition (Gustin et al., 2012).

In the LE region, a distinct cluster of sites near the Atlantic coast (including parts of the states of Maryland, Pennsylvania, New Jersey, Virginia, West Virginia, and New York) had mostly negative annual rates of change (slopes) for Hg concentration across all time periods considered (Fig. 2). This region is distinctive because it is seasonally affected by continental outflow (Li et al., 2005), and Hg models indicate that the entire region from the Ohio River Valley to the Mid-Atlantic Seaboard should be most affected by domestic Hg emissions in wet deposition (Zhang et al., 2012; Zhang and Jaeglé, 2013). Using  $\text{SO}_4^-$  concentrations in wet deposition as an indicator of the extent of influence from U.S. anthropogenic emissions, sites with larger correlation coefficients from a linear regression between the log of weekly Hg and the log of weekly  $\text{SO}_4^-$  concentrations were interpreted as being better receptors of these Hg emissions. Fig. 5 shows the 2008–2013 slopes in Hg concentration (same colors as in Fig. 2F) with distinctions made for different ranges in the values of correlation coefficients (R) from  $\log\text{Hg}:\log\text{SO}_4^-$  linear regressions over this time period. Only co-located MDN-NTN sites are shown and the map is focused on the east-northeast U.S. region. Note that the largest values of the  $\log\text{Hg}:\log\text{SO}_4^-$  correlation coefficient were from sites with mostly negative annual rates of change in Hg concentration (PA00 and NY20 are notable exceptions with positive trends in Hg). The mean slope from sites with  $R > 0.6$  was  $-1.0 \pm 1.7\% \text{ year}^{-1}$  ( $N = 9$ ), and these were located along the northeastern seaboard and one site near Chicago (WI99) (Fig. 5). This mean slope was significantly different ( $p < 0.05$ , two-sample t-test) than the mean slopes from the other two ranges of R values from  $\log\text{Hg}:\log\text{SO}_4^-$  linear regressions, which were  $+2.5 \pm 2.5\% \text{ year}^{-1}$  ( $N = 11$ ) for  $R = 0.5\text{--}0.6$ , and  $+1.4 \pm 0.8\% \text{ year}^{-1}$  for  $R < 0.5$  ( $N = 5$ ). These results indicate that although there appears to be an increase in

Hg concentrations in wet deposition over the central U.S. during 2008–2013, the sites that are perhaps most influenced by local and regional scale anthropogenic emissions had predominantly negative slopes in Hg concentration in wet deposition, in agreement with the reduction in Hg emissions as indicated by North American emissions inventories for this period (Fig. 1). This result is also consistent with a recent paper that shows negative trends in annual averages of  $\text{SO}_2$  and GOM concentrations in air and emissions from CFPPs in upwind states, as observed at the MD08 site in Maryland (Castro and Sherwell, ES&T, in press). As a caution though, many of the region's sites are not testable (i.e. do not have paired  $\text{SO}_4^-$  measurements) and may not follow this pattern, and PA00 and NY20 were exceptions, having slopes that were opposite in sign with high Hg: $\text{SO}_4^-$  correlation.

#### 3.4. Trends in Hg air concentrations

Data for calculating trends in TGM (or GEM) are sparse temporally and spatially (not many sites and few of those with multiyear records) compared to Hg in wet deposition. Thus, GEM monthly medians from 33 sites across North America were joined to make a data set that spanned 1998–2013 in order to investigate trends that might agree with the observed trends in Hg concentration in wet deposition. We justify this approach because monthly median GEM for most non polar sites typically only varies between  $1.3\text{--}1.7 \text{ ng m}^{-3}$  (Cole et al., 2014) a variation of only 13%. Hg concentrations in wet deposition in this work varied from  $2.2\text{--}19.4 \text{ ng L}^{-1}$  for the precipitation weighted mean by site (Table S-1), a variation of 80%. There were also regional differences in Hg concentration in wet deposition (SE vs. UE in Table S-1) that are not present for GEM since it is more globally mixed. Fig. 6 shows the locations and mean GEM concentrations for all 42 sites where data were collected for varying lengths between 1998 and 2013. The sites shown in red ( $N = 9$ ) had mean GEM concentration  $> 1.7 \text{ ng m}^{-3}$  and were excluded from the composite data set upon which trend analysis was done due to suspected influence from local sources. The predominance of these sites were in the WE

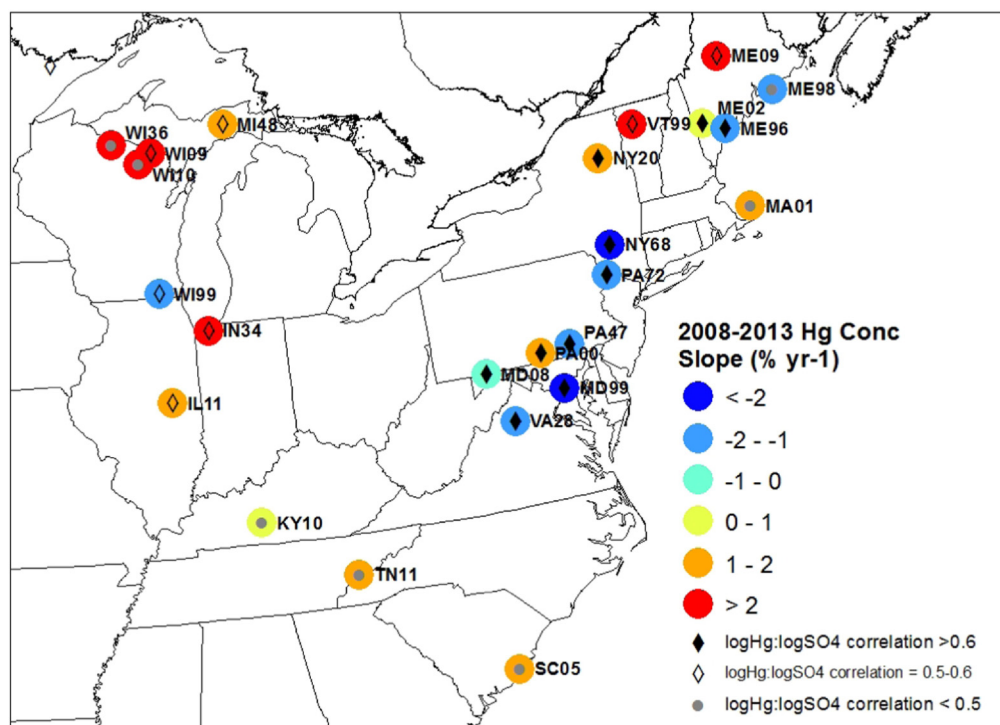
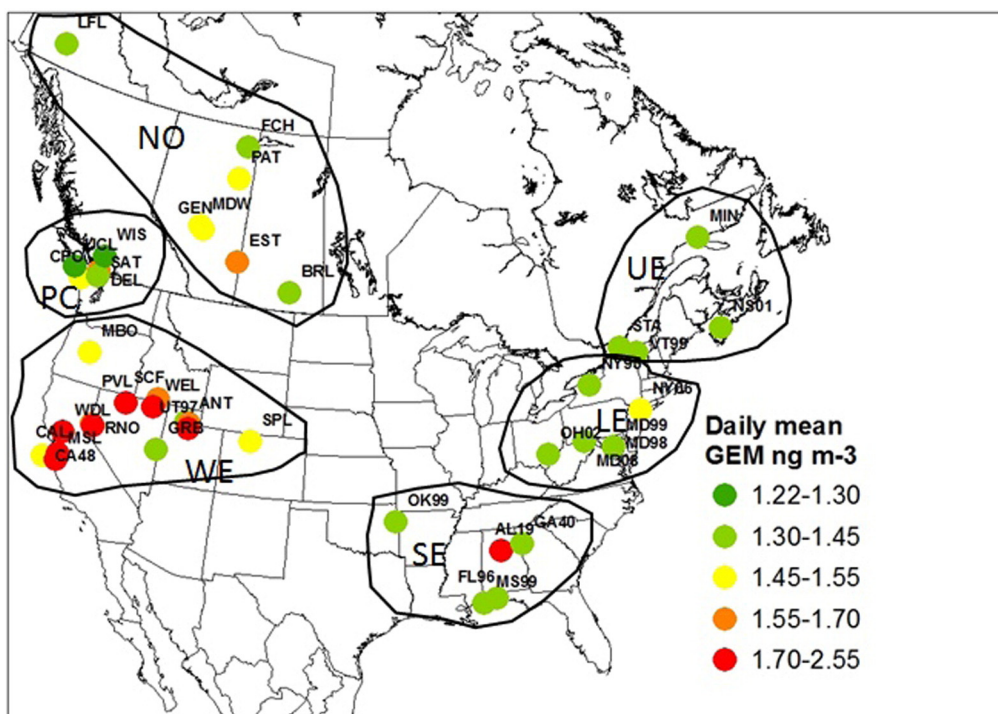


Fig. 5. Annual rates of change in PWM residual Hg concentration over the period 2008–2013 for co-located Mercury Deposition Network and National Trends Network sites in the northeastern U.S. Symbols indicate the site-specific linear correlation coefficients (R) obtained from a regression between weekly log Hg and weekly log  $\text{SO}_4^-$  concentrations (not residuals) over the 2008–2013 period.

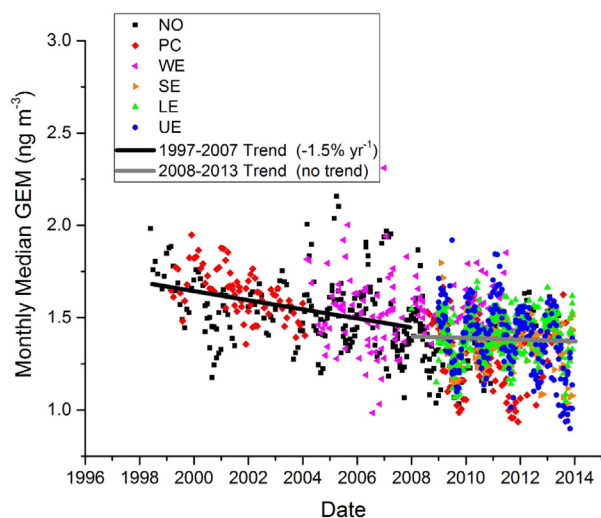




**Fig. 6.** Locations, site IDs, region IDs, and mean GEM concentrations at sites from which data were taken for this study. Table S-2 gives the standard deviations of the mean GEM concentrations, the site names, and the start-stop dates for each site's data set. [NO, Northwest region, WE, West region, all other region IDs defined in Table S-1].

region and may reflect the importance of historical and current mining sources.

Trend results shown in Fig. 7 are for pre- and post-2008 time periods. GEM concentrations in the 1998–2007 time period displayed a significant negative trend ( $-1.5 \pm 0.2\% \text{ year}^{-1}$ ,  $p < 0.05$ ), whereas for GEM concentrations in the 2008–2013 time period, an essentially flat slope was found ( $-0.3 \pm 0.1\% \text{ year}^{-1}$ ,  $p > 0.05$ ). However, caution must be used in interpreting this finding since data from the early time period came from only three regions, whereas starting in 2009 the AMNet data were incorporated from many more sites, and this has an unknown effect on the observed trends. But, the results represent a consistent



**Fig. 7.** Monthly median GEM concentrations from all sites shown in Fig. 6 grouped by region ID, except for the sites denoted with red symbols (mean GEM  $> 1.7 \text{ ng m}^{-3}$ ). Also shown are the SMK trends on monthly medians (not residuals) separated into pre- and post-2008 time periods. The 1997–2007 trend is significant with  $p < 0.05$ .

temporal development to that seen for Hg concentrations in wet deposition, with trends generally becoming more positive in the recent time periods. Similarly, a less negative trend in TGM concentration at Mace Head, Ireland, was observed by Weigelt et al. (2015) for data beginning around 2005.

#### 4. Conclusions

Performing trend analysis of Hg in wet deposition data from the MDN involved a balance between few sites clustered in the eastern U.S. with reasonably long records ( $>13$  years) and more sites with better spatial coverage, but with shorter data records (6–7 years). Long-term trends in Hg concentration at many sites in the U.S. and Canada were significantly negative (53% of sites for 1997–2013 and 31% of sites for 2001–2013) whereas only one site displayed significant positive trends for these time periods. This was in general agreement with previous studies that revealed negative trends in both Hg concentrations in wet deposition and Hg air concentrations for MDN and EC data going up to about 2010. However, Hg concentrations trends calculated on more recent data show more numbers of sites with significant positive trends compared to the number of sites with significant negative trends (12 positive versus 9 negative for 2007–2013 and 24 positive vs. 5 negative for 2008–2013). Regional trend analysis of MDN data revealed that the central area of the U.S. which includes the RM and UW regions displayed significant positive regional trends in Hg deposition for the most recent time periods that appears to be partly driven by significant positive regional trends in Hg concentration. Clearly, many sites and regions of North America were exhibiting more positive/less negative trends (or tendencies) with time. We hypothesize that the location of these regions with the largest positive trends in the center of the continent is consistent with a contribution from long-range transported Hg emissions in the free troposphere.

Mean regional trends in  $\text{SO}_4^{2-}$  concentrations in wet deposition were consistently negative across all regions, primarily after 2005, which is consistent with the steepest declines in  $\text{SO}_2$  emissions from

anthropogenic sources in the U.S. and Canada. We note the lack of general agreement in trends in  $\text{SO}_4^-$  and Hg concentrations in wet deposition, which indicates that recent increases in Hg concentrations are not due to rising Hg emissions from sources in the U.S. or Canada. However, the LE region which includes the upper Ohio River Valley and Pennsylvania has many sites that showed significant negative trends in Hg concentrations through the 2008–2013 period accompanied by relatively strong correlations with  $\text{SO}_4^-$  concentrations in wet deposition. This suggests that reported coal-combustion related anthropogenic Hg emissions reductions during the 2008–2013 period were detectable in Hg concentration in wet deposition trend in this region.

The temporal trend of GEM in air was calculated by combining the data records from 33 sites considered representative of the background across the U.S. and Canada with varying data term lengths. The composite GEM data from all sites covering 1998–2007 produced a significant trend on monthly medians of  $-1.5 \pm 0.2\% \text{ year}^{-1}$  ( $p < 0.05$ ), whereas the data from all sites covering 2008–2013 produced a rate of change of  $-0.3 \pm 0.1\% \text{ year}^{-1}$  ( $p > 0.1$ ) (not significant). While there may be biases inherent in combining data sets from different sites, the overall pattern of more positive/less negative trends is consistent with other long-term TGM measurements from Mace Head, Ireland, in addition to our observations of trends in MDN Hg concentration and deposition.

We speculate that many drivers of Hg concentration in wet deposition will act to produce positive trends in the future if one considers 1) rising Hg emissions from emerging economies, 2) increasing oceanic, soil, and biomass burning emissions of Hg due to warming temperatures, and 3) greater oxidation of gaseous elemental Hg due to increasing levels of atmospheric oxidants. Thus, continuing monitoring efforts such as the MDN are vital in addition to establishing more sites in critical regions (i.e. Western North America).

## Acknowledgments

We thank the many state, provincial, federal, and non-governmental institutions that collaboratively fund and provide logistical support the MDN, NTN, AMNet, and other networks, which provided much of data for this study. This paper was made possible by funding support through EPRI. We thank the following for contributing data to this project: Eric Edgerton, Winston Luke, Mark Castro, Kevin Crist, Rob Tordon, Dirk Felton, Gary Conley, Ryan Callison, Kevin Perry, Bowen Call, Miriam Pendleton, Eric Miller, Alexandra Steffen, Martin Pilote, Dan Jaffe, Daniel Obrist, Sarah Rothenberg, Key-Young Choe, and Mike Abbott. We thank Greg Wetherbee and Greg Lorenz for their quality control analysis on Hg concentration data from the MDN. We thank Leonard Levin for helpful comments and for providing the EPRI Hg emissions data, and John Jansen, Janet Carter, Keith Lucey, and Mark Nilles for helpful comments on the manuscript. We also thank three anonymous reviewers for their constructive comments. This work was conducted as a part of the Western North American Mercury Synthesis Working Group supported by the John Wesley Powell Center for Analysis and Synthesis, funded by the U.S. Geological Survey. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of the NADP, including its member agencies. This article has been peer reviewed and approved for publication consistent with USGS Fundamental Science Practices (<http://pubs.usgs.gov/circ/1367/>).

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.01.061>.

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