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Impact of climate change on mercury concentrations and deposition in the eastern United States

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HIGHLIGHTS

- Rainfall changes will dominate the future climate-related changes of Hg deposition.
- The Hg deposition changes will be quite variable in space.
- Increases of Hg deposition are expected in the Eastern US due to climate change.
- Local Hg^{2+} levels may change up to 50% in the future due to climate change.
- Climate change will have a minor impact on elemental mercury levels.

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ABSTRACT

The global–regional climate–air pollution modeling system (GRE-CAPS) was applied over the eastern United States to study the impact of climate change on the concentration and deposition of atmospheric mercury. Summer and winter periods (300 days for each) were simulated, and the present-day model predictions (2000s) were compared to the future ones (2050s) assuming constant emissions. Climate change affects Hg^{2+} concentrations in both periods. On average, atmospheric Hg^{2+} levels are predicted to increase in the future by 3% in summer and 5% in winter respectively due to enhanced oxidation of Hg^0 under higher temperatures. The predicted concentration change of Hg^{2+} was found to vary significantly in space due to regional-scale changes in precipitation, ranging from −30% to 30% during summer and −20% to 40% during winter. Particulate mercury, Hg(p) has a similar spatial response to climate change as Hg^{2+}, while Hg^0 levels are not predicted to change significantly. In both periods, the response of mercury deposition to climate change varies spatially with an average predicted increase of 6% during summer and 4% during winter. During summer, deposition increases are predicted mostly in the western parts of the domain while mercury deposition is predicted to decrease in the Northeast and also in many areas in the Midwest and Southeast. During winter mercury deposition is predicted to change from −30% to 50% mainly due to the changes in rainfall and the corresponding changes in wet deposition.

1. Introduction

Mercury (Hg) can accumulate in the food chain in the form of methylmercury, a neurotoxin to living organisms and human beings (Satoh, 2000). Significant amounts of mercury have been found in fish even in remote water bodies (Stephens, 1995), indicating the importance of long-range transport of mercury to locations far from its emission sources. Most of the mercury in the atmosphere (>95%) is in the gas phase (Baya and Van Heyst, 2010) as elemental mercury (Hg^0). Smaller amounts are present in the +2 oxidation state referred to as gaseous oxidized mercury (Hg^{2+}). Another important form of mercury in the atmosphere is particulate mercury (Hg(p)). Particulate mercury is either emitted directly from anthropogenic sources (Schroeder and Munthe, 1998) or produced from Hg^0 or Hg^{2+} adsorbed onto particulate matter (PM) (Schroeder and Munthe, 1998; Seigneur et al., 2004a). Elemental mercury is the predominant species because it has a long atmospheric lifetime (0.5–2 years) (Lindberg et al., 2007) due to its low solubility in water and low chemical reactivity. It is vertically well mixed in the

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troposphere and can be transported over long distances. On the other hand, Hg^{2+} is highly water soluble, reactive and less volatile than Hg^0, having a much shorter atmospheric lifetime and is rapidly removed via wet and dry deposition. Particulate mercury, Hg(p), is mostly present in fine particulate matter ($PM_{2.5}$), although some Hg(p) may be present in coarse PM (Landis and Keeler, 2002). Similar to Hg^{2+}, Hg(p) has a relatively short atmospheric lifetime and deposits closer to emission sources by wet and dry deposition.

Numerous modeling studies have been conducted to understand the transport, chemistry and deposition of atmospheric mercury at regional (Baker and Bash, 2012; Bash et al., 2010; Bullock and Brehme, 2002; Bullock et al., 2009; 2008; Cohen et al., 2004; Gbor et al., 2007; 2006; Landis and Keeler, 2002; Lee et al., 2001; Lin and Tao, 2003; Lin et al., 2007; Lohman et al., 2006; Myers et al., 2013; Pai et al., 1997; Pongprueksa et al., 2008; Seigneur, 2003; Seigneur et al., 2001, 2003, 2004b; Selin and Jacob, 2008; Sillman et al., 2007; Vijayaraghavan et al., 2007; Xu et al., 2000b; Zhang et al., 2012a, 2012b) and global scales (Amos et al., 2012; Bergan and Rodhe, 2001; Bergan et al., 1999; Dastoor and Larocque, 2004; Holmes et al., 2006; Seigneur et al., 2006; Selin et al., 2008; Shia et al., 1999; Soerensen et al., 2010; Strode et al., 2007). Xu et al. (2000a) applied a three-dimensional chemical transport model (CTM) over an area of the northeastern United States, for a summer and a winter week to study the atmospheric transport and transformation of mercury. Their model predictions were evaluated against measurements from eight monitoring stations in Connecticut and the model was able to capture the spatial variation of total gaseous mercury (TGM, $Hg^0 + Hg^{2+}$) concentrations. Hg(p) levels were overpredicted suggesting an overestimation of Hg(p) emissions from point sources or an underestimation of dry deposition. Vijayaraghavan et al. (2008) applied a plume-in-grid model to selected power plants in the continental United States. Their results showed an improved model performance with the inclusion of the advanced plume treatment, in comparison with mercury wet deposition data from the Mercury Deposition Network (MDN) sites (National Atmospheric Deposition Program, 2003), especially in Pennsylvania. A recent study in the same area was performed by Holloway et al. (2012) who employed a three-dimensional CTM to examine how local emissions, meteorology, atmospheric chemistry, and deposition affect mercury concentration and deposition over the Great Lakes region. Their model underpredicted Hg^0 by 6% at a rural site and 36% at an urban site in Wisconsin and overpredicted reactive mercury ($RHg = Hg^{2+} + Hg(p)$) concentrations with annual average biases >250%. In addition, the modeled Hg wet deposition agreed reasonably well against measurements from the MDN sites in this region, with an underprediction of 21% on an annual basis.

Seigneur et al. (2004a) used a multiscale modeling system consisting of a global chemical transport model (CTM) and a nested continental CTM to simulate the global atmospheric fate and transport of mercury and its deposition over the United States. Their model reproduced observed TGM concentrations within 0.1 ng m^{-3} in the eastern US but there were overpredictions in the Midwest and Northwest. In addition, they estimated that North American anthropogenic sources contribute only 25 to 32% to the total mercury deposition over the continental US. Selin et al. (2007) used a global CTM to interpret worldwide observations of TGM. The mean annual TGM concentration observed at 22 land-based sites (1.58 ± 0.19 ng m^{-3}) was reproduced by their model with little mean bias (1.63 ± 0.10 ng m^{-3}), while the model accounted for 51% of the spatial variance in the measurements. In addition, the model reproduced the magnitude of annual wet deposition over the US within 10%.

These modeling studies have greatly advanced our understanding on the behavior of mercury in the atmosphere however the simulation of the fate, transport and deposition of mercury remains a challenging issue. A fundamental limitation of current models is the uncertainty in the atmospheric chemistry of mercury (Ariya et al., 2009; 2008; Lin et al., 2006; Subir et al., 2011). In many modeling studies, the gas-phase oxidation of Hg^0 by OH and ozone has been assumed to be the major pathway for Hg^{2+} formation (Bergan and Rodhe, 2001; Cohen et al., 2004; Holloway et al., 2012; Seigneur et al., 2006). Aqueous-phase reduction of Hg^{2+} to Hg^0, mainly via reaction with hydroperoxyl radicals (HO_2), competes with deposition as a sink for Hg^{2+} (Holloway et al., 2012; Lin et al., 2006; Seigneur et al., 2006; 2004a; Selin et al., 2007). However, recent studies suggest that the gas-phase oxidation reactions by O_3 and OH may not be the dominant pathways (Calvert and Lindberg, 2005; Goodsite et al., 2004; Hynes et al., 2009), that govern the gas-phase chemistry of Hg. In addition, the aqueous-phase reduction of Hg^{2+} to Hg^0 remains uncertain with no accepted kinetics or mechanism (Ariya et al., 2009; Gardfeldt and Johnson, 2003; Goodsite et al., 2004; Hynes et al., 2009). Several studies have focused on the role of bromine in the atmospheric mercury cycle. Holmes et al. (2010, 2006) have demonstrated that gas-phase Br atoms might be an important oxidant of Hg^0 on a global scale. Their conclusions are supported from several pieces of evidence (Goodsite et al., 2004; Holmes et al., 2009; Sinnhuber et al., 2005; Steffen et al., 2008). A large range of kinetics has been reported in the literature for the reaction of Hg^0 with bromine (Ariya et al., 2008; Hynes et al., 2009), while several models have included this oxidation pathway of Hg^0 in their chemistry modules (Dastoor et al., 2008; Seigneur and Lohman, 2008; Zhang et al., 2012b).

The emission rates of mercury from anthropogenic sources are continuously revised and improved (Pacyna et al., 2010; 2006; Seigneur et al., 2004a). Nevertheless, significant uncertainties still remain in these estimates, regarding the emission speciation of mercury and the lack or inaccuracy in reported emission data (Lin et al., 2006). Emissions of mercury from natural sources have been overlooked or estimated as a certain fraction of the deposited mercury in previous modeling studies (Bergan and Rodhe, 2001; Bullock and Brehme, 2002; Seigneur et al., 2004a). In order to reduce this uncertainty, there have been several modeling efforts estimating mercury emissions from various natural sources (vegetation, soil, water surfaces, etc.) (Bash et al., 2004; Gbor et al., 2007; Lin et al., 2005), indicating that natural mercury emissions can be comparable to those from anthropogenic sources, especially during warm months.

Mercury deposition processes and their simulation are additional sources of uncertainty. For example, the dry deposition velocity of Hg^0 is often neglected (Bergan and Rodhe, 2001; Bullock and Brehme, 2002), assigned a very small value (Lee et al., 2001), or calculated using a detailed treatment on the air-surface exchange of Hg^0 (Lin and Tao, 2003). Uncertainties in the atmospheric chemistry of mercury, the emission rates and the mercury deposition processes have been the focus of a number of review studies (Ariya et al., 2009; 2008; Lin et al., 2007; 2006; Pongprueksa et al., 2008; Subir et al., 2011) aiming to improve models simulating atmospheric mercury.

The impact of climate change on mercury concentration and deposition has received relatively little attention. Despite the fact that there have been several studies of how climate change may influence regional and global air quality (Avise et al., 2009; Chen et al., 2009; Dawson et al., 2009; 2007; Forkel and Knoche, 2006; Giorgi and Meleux, 2007; Heald et al., 2008; Hogrefe et al., 2004; Jacob and Winner, 2009; Jiang et al., 2010; Kunkel et al., 2008; Lam et al., 2011; Leung and Gustafson, 2005; Liao et al., 2006; Mahmud et al., 2010; Meleux et al., 2007; Mickley et al., 2004; Murazaki and Hess, 2006; Nolte et al., 2008; Prather et al., 2003; Pye et al., 2009; Racherla and Adams, 2009; 2008; 2006; Steiner et al., 2006; Tagaris et al., 2009; 2008; 2007; Tsigaridis and Kanakidou, 2007; Wu et al., 2008; Zeng et al., 2008; Zhang et al., 2008), the majority of them focused on the effects of climate change on ozone and particulate matter (PM) concentrations.

In this study, we use a coupled modeling system, GRE-CAPS, to study the spatial and seasonal responses of mercury concentration and deposition, to future climate change, with a focus on the eastern United States. GRE-CAPS is well suited for this purpose since it has been used in similar studies in the past (Dawson et al., 2008) and reproduced present ozone and PM as well as CTMs driven by assimilated meteorology.