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A simulation study of atmospheric mercury and its deposition in the Great Lakes

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HIGHLIGHTS

- The study examines total mercury deposited to the Great Lakes.
- Sensitivity test is done to assess source contribution.
- Wet and dry deposition are significant pathways affecting the mercury budget.
- Global background is the dominant source impacting the northern lakes.
- IPM utilities represent the highest contributor to Lakes Erie and Michigan.

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ABSTRACT

The Great Lakes eco-region is one of the largest sources of fresh water in North America; however it is chronically exposed to heavy metal loadings such as mercury. In this study a comprehensive model evaluation was conducted to determine mercury loadings to the Great Lakes. The study also evaluated the relative impact of anthropogenic mercury emissions from China, regional and global sources on deposition to the Great Lakes. For the 2005 study period, CMAQ 4.7.1 model estimated a total of 6.4 ± 0.5 metric tons of mercury deposited in the Great Lakes. The total deposition breakdown showed a net loading for Lake Superior of 1906 ± 246 kg/year which is the highest of all the lakes. Lake Michigan followed with 1645 ± 203 kg/year and 1511 ± 107 kg/year in Lake Huron. The lowest total deposition was seen in Lakes Erie and Ontario amassing annual totals of 837 ± 107 kg and 506 ± 63 kg, respectively. Wet and dry deposition of mercury were both significant pathways and exhibited strong seasonal variability with higher deposition occurring in the warmer months (June–November) and the lowest in winter. Wet deposition of RGM significantly influenced the deposition proportions accounting for roughly 90% of all mercury deposited. Of the three emission sources (global background, integrated planning management (IPM) and Chinese), global background concentrations represented the maximum impact to deposition loading in the Great Lakes, except for Lake Erie and parts of Lake Michigan. There was minimal seasonality for the global background, but differences in percentage contribution between dry (28–97%) and wet deposition (43–98%) was predicted. The contributions were seen mainly in the northern sections of the Great Lakes further away from IPM point sources. These findings suggest strong localized impact of IPM sources on the southernmost lakes. Deposition as a result of emissions from China exhibited seasonality in both wet and dry deposition and showed significant contributions ranging from 0.2 to 9%.

1. Introduction

Mercury (Hg), liquid at almost all temperatures, is chemically stable, possesses high surface tension, forms amalgams readily (except iron, nickel and cobalt) and has good electrical conductivity (Mohapatra et al., 2007; Zhang et al., 2002). These exceptional properties make it useful for many applications. Despite its many

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uses, mercury is a toxic persistent heavy metal which methylates in aquatic eco-systems forming methylmercury. This species, particularly in its organic form, bioaccumulates and biomagnifies in aquatic biota. In humans, impaired neurobehavioral functions and birth defects have been reported as a result of mercury exposure (ASTDR, 1999; Clarkson, 1993, 2002).

The Great Lakes, a major source for potable water and fish for parts of the United States and Canada (Mohapatra et al., 2007), has been burdened with elevated levels of mercury for decades (Chalmers et al., 2011). In an attempted to rectify this trend and stave off the potential deleterious effects mercury introduces, agreements between the states and provinces bordering the lakes were made to reduce direct loading of mercury species entering the Lakes (Leah and Kulperger, 2004). While showing a decrease over the 1969–2005 period, the concentration of mercury in the lakes often exceeds tolerable limits prompting intermittent advisories from authorities (Great Lakes Commission, 2011).

Examination of potential sources and means of mercury entering the Great Lakes indicated that up until the early 90s, direct discharge of mercury contaminated substances was a major contributor to elevated concentrations of mercury (Mohapatra et al., 2007). However, with new restrictions on direct discharge and increased combustion of coal and other fossil fuels, atmospheric mercury deposition became the dominant pathway for mercury and mercury species entering the Great Lakes (Chalmers et al., 2011; Cohen et al., 2004; Landis and Keeler, 2002; Rolfhus et al., 2003).

Mercury enters the atmosphere through natural and anthropogenic activities and exists primarily in three forms in the atmosphere: elemental (GEM), reactive (RGM) and particulate bound (HGp). Divalent and particulate mercury are readily scavenged from the atmosphere due to their physiochemical properties, while elemental mercury which is only slightly soluble and more volatile remains in the atmosphere for longer periods with atmospheric residence time ranging from 0.5 to 2 years (Schroeder and Munthe, 1998). With this extended lifetime, mercury is likely to undergo long-range transport and has the potential of enhancing mercury levels in remote locations. Thus curtailing of mercury usage and subsequently emissions has been prescribed in North American and European countries. However, with population growth and increased industrial productivity in developing countries, release of mercury species to the atmosphere has increased and is expected to continue in this vein (Streets et al., 2009)

In this study a comprehensive model evaluation was conducted to determine mercury deposited using a global transport model, Model for Ozone and Related Chemical Tracers (MOZART) and regional Environmental Protection Agency (EPA) recommended model, Community Multi-scale Air Quality (CMAQ). The efforts of this work also included an assessment of the impact of mercury emissions from China, global sources (including China), and local Integrated Planning Model (IPM) utilities on the mercury deposition into the Great Lakes.

1.1. Mercury sources

1.1.1. Global emissions

Existing gaps in global mercury emission sources, particularly from countries where mercury is unregulated, makes quantification of the actual emissions challenging. Despite this, global estimates are made based on approximations and reported release data. Taking into the consideration the limitations, in 1995 an estimated 1900 metric tons of anthropogenic mercury was emitted globally (Pacyna and Pacyna, 2002); in 2000 approximately 2189.9 metric tons (Pacyna et al., 2006). In 2005 the United Nations Environment Programme (UNEP) reported an average estimate of 1930 metric tons (range 1230–2890 tons) for anthropogenic mercury that was emitted globally (UNEP Chemicals Branch, 2008). A re-analysis study of the global inventories indicated that global mercury emissions decreased by 46 metric tons from 1990 to 2005 (UNEP, 2010). While imposed regulations led to reduced mercury emissions in North America and Europe, a higher contribution from Asian countries was observed (UNEP, 2010).

1.1.2. Emissions from China

Driven to explore emissions sources contributing to the global mercury pool, Pacyna et al. (2006) looked at likely major sources and found that Asian countries are the largest contributors to the global anthropogenic mercury emissions amassing 54% of the total. Of the major sources of anthropogenic mercury emissions studied, China's contribution ranged from 26 to 28% (Pacyna et al., 2006; Pirrone et al., 2010), making it the largest contributor. The US and India are the second and third largest emitters, respectively, but the combined total is only one-third the amount released from China (UNEP Chemicals Branch, 2008). The elevated mercury emissions from China is believed to be associated with the large number of stationary coal combustion units, which have mercury content ranging from 0.02 to 1.95 mg/kg (Zhang et al., 2002).

In a study examining trans-pacific transport of mercury species from Asian countries it was found that elementary mercury largest influence on North America is mainly observed in Alaska, western Canada and the North-western United States (Strode et al., 2008). From that study, it was found that elementary mercury contributes up to 14% increase in the mercury deposited in the United States. Drewniak et al. (2008) used MOZART (Model for Ozone and Related Chemical Tracers) with $2.8^\circ \times 2.8^\circ$ spatial gridding and showed that mercury deposition in the US is impacted by mercury emissions from global sources as well as China which varies seasonally from 5 to 9%. From a more regional perspective, this paper implemented CMAQ chemical transport model (CTM) for mercury with a higher resolution spatial grid, 36 km $\times$ 36 km, and assessed the impact of these sources on the Great Lakes.

1.1.3. Integrated Planning Model (IPM) utilities

Utilities in the electric sector under the Environmental Protection Agency's IPM, particularly fossil fuel-fired plants, are a major contributor to local and regional ambient mercury concentrations and subsequent deposition loadings (Keeler et al., 2006). Electric generation, metallurgical processes and incineration of waste have the largest impact on local anthropogenic mercury emissions in the United States and Canada combined (Cohen et al., 2004). On the Eastern seaboard of the US and states adjoining the Great Lakes, there is a significant number of IPM units which according to the 2008 national emissions inventory (NEI) released approximately 34 metric tons of mercury species. Source-receptor model analyses indicate that these local anthropogenic mercury emissions sources contribute to the mercury deposited into the Great Lakes (Cohen et al., 2004). As part of the plan for limiting mercury emissions from new and existing coal and oil-fired power plants, the US EPA promulgated new Mercury and Air Toxics Standards (MATS) in 2012. The rule sets limits for newly built power plants and gives existing sources up to 4 years to comply. Thus, prior to the implementation of the MATS, it is important to gauge the state of the mercury deposition in the lakes as a platform for further studies assessing the impact of the new rule.

2. Methods

Global simulation using MOZART modified to include gas-phase Hg chemistry (Drewniak et al., 2008) was performed to estimate background mercury concentration. The output from the model