Science of the Total Environment xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Surface-air mercury fluxes across Western North America: A synthesis of spatial trends and controlling variables

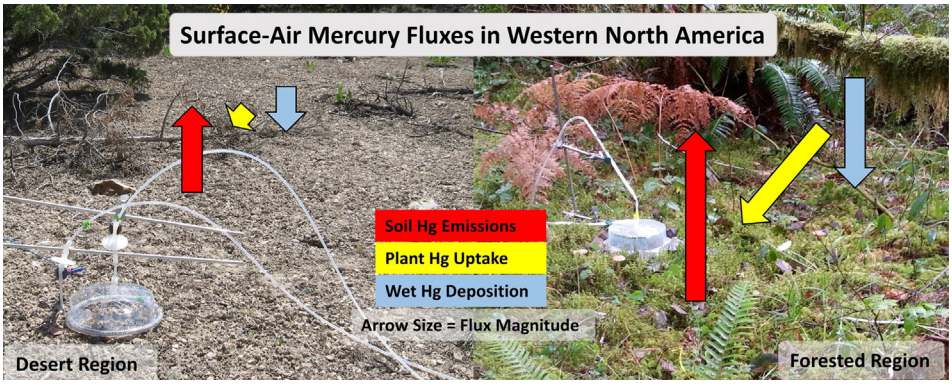
Chris S. Eckley [a,*], Mike T. Tate [b], Che-Jen Lin [c], Mae Gustin [d], Stephen Dent [e], Collin Eagles-Smith [f], Michelle A. Lutz [b], Kimberly P. Wickland [g], Bronwen Wang [h], John E. Gray [i], Grant C. Edwards [j], Dave P. Krabbenhoft [b], David B. Smith [i]

[a] US Environmental Protection Agency, Region-10, Seattle, WA 98101, USA
[b] US Geological Survey, Middleton, WI 53562, USA
[c] Center for Advances on Water and Air quality, Lamar University, Beaumont, TX 77710, USA
[d] Department of Natural Resources & Environmental Science, University of Nevada, Reno, NV 89557, USA
[e] CDM Smith, Portland, OR 97205, USA
[f] US Geological Survey, Corvallis, OR 97331, USA
[g] US Geological Survey Boulder, CO 80303, USA
[h] US Geological Survey, Anchorage, AK 99508, USA
[i] US Geological Survey, Denver, CO 80225, USA
[j] Department of Environment and Geography, Macquarie University, North Ryde, NSW 2109, Australia

HIGHLIGHTS

- Soil-air Hg fluxes are an important component of the global atmospheric Hg budget.
- A database of soil-air Hg flux measurements for Western North America was created.
- Ecosystem Hg fluxes were influenced by vegetation, light, and soil Hg and moisture.
- Vegetation had a large effect on net-ecosystem fluxes due to shading and uptake.
- Hg emission from sparsely vegetated landscapes was similar to Hg wet deposition.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 October 2015
Received in revised form 4 February 2016
Accepted 17 February 2016
Available online xxxx

Keywords:
Mercury
Dynamic flux chamber

ABSTRACT

Mercury (Hg) emission and deposition can occur to and from soils, and are an important component of the global atmospheric Hg budget. This paper focuses on synthesizing existing surface-air Hg flux data collected throughout the Western North American region and is part of a series of geographically focused Hg synthesis projects. A database of existing Hg flux data collected using the dynamic flux chamber (DFC) approach from almost a thousand locations was created for the Western North America region. Statistical analysis was performed on the data to identify the important variables controlling Hg fluxes and to allow spatiotemporal scaling. The results indicated that most of the variability in soil-air Hg fluxes could be explained by variations in soil-Hg concentrations, solar radiation, and soil moisture. This analysis also identified that variations in DFC methodological approaches were

* Corresponding author.
E-mail address: eckley.chris@epa.gov (C.S. Eckley).

http://dx.doi.org/10.1016/j.scitotenv.2016.02.121
0048-9697/Published by Elsevier B.V.

Emission
Deposition
Western North America

detectable among the field studies, with the chamber material and sampling flushing flow rate influencing the magnitude of calculated emissions. The spatiotemporal scaling of soil-air Hg fluxes identified that the largest emissions occurred from irrigated agricultural landscapes in California. Vegetation was shown to have a large impact on surface-air Hg fluxes due to both a reduction in solar radiation reaching the soil as well as from direct uptake of Hg in foliage. Despite high soil Hg emissions from some forested and other heavily vegetated regions, the net ecosystem flux (soil flux + vegetation uptake) was low. Conversely, sparsely vegetated regions showed larger net ecosystem emissions, which were similar in magnitude to atmospheric Hg deposition (except for the Mediterranean California region where soil emissions were higher). The net ecosystem flux results highlight the important role of landscape characteristics in effecting the balance between Hg sequestration and (re-)emission to the atmosphere.

Published by Elsevier B.V.

1. Introduction

The bi-directional flux of mercury (Hg) between terrestrial surfaces and the atmosphere is an important component of the global mercury budget. The magnitude of soil Hg emissions is related to the soil Hg concentration (Coolbaugh et al., 2002; Eckley et al., 2011b; Gustin et al., 2003; Nacht and Gustin, 2004; Zehner and Gustin, 2002), as well as other soil properties such as moisture content, temperature, mineralogy, disturbance and grain size (Eckley et al., 2011a; Gustin and Stamenkovic, 2005; Lin et al., 2010; Nacht and Gustin, 2004). Meteorological variables such as solar radiation, air temperature, relative humidity (RH), wind speed/turbulence, and air Hg and oxidant concentrations can also affect soil-air Hg fluxes (Carpi and Lindberg, 1997; Engle et al., 2005; Poissant et al., 1999; Xin and Gustin, 2007). These factors can vary substantially across the landscape, resulting in significant heterogeneity in soil-air Hg fluxes that can influence large-scale flux estimates and their contribution to local, regional, and global Hg cycling. Western North America in particular contains a tremendous gradient in climatological, geological, and land use characteristics that may result in extensive variation in site-specific soil-air Hg fluxes.

In geologically enriched regions, oxidized Hg (mostly Hg^{2+}) can exist in mineral forms such as cinnabar, metacinnabar, corderoite among others (Jew et al., 2014; Kim et al., 2000; Lowry et al., 2004). Most Hg in background soil is also in an oxidized form and bound to organic material (Grigal, 2003; Richardson et al., 2013; Skyllberg et al., 2009) though some gaseous elemental Hg (GEM or Hg^0) can also be loosely sorbed within the soil matrix (Carpi and Lindberg, 1997; Xin and Gustin, 2007; Zhang et al., 2008; Zhang et al., 2001). Mercury emitted from terrestrial surfaces primarily consists of Hg^0 due to its high volatility (Carpi and Lindberg, 1998; Gustin, 2003). Photo-reduction of Hg^{2+} to Hg^0 via sunlight exposure is well documented mechanism associated with the release of soil bound Hg to the air (Carpi and Lindberg, 1997; Xin and Gustin, 2007; Zhang and Lindberg, 1999); however, other processes occurring in the absence of light may also occur and may be related to biotic and abiotic processes (Barkay et al., 2003; Choi and Holsen, 2009a; Mazur et al., 2015).

Soil-air Hg flux is not always net emission. Numerous studies have also observed net deposition of gaseous Hg, particularly under low-light conditions and/or during periods of elevated ambient air Hg concentrations (Eckley et al., 2015a,b; Edwards and Howard, 2013; Ericksen et al., 2006; Gustin et al., 2006; Kuiken et al., 2008b). Hg released from soils may have been an original component of the substrate (geogenic) or it may represent re-emission of previously deposited Hg from the atmosphere (Eckley et al., 2015a,b; Ericksen et al., 2005).

Several studies have used soil-air Hg chamber flux data to scale-up emission estimates spatially and temporally. Some have focused on scaling over relatively small areas exhibiting anthropogenic impacts, such as mining sites (Eckley et al., 2015a,b; Eckley et al., 2011b; Engle and Gustin, 2002; Kocman and Horvat, 2011; Miller et al., 2011). These studies have relied on field and/or laboratory Hg flux data to develop correlations with environmental parameters and then utilized datasets on substrate Hg concentrations and other environmental variables to scale emissions over space and time. A similar approach has also been used to scale Hg fluxes across larger areas such as the State of Nevada, for which an extensive database of substrate Hg concentrations was available associated with mineral exploration (Zehner and Gustin, 2002). Scaling soil-air Hg fluxes has also occurred over large areas consisting of low-Hg content background soils (Denkenberger et al., 2012; Hartman et al., 2009). These efforts have relied on variations in land cover types and meteorological variables, but not soil Hg concentrations, to scale fluxes annually across regions of the US and Canada. Because vegetation can accumulate Hg from the air (Fleck et al., 1999; Rea et al., 2002; Stamenkovic and Gustin, 2009), estimations of the net ecosystem Hg flux must consider both the releases of Hg from soil as well as the uptake by plants (Hartman et al., 2009). The Hg taken up by plants can originate from soil Hg emission within an ecosystem as well as externally from atmospheric sources.

Within the last decade, there have been two regional Hg syntheses in North America, the first on the northeastern United States and eastern Canada (Evers and Clair, 2005) and the second on the Great Lakes regions of the US and Canada (Wiener et al., 2012). This study is part of a third Hg synthesis project that encompasses the Western North American region. The overall focus of the effort is to gather existing data collected over the past few decades (published and unpublished) from the region for the purpose of conducting a landscape-scale synthesis of Hg in abiotic and biotic resources. Our paper is one component of this effort and specifically focuses on surface-air Hg flux data. The Great Lakes Hg synthesis project included a similar regionally focused manuscript on surface-air Hg fluxes (Denkenberger et al., 2012).

Variables affecting Hg fluxes in Western North America are distinct due to this region's wide range of climate, vegetation/land cover, and relative abundance of geologically Hg enriched areas due to geothermal processes occurring along the Pacific tectonic plate boundary (Schluter, 2000). These diverse conditions facilitate testing the hypothesis that spatiotemporal trends in surface-Hg fluxes are controlled by variations in soil Hg concentrations, solar radiation, and soil moisture, and that vegetation patterns influence the net-ecosystem exchange of Hg with the atmosphere. Furthermore, because surface-air Hg fluxes have been measured using a range of methodological approaches, the gathering of flux data from numerous studies allows the opportunity to test a second hypothesis that the operating parameters used to measure Hg flux can have an identifiable effect on the magnitude of the calculated fluxes as shown by Eckley et al. (2010). These questions will be addressed by creating a database of all known surface-air Hg flux measurements conducted in Western North America, performing statistical analysis of the database to identify the key variables controlling fluxes and using this information to scale fluxes spatially and temporally.

Our study is unique from previous efforts to scale Hg emissions because of the broad geographic focus on Western North American landscapes, inclusion of recent findings on the role of soil moisture on Hg emission (Briggs and Gustin, 2013), and air-vegetation Hg uptake rates (Mao et al., 2008; Risch et al., 2012), and utilization of a newly available USGS database of soil Hg concentrations that has coverage across the conterminous United States (Smith et al., 2014). As the understanding of processes controlling Hg fluxes advances and new

Please cite this article as: Eckley, C.S., et al., Surface-air mercury fluxes across Western North America: A synthesis of spatial trends and controlling variables, Sci Total Environ (2016), http://dx.doi.org/10.1016/j.scitotenv.2016.02.121