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Continuous proxy measurements reveal large mercury fluxes from glacial and forested watersheds in Alaska

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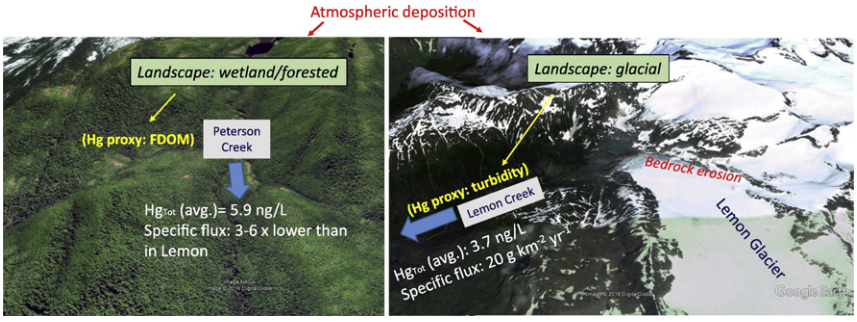
HIGHLIGHTS

- Total Hg fluxes were determined in a glacial stream by proxy monitoring of turbidity.
- Total Hg fluxes were determined in non-glacial stream by proxy monitoring of FDOM.
- Filtered Hg concentrations were consistently higher in non-glacial stream.
- Glacial stream had the highest specific mercury flux ever reported.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a stream from a glacially dominated watershed and one from a wetland, temperate forest dominated watershed in southeast Alaska were continuously monitored for turbidity and fluorescence from dissolved organic matter (FDOM) while grab samples for unfiltered (UTHg), particulate (PTHg), and filtered mercury (FTHg) where taken over three 4-day periods (May snowmelt, July glacial melt, and September rainy season) during 2010. Strong correlations were found between FDOM and UTHg concentrations in the wetland, temperate forest watershed ($r^2 = 0.81$), while turbidity and UTHg were highly correlated in the glacially dominated watershed ($r^2 = 0.82$). Both of these parameters (FDOM and turbidity) showed stronger correlations than concentration-discharge relationships for UTHg ($r^2 = 0.55$ for glacial stream, $r^2 = 0.38$ for wetland/forest stream), thus allowing for a more precise determination of temporal variability in UTHg concentrations and fluxes. The association of mercury with particles and dissolved organic matter (DOM) appears to depend on the watershed characteristics, such as physical weathering and biogeochemical processes regulating mercury transport. Thus employing watershed-specific proxies for UTHg (such as FDOM and turbidity) can be effective for quantifying mercury export from watersheds with variable landcover. The UTHg concentration in the forest/wetland stream was consistently higher than in the glacial stream, in which most of the mercury was associated with particles; however, due to the high specific discharge from the glacial stream during the melt season, the watershed area normalized flux of mercury from the glacial stream was 3–6 times greater than the wetland/forest stream for the three sampling campaigns. The annual specific flux for the glacial watershed was 19.9 g UTHg km^{-2} y^{-1}, which is higher

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than any non-mining impacted stream measured to date. This finding indicates that glacial watersheds of southeast Alaska may be important conduits of total mercury to the Gulf of Alaska.

1. Introduction

Like many pristine, high-latitude regions, the watersheds ringing the Gulf Of Alaska (GOA) are subject to atmospheric mercury (Hg) deposition via long range transport (Fitzgerald et al., 2005). Many of these watersheds are blanketed by glaciers, which account for nearly 20% of the land area and 50% of the freshwater discharge draining to the GOA (Neal et al., 2010). Non-glacial watersheds with peatlands on shallow slopes and upland conifer forests on steeper aspects are also abundant in this region and can be characterized by high dissolved organic carbon (DOC) concentrations in streamwater (D'Amore et al., 2015). This wide spectrum of landscape types translates into diverse biogeochemical conditions among watersheds in the region that variably influence storage, export, and methylation of atmospherically derived mercury. Understanding how watershed landcover influences the dynamics of riverine Hg export in southeast Alaska is of particular importance given that climate-driven changes in glacier volume and precipitation are projected to substantially alter land-to-ocean fluxes of freshwater in the region (Shanley et al., 2015).

On a global scale, nearly half of atmospheric mercury originates from fossil fuel combustion, of which >60% originates from Asia (excluding Russia), mainly from burning coal as fuel (Horowitz et al., 2014; Jaffe et al., 2005). Previous research has shown that the particulate/aerosol Hg released from coal burning can be carried via atmospheric currents to the North American northwest coast where deposition occurs (Durnford et al., 2010; Munthe et al., 2011). This mechanism is thought to contribute to atmospheric Hg deposition in the Coast Mountains of southeast Alaska (Lamborg et al., 2013) and northern British Columbia (Karlsson, 2014), which are located nearly 10,000 km east of the Asian continent. Furthermore, lake sediment cores in this region show a pronounced increase in Hg concentrations since the 1940s (Engstrom et al., 2014). Runoff from the coastal mountains in southeast Alaska is extremely high (~2 m y^{-1}; Hill et al., 2015) as a result of large amounts of regional rainfall combined with abundant glacial melt water. This creates the potential for high riverine mass fluxes of dissolved and particulate mercury even when streamwater Hg concentrations are low.

Recent research in southeast Alaska has shown that streamwater derived from glacially influenced or recently deglaciated landscapes in southeast Alaska have lower filtered (FTHg) and biotic total mercury concentrations, and higher particulate total mercury (PTHg) concentrations, compared to streams draining forested and wetland watersheds (Nagorski et al., 2014). The role of forest and wetland ecosystems in the storage, transformation, and export of Hg is relatively well documented (e.g. Fostier et al., 2000; Lawson et al., 2001); however Hg cycling in glacier ecosystems like those found in southeast Alaska is not well understood. Glacial watersheds lack most of the features that promote the physical and biological retention of atmospherically deposited Hg in forested watersheds with well-developed soils (e.g. Demers et al., 2007; Obrist et al., 2011), and therefore, could directly release Hg during times of glacial melt. In addition, physical weathering by glaciers can mobilize geogenic Hg (Zdanowicz et al., 2013; Bełdowski et al., 2015). The few studies conducted on mercury in glaciated watersheds suggest that glacial meltwater can act as a source of total Hg to downstream freshwater and marine environments. For example, in the Arctic near Svalbard, glacial runoff appears to be an important source of total Hg to downstream fjords (Bełdowski et al., 2015).

Mercury is not routinely measured in most watersheds, making it difficult to accurately characterize riverine Hg fluxes. In southeast Alaska, this issue is compounded by the difficulty in consistently accessing rugged, remote watersheds. Correlating mercury concentrations to a stream characteristic that is easy and inexpensive to measure can improve the ability to characterize seasonal and event-based changes in Hg concentrations and ultimately quantify riverine Hg export. Unfiltered total Hg (UTHg) can be correlated with discharge (e.g. references within Table 2); however, the strength of this relationship is often poor, leading to large uncertainties in UTHg fluxes. While the utility of traditional concentration-discharge relationships for UTHg may be limited, other relatively easy to measure water quality parameters may correlate better with UTHg and provide more robust estimates of Hg export. For example, binding of Hg to dissolved organic matter (DOM) ligands appears to be a dominant interaction, and thus an export vector for Hg when DOC concentrations are above 3 mg C L^{-1} for many streams (Dong et al., 2011). Concentrations of DOC in forested and wetland watershed streams have been shown to be significantly correlated with FTHg concentrations (Dittman et al., 2009; Nagorski et al., 2014; Bergamaschi et al., 2012). The effectiveness of DOC as a tracer, or proxy, for FTHg and UTHg appears to be somewhat dependent on stream size, as shown by the variability in the strength of the DOC-FTHg relationship across 1st to 4th order streams in a single watershed in Vermont (Schuster et al., 2008). In glaciated watersheds, the predominance of particulate species of Hg in streamwater (Nagorski et al., 2014; Bełdowski et al., 2015) suggest that total suspended sediment may be an effective proxy for riverine Hg export, although the strength of this relationship has not been explored.

Glaciers in the Coast Mountains of southeast Alaska are rapidly thinning and retreating, and being replaced by temperate forests and peatlands. It is important to assess how ongoing landscape evolution is altering the sensitivity of coastal watersheds to atmospheric Hg inputs. Here we quantify the mercury concentrations, fluxes, and partitioning in two coastal watersheds, one heavily glaciated (Lemon Creek) and one dominated by temperate forest and wetlands (Peterson Creek), using continuous, in-situ measurements of water quality parameters as proxies. Our hypotheses are that: (1) FDOM will serve as a robust proxy for unfiltered total mercury (UTHg) concentrations in the temperate forest/wetland watershed due to the association of Hg with DOC, (2) turbidity will serve as a robust proxy for [UTHg] in the glaciated watershed due to the association of Hg with particles, (3) Hg partitioning in the glaciated watershed will be dominated by particle-associated Hg, while the dissolved phase will contain the majority of Hg in the forest/wetland watershed, and (4) the specific flux of UTHg will be greater from the glacial watershed due to higher rates of specific discharge.

2. Experimental

2.1. Sample sites

Mercury measurements were made in two different streams, Peterson Creek (wetland/upland forest) and Lemon Creek (glacial), during three 4-day periods in 2010. The sampling periods occurred in May (18 May–21 May), July (20 July–23 July), and September (24 September–27 September), and were chosen to characterize the three primary hydrologic regimes during the summer runoff season: snowmelt (May), glacial melt (July), and the Fall rainy season (September). In order to not target any specific event the dates were chosen well in advance of the field campaign. Peterson Creek and Lemon Creek are located within 15 km of one another along the Juneau, Alaska road system (Fig. 1) and are subject to similar weather systems, which typically originate in the Gulf of Alaska. Lemon Creek was sampled and monitored about 7 linear km upstream of the creek mouth in Gastineau Channel