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Anthropogenic mercury deposition in Flin Flon Manitoba and the Experimental Lakes Area Ontario (Canada): A multi-lake sediment core reconstruction

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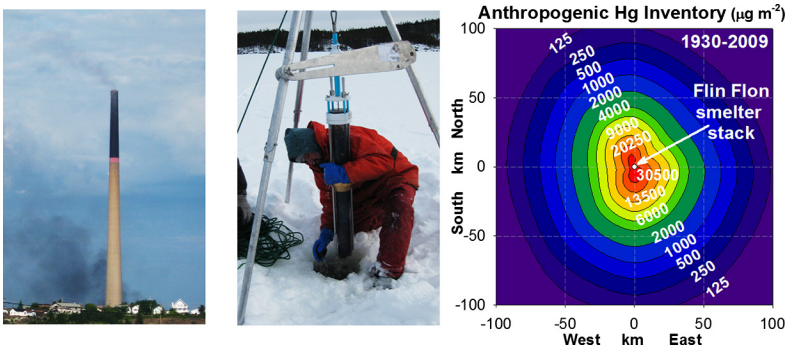
HIGHLIGHTS

- Multiple lake sediment cores used as multi-receptors of atmospheric Hg deposition.
- Conducted in a remote region and near a major Hg point-source.
- Spatial-temporal anthropogenic Hg inventory near the Flin Flon smelter estimated
- Landscape re-emission/remobilization of legacy Hg is a major regional source of Hg.

GRAPHICAL ABSTRACT



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ABSTRACT

High-resolution records of anthropogenic mercury (Hg) deposition were constructed from 9 lakes located 5–75 km from the Flin Flon, Manitoba smelter (formerly one of North America's largest atmospheric Hg point sources) and 5 lakes in Experimental Lakes Area (ELA), Ontario; a region remote from major Hg point sources. Anthropogenic Hg deposition, as both a flux and inventory, was determined after accounting for lake-specific natural Hg background concentrations, changes in sedimentation and sediment focusing. Results show that records of anthropogenic flux and inventory of Hg were remarkably consistent among the ELA lakes, but varied by 2 orders of magnitude among Flin Flon lakes. The relation between Hg inventories (normalized for prevailing wind direction) and distance from the smelter was used to estimate the total Hg fallout within a 50 km radius in 5 year time-steps, thus providing a quantitative spatial-temporal Hg depositional history for the Flin Flon region. The same relation solved for 8 cardinal directions weighted by the inverse of the previously applied wind direction normalization generates a map of Hg inventory and deposition on the landscape (Supplementary video). This novel application of sediment core data constructs a landscape model and allows for a visualization of contaminant deposition with respect to a point major source in both space and time. The propensity for Hg to

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undergo long-range, even global transport explains why Hg deposition within 50 km of Flin Flon was ~11% of estimated releases. That is until smelter releases were reduced >10-fold (post-2000), after which observed deposition exceeded smelter releases, suggesting landscape re-emission/remobilization of legacy Hg is a major ongoing regional source of Hg.

1. Introduction

Mercury is a global pollutant, and recent estimates of annual anthropogenic mercury (Hg) releases to air are 1000–4100 MT, over an order of magnitude larger than primary natural releases (Amos et al., 2015). As Hg releases are principally elemental Hg (Hg^0), Hg released has a long atmospheric residence time (~1 year), and the propensity for long-range and even global transport. Volatilization of previously deposited Hg leads to recycling of the primary Hg released through land, water and atmospheric reservoirs such that secondary Hg emissions are estimated to comprise 60% of the total annual Hg releases to air, with deep oceanic burial being the primary route of return to the Earth's interior (Selin 2009; UNEP 2013). The large primary releases of anthropogenic sourced Hg will similarly cycle through short and medium term reservoirs of vegetation, soils and surface waters such that globally, an augmented supply of Hg shall persist in the biosphere for a prolonged period of time after reductions or eliminations of anthropogenic Hg sources (Selin 2009; UNEP 2013; Amos et al., 2013; Amos et al., 2015).

Precious and base metal (gold, silver, copper, zinc, lead, and mercury) ore smelting and refining have historically been the major anthropogenic sources of atmospheric Hg emissions (Selin 2009; Streets et al., 2011; UNEP 2013: Amos et al., 2015). It is estimated that between 1850 and 2008, ~76% or 215 Gg of anthropogenic Hg emissions was attributable to these sources (Streets et al., 2011). While there is confidence in the prominence of metal extraction and refining as a dominant historical Hg emission source, the quantities of emissions, reservoirs, and deposition rates of Hg (as well as re-emission rates) currently and particularly in the past have considerable uncertainties and is an ongoing subject of research and controversy (Streets et al., 2011; Durnford and Dastoor, 2011; Zhang et al., 2012a; UNEP 2013; Amos et al., 2013, 2015; Engstrom et al., 2014).

Hg deposition is comprised of both dry and wet deposition, with only the latter being comparatively straightforward to measure, and a limitation is that historical measurements extend only back to the 1990s (Zhang et al., 2012a,b; Cole et al., 2014). Re-emission of freshly deposited Hg and older "legacy Hg" further complicates contemporary estimates of net deposition (Durnford and Dastoor, 2011; Zhang et al., 2012a,b), as well as the long-term effect of human activities on the global Hg cycle (UNEP 2013; Amos et al., 2013, 2015). As the monitoring record of atmospheric Hg content and deposition is brief, and natural as well as anthropogenic Hg emission estimates have considerable uncertainties, paleo-reconstructive methods are needed to determine the historical and natural deposition rates of Hg, and a wide variety of other contaminants, as well as help constrain contemporary modeling of Hg deposition and cycling between reservoirs (Biester et al., 2007; Engstrom et al., 2014; Amos et al., 2015).

The objective of this study was to reconstruct the history of the atmospheric Hg deposition sourced from human activities deposited in the Experimental Lakes Area (ELA) of Northwestern Ontario, and the area of Flin Flon, Manitoba (MB) using a landscape-scale, multi-lake approach with 14 cores collected from the ELA and Flin Flon regions. Remote (>200 km) from major centres of population and industrial and mining centres, the ELA is located ~55 km east of Kenora, Ontario, Canada (Fig. 1), and has been a world renowned centre for the study of environmental research since 1968 (Blanchfield et al., 2009). Monitoring data and atmospheric modeling have confirmed the ELA as suitable background site with comparatively low Hg deposition compared to the larger region (Hall et al., 2005; Zhang et al., 2012b). The ELA receives long-range transport from both Canadian and American industrial activity in the Great Lakes Basin, in addition to global sources. In contrast, Flin Flon MB has been a major copper and zinc mining, smelting, and processing centre for 80 years, and was the largest Canadian Hg emission source contributing as much 6% of the North American anthropogenic Hg releases to air during the smelter period of the peak emissions (~1980; Pirrone et al., 1998; Clarry, 2015). Otherwise, Flin Flon is remote (>250 km) from industrial and urban centres, making it an ideal site to study point source emission history as archived in lake sediments. Both Flin Flon and the ELA are well positioned to provide insights into the response of aquatic systems to widespread reductions in Hg point source emissions already occurring in North America, in a large part due to closures of many coal-fired generating stations in both Canada and USA (EPA, 2011; Bill 138, 2013; Weiss-Penzias et al., 2016).

After accounting for background Hg content, variable sedimentation rates and within lake sediment focusing rates, anthropogenic Hg fluxes (deposition per year), and inventories (total deposition post industrial development) were compared with Hg wet and dry deposition data (from snowpack and precipitation measurements), and smelter emission estimates. For the Flin Flon region, we were able to integrate the strong exponential relation between anthropogenic Hg inventory ($\mu g\ m^{-2}$) and distance from point source to estimate changes in Hg deposition over 5-year time steps within 50 km of the smelter for the 80 years of smelter operations. Finally, we produced a time series of Hg deposition maps for the Flin Flon region. While multiple lake sediment core reconstructions of atmospheric Hg fluxes have previously been performed for discrete background regions (Fitzgerald et al., 2005), or sub-continental scale regions (Muir et al., 2009; Drevnick et al., 2016), the work presented here is a quantitative spatial-temporal reconstruction of contaminant deposition and inventory with respect to a point source has been performed using lake sediment cores. The multi-lake approach using high fidelity lake sediment cores applied here is eminently suitable to assess Hg transport and deposition processes as it incorporates multiple receptors producing a coherent landscape signal. Furthermore, our approach is suitable to assess mercury contaminated site inventories and evaluate the success of Hg emission reductions from point sources and decommissioning/cessation of primary Hg mining and Hg intense industries, and from point sources as required by the Minamata Convention (articles 8 and 12; UN 2013; UNEP 2014).

2. Materials and methods

2.1. Study sites

Lake sediment cores were collected from two regions of central Canada (Fig. 1, Table S1), the Experimental Lakes Area (ELA; ~49.8°N, 93.8°W) and Flin Flon, Manitoba (~54.5°N, 101.8°W). The ELA is located within the Wabigoon Subprovince of the Superior Archean Craton characterized by granitic rocks and Greenstone belts 2.8–3.1 Ga years old (Tomlinson et al., 2004). The area of Flin Flon Manitoba contains several volcanogenic massive sulphide (VMS) deposits hosted within Paleoproterozoic volcanic rocks (formed ~1.89 Ga years ago) of the Trans-Hudson Orogen flanked by the Hearne and Superior Archean Cratons to the west and east respectively (Simard and MacLachlan, 2009). The Flin Flon copper smelter and zinc extraction plant was recognized as a large source of gaseous and particulate air pollution contributing heavy metals and other contaminants to the environment (Zoltai,

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