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Atmospheric mercury measurements at a suburban site in the Mid-Atlantic United States: Inter-annual, seasonal and diurnal variations and source-receptor relationships

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HIGHLIGHTS

- Decreases in [GEM], [GOM], [PBM], and Hg wet deposition over 2007–2015 were observed.
- Trajectory analysis shows correlation between Hg emissions and observed mercury.
- Two possible sources of GOM include direct emissions and photochemical oxidation.

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ABSTRACT

Different atmospheric mercury forms have been measured at a suburban site in Beltsville, Maryland in the Mid-Atlantic United States since 2007 to investigate their inter-annual, seasonal and diurnal variabilities. Average concentrations and standard deviations of hourly measurements from 2007 to 2015 were 1.41 ± 0.23 ng m^{-3} for gaseous elemental mercury (GEM), 4.6 ± 33.7 pg m^{-3} for gaseous oxidized mercury (GOM), and 8.6 ± 56.8 pg m^{-3} for particulate-bound mercury (PBM). Observations show that on average, the rates of decrease were 0.020 ± 0.007 ng m^{-3} yr^{-1} (or 1.3 ± 0.5% yr^{-1}, statistically significant, p-value < 0.01) for GEM, 0.54 ± 0.19 pg m^{-3} yr^{-1} (or 7.3 ± 2.6% yr^{-1}, statistically significant, p-value < 0.01) for GOM, and 0.15 ± 0.35 pg m^{-3} yr^{-1} (or 1.6 ± 3.8% yr^{-1}, statistically insignificant, p-value > 0.01) for PBM over this nine-year period. In addition, the collocated annual mercury wet deposition decreased at a rate of 0.51 ± 0.24 μg m^{-2} yr^{-2} (or 4.2 ± 1.9% yr^{-1}, statistically insignificant, p-value > 0.01). Diurnal variation of GEM shows a slight peak in the morning, likely due to the shallow boundary layer. Seasonal variation of GEM shows lower levels in fall. Both diurnal variations of GOM and PBM show peaks in the afternoon likely due to the photochemical production of reactive mercury from the oxidation of GEM and the influence of boundary layer processes. Seasonally, GOM measurements show high levels in spring and constant low levels in the other three seasons, while PBM measurements exhibit higher levels from late fall to early spring and lower levels from late spring to fall. These measurement data were analyzed using the HYSPLIT back trajectory model in order to examine possible source-receptor relationships at this suburban site. Trajectory frequency analysis shows that high GEM/

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GOM/PBM events were generally associated with high frequencies of the trajectories passing through areas with high mercury emissions, while low GEM/GOM/PBM levels were largely associated the trajectories passing through relatively clean areas. This study indicates that local and regional sources appear to have a significant impact on the site and these impacts appear to have changed over time, as the local/regional emissions have been reduced.

1. Introduction

Mercury (Hg) is a ubiquitous and neurotoxic pollutant and exists in the environment for long periods by cycling between the air, water, and soil in different chemical forms. Atmospheric emissions of mercury are important, as atmospheric deposition is the most significant loading pathway for many ecosystems (UNEP, 2013). After deposition to watersheds and receiving waters, mercury can be converted to methylmercury, a highly toxic form. Methylmercury is incorporated into the food chain and increases with trophic levels through bioaccumulation (Morel et al., 1998; Fitzgerald et al., 1998). Humans are exposed to methylmercury primarily through consuming contaminated fish and other aquatic organisms (Sunderland, 2007; Choi and Grandjean, 2008; Selin, 2009). Methylmercury can adversely affect the nervous system, particularly those of fetuses and young children (Choi and Grandjean, 2008).

The chemical composition of atmospheric mercury is not completely known and consists of three operationally defined forms: gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and particulate-bound mercury (PBM). The absolute levels and relative proportions of GEM, GOM, and PBM in the atmosphere vary geographically due to different land use patterns, human activities, and numerous physical and chemical processes. GEM is the predominant mercury forms in the atmosphere and typically accounts for >90% of total mercury (Schroeder and Munthe, 1998). Measurements of atmospheric mercury composition and other chemical and meteorological parameters can help us to assess both regional and global atmospheric budgets and cycling of mercury. A declining GEM concentration trend has been observed at many surface sites (Sprovieri et al., 2010; Zhang et al., 2016). In North America, studies have shown the correlation of power-plant emission controls and reducing atmospheric mercury concentrations (Castro and Sherwell, 2015; Zhang et al., 2016), while mercury data observed in China suggest an increasing trend over the last decade (Fu et al., 2015). Long-term monitoring of atmospheric mercury is thus critical to assemble a publicly available data record for model evaluation and to discern trends in atmospheric mercury concentrations. It is also important to establish correlation with meteorology and ancillary trace gases to better understand the emissions, transport, transformation, and fate of mercury in the atmosphere. Ultimately, these investigations can help to elucidate mercury source-receptor relationships so that policy-makers and regulators can assess the impacts of potential changes in mercury emissions with more certainty.

Atmospheric mercury forms have been measured at a suburban site near the Washington Metropolitan area in the Mid-Atlantic United States since 2007. In this work, an analysis of multi-year continuous measurements of atmospheric mercury was performed. Back trajectory simulations were conducted to examine the mercury source-receptor relationships in this suburban environment. The main purpose of this study is to increase understanding of how different processes influence atmospheric mercury concentrations.

2. Measurement and model description

2.1. Site

The monitoring station is located at the National Oceanic and Atmospheric Administration (NOAA)'s Beltsville site near Beltsville, Maryland (39.0284°N, 76.8172°W) on the campus of the United States Department of Agriculture's Beltsville Agricultural Research Center, and bordering the U.S. Fish and Wildlife Service's Patuxent National Wildlife Refuge (NWR). It is one of the National Atmospheric Deposition Program (NADP)'s Atmospheric Mercury Network (AMNet) sites (site ID: MD99). The site is located on an agricultural area embedded within a suburban portion of the Washington, DC metropolitan area and is representative of much of the semi-urban nature of the Chesapeake Bay watershed. The area near the site contains a few small experimental agricultural plots and some small forests. The location of the monitoring site and major regional point sources of mercury are shown in Fig. 1.

A 10-m walk-up tower was established in a clearing surrounded by grassland. All chemical analyzers were housed in a climate-controlled shelter adjacent to the tower. Measurements of atmospheric mercury forms (GEM, GOM, and PBM) were made from the top of the tower with an inlet height of 10.6 m above ground to minimize local surface effects. The site also hosts measurements under the United States Environmental Protection Agency (EPA)'s Clean Air Status and Trends Network (CASTNet) (including meteorological parameters and trace gases that consist of sulfur dioxide (SO_2), ozone (O_3), carbon monoxide (CO, whose measurements were terminated in September 2012), and total reactive nitrogen (NO and NO_y) (US EPA, 2016); NADP's Mercury Deposition Network (MDN) for mercury wet deposition (NADP, 2015); and NADP's National Trends Network (NTN) for major ions in precipitation.

2.2. Measurements

2.2.1. Measurements of mercury forms

At the Beltsville site two Tekran speciation systems (Tekran Instrument Corporation, Ontario, Canada) were used to measure GEM, GOM and PBM over 2007–2015. Each system uses a Tekran 1130/1135 speciation unit coupled with a Tekran 2537 Cold Vapor Atomic Fluorescence Spectrometer (CVAFS). Details of the system have been described by Landis et al. (2002) and Lindberg et al. (2002). Briefly, as ambient air flows through the system, GOM is collected on a KCl-coated annular denuder followed by the collection of PBM (with particle diameter < 2.5 μm) on a quartz regenerable particle filter (RPF) and GEM on gold traps. The collected GOM on the denuder and PBM on the quartz filter are then thermally desorbed and quantitatively converted to GEM, which is then analyzed by the Tekran 2537. Every 2 h each mercury speciation system provides twelve 5-min consecutive GEM measurements