

## Mercury Export from the Yukon River Basin and Potential Response to a Changing Climate

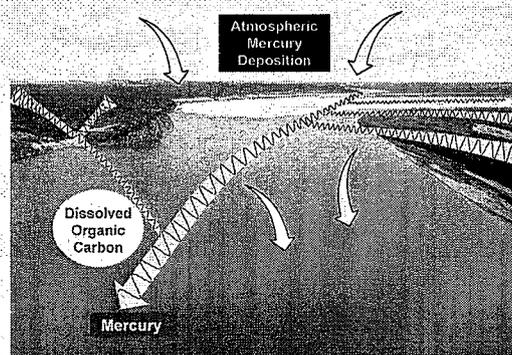
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**S** Supporting Information

**ABSTRACT:** We measured mercury (Hg) concentrations and calculated export and yield from the Yukon River Basin (YRB) to quantify Hg flux from a large, permafrost-dominated, high-latitude watershed. Exports of Hg averaged  $4400 \text{ kg Hg yr}^{-1}$ . The average annual yield for the YRB during the study period was  $5.17 \mu\text{g m}^{-2} \text{ yr}^{-1}$ , which is 3–32 times more than Hg yields reported for 8 other major northern hemisphere river basins. The vast majority (90%) of Hg export is associated with particulates. Half of the annual export of Hg occurred during the spring with about 80% of 34 samples exceeding the U.S. EPA Hg standard for adverse chronic effects to biota. Dissolved and particulate organic carbon exports explained 81% and 50%, respectively, of the variance in Hg exports, and both were significantly ( $p < 0.001$ ) correlated with water discharge. Recent measurements indicate that permafrost contains a substantial reservoir of Hg. Consequently, climate warming will likely accelerate the mobilization of Hg from thawing permafrost increasing the export of organic carbon associated Hg and thus potentially exacerbating the production of bioavailable methylmercury from permafrost-dominated northern river basins.



### INTRODUCTION

Atmospheric deposition of mercury (Hg) and its subsequent export from watersheds is a critical concern to aquatic and terrestrial food webs.<sup>1</sup> This concern is of particular significance in northern latitudes where arctic rivers presently deliver substantial amounts of both organic matter and Hg to the Arctic Ocean, where elevated foodweb levels of Hg are particularly problematic.<sup>2</sup> Future export of Hg by these systems may potentially be influenced by two factors. First, the landscapes of northern regions are changing as a result of a warming climate.<sup>3</sup> Frozen soils in this region contain large stores of both organic matter<sup>4</sup> and Hg that may be mobilized from thawing permafrost.<sup>5</sup> Second, it is anticipated that atmospheric deposition of Hg in northern regions will increase due to rapidly expanding Eurasian industrialization.<sup>6</sup> Thus, it is important to measure the current exports and yields of Hg from northern river basins so that a baseline is established to compare against future conditions.

Much of what is known about Hg transport in rivers is derived from studies of small streams and lakes at lower latitudes.<sup>7,8</sup> In many of these systems, Hg and organic matter concentrations are strongly correlated,<sup>9</sup> and it is generally accepted that interactions of Hg with organic matter in soils and stream waters are major factors controlling Hg export from a watershed.<sup>8,10–12</sup> Boreal forests contain approximately one-third of the world's terrestrial organic carbon, and DOC concentrations and fluxes in northern streams draining boreal forest catchments are generally greater

than those at lower latitudes.<sup>13</sup> In these systems, changes in climate are resulting in permafrost thaw<sup>14</sup> and increased fire frequency.<sup>15,16</sup> In turn, both the biogeochemical activity within soils, which controls the fate of organic matter, and the amount and timing of water discharge ( $Q$ ) from a watershed are being altered.<sup>17,18</sup>

Here, we present Hg export data for the Yukon River, a major northern river draining to the Bering Sea and, ultimately, the Arctic Ocean. The Yukon River, the subject of U.S. Geological Survey investigations since 2001 (see Supporting Information), provides a unique opportunity to study the cotransport of Hg and organic matter in a large, high latitude boreal river. It is the longest free-flowing river in the world,<sup>19</sup> and with little development along its 3200 km reach, it is considered relatively pristine. In addition, nearly 75% of the Yukon River Basin (YRB) is covered by organic-rich permafrost soils. These exceptional characteristics along with vast reservoirs of sequestered carbon, complex geologic terrain, and naturally high suspended sediment loads provide a unique setting to examine Hg dynamics at a large scale. These data will serve as a baseline by which to compare future conditions, increase our understanding of correlations of

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Hg and organic carbon (OC) at large scales, and establish the basis for utilization of the organic matter concentrations and water yield to be used as proxy measures of Hg yield at large scales.

## EXPERIMENTAL SECTION

The Yukon River is the 19th longest river in the world (3200 km), draining the fourth largest basin (853 500 km<sup>2</sup>) with the fifth largest average annual discharge ( $Q$ ) (6500 m<sup>3</sup> s<sup>-1</sup>) in North America (see Supporting Information for an overview of YRB characteristics). The YRB is located in Arctic and Subarctic latitudes (60–68° N) that include most of interior central Alaska and the Yukon Territory of Canada (see Supporting Information, Figure S1). Discharge was monitored continuously for the Yukon River at Pilot Station, Alaska (YRP) by the U.S. Geological Survey (gaging station 15565447; <http://waterdata.usgs.gov/ak/nwis/uv/15565447>). In addition,  $Q$  was measured during water sampling using an Acoustic Doppler Current Profiler (ADCP).<sup>20</sup> Surface water grab samples were collected in the centroid of flow off the bow of a small boat that was headed slowly into the current. For all organic matter sampling, surface water was sampled using the USGS EDI method<sup>21</sup> and processed according to USGS protocols.<sup>22</sup> Samples were filtered in the field, stored chilled, and shipped for analyses as soon as possible after collection.

Discharge at YRP is operationally defined as the outflow of the YRB because (1) this is the furthest downstream site having no tidal influence and (2) the river is confined to a single channel providing the ability to accurately measure  $Q$ . River water at this site is composed of surface and groundwater from three general sources: (1) snowmelt and glacial meltwater that has a high sediment load and low dissolved organic carbon (DOC); (2) surface water originating from terrestrial landscapes dominated by permafrost and/or peat and has a high DOC but low sediment load; and (3) water derived from groundwater sources that are low in sediment and DOC but high in dissolved inorganic carbon (DIC).

Water samples were collected from the YRP about 100 miles upstream from the Yukon Delta 7–8 times a year, once in March or April (under ice base flow) and then every 2–3 weeks during open water from October 2001 through September 2005.<sup>23</sup> During this time, filtered total mercury (FHg) and particulate total mercury (PHg) were measured in 38 samples. Accurate estimation of average exports and yields required measurements of Hg and OC over a range of hydrologic conditions (abbreviations of Hg species are defined in Table 2). The 2001–05 data set captured a robust representation of end member or extreme flow events (see Supporting Information, Figure S2) and also included 4 years in which average flow conditions closely matched the 29 year average (see Supporting Information, Figure S3). As with all remote areas of the world, sampling logistics can be problematic. Thus, not all flow regimes could be sampled (i.e., very few samples between 37 and 82% of the time that  $Q$  was equaled or exceeded). Because a main objective of this research was to calculate annual exports as accurately as possible, we concentrated on sampling during high flows. The load (or export) estimating program used in this study (LOADEST)<sup>24</sup> requires 12 concentration measurements with half of them as close to peak flow as possible. Thus, most of the measurements are concentrated between 0 and 50% of the time that  $Q$  was equaled or exceeded.

## ANALYTICAL APPROACH

All Hg analyses were performed at the USGS Mercury Research Laboratory (MRL) in Middleton, Wisconsin.<sup>25</sup> Dissolved organic carbon (DOC) analyses were performed by the USGS National Research Program (NRP) laboratory in Boulder, Colorado.<sup>23,26</sup> POC analyses were performed at the USGS National Water Quality Laboratory and also at the Nutrient Analytical Services Lab (NASL), Chesapeake Bay Laboratory, Maryland, using the same methodologies described in Zimmerman et al.<sup>27</sup>

Annual exports (also referred to as fluxes) (mass yr<sup>-1</sup>) and yields (mass m<sup>-2</sup> yr<sup>-1</sup>) of Hg were calculated using two independent approaches. In the first approach, LOADEST was used to calculate daily exports as described in Striegl et al.<sup>28</sup> and Dornblaser and Striegl.<sup>29,30</sup> Exports were estimated from 38 measurements of Hg concentrations and continuous  $Q$  over a wide range of flow conditions between 2001 and 2005 (see Supporting Information, Figure S2). In a second approach, linear regressions were developed between DOC and FHg and POC and PHg. The regression equations were used to estimate FHg and PHg exports and yields based on dissolved and particulate carbon concentrations, respectively. Mercury yields were calculated by dividing export by the watershed area.

## RESULTS AND DISCUSSION

**Hydrology.** Average annual Hg and OC exports and yields were determined over a range of hydrologic regimes. During the 5 years of study (2001–2005), continuous  $Q$  was measured at YRP and compared closely with  $Q$  measured over the 29 year long-term record. The study period captured record low and high annual flows and 3 years of average flows that matched closely to the 29 year average (see Supporting Information, Figure S3). Nearly one-third of the total annual  $Q$  from the YRB is from snowmelt occurring from early April to late June. Furthermore, 87% of annual water export occurs in less than half the water year (WY) (Oct. 1 through Sept. 30). Therefore, to obtain the best estimates of annual geochemical exports and yields, sample collection was coordinated with maximum flow. Additional samples were collected in the late winter under ice (see Supporting Information, Figure S2, plotted as greater than 80% on the flow duration curve). Because  $Q$  is at its lowest during the early spring, samples collected during this time represent mostly base flow (groundwater) for more than 200 days of the water year.

**Concentrations of Hg.** Hg concentrations were dominantly in particulate phase (90%) with annual discharge weighted PHg concentrations averaging 9.6 ng L<sup>-1</sup> ( $n = 34$ ), whereas FHg concentrations averaged 1 ng L<sup>-1</sup> ( $n = 38$ ), with observed increases of 24 and 9 fold, respectively, from winter base flow to peak spring flow (Table 1). Compared to other large Northern hemisphere rivers (Table 2) these relatively high Hg concentrations observed in the YRB suggest contributions from geogenic and/or other terrestrial-based sources in addition to atmospheric Hg deposition. About 80% of the 34 samples measured for THg at the YRP, with a mean value of 21 ng L<sup>-1</sup>, exceeded the USEPA aquatic life THg standard for adverse chronic effects to biota (12 ng L<sup>-1</sup>).<sup>31</sup> Forty percent of these exceeded values occurred during the spring, in advance of the fish migration and spawning season. Concentrations of filtered (dissolved) methylmercury (FMeHg) were generally below the method detection limit (MDL) of 0.04 ng L<sup>-1</sup> ( $n = 38$ ). The weighted average annual

**Table 1. Seasonal Exports of Filtered Mercury (FHg) ( $\text{kg yr}^{-1}$ ) and Particulate (PHg) ( $\text{kg yr}^{-1}$ ) and Dissolved Organic Carbon (DOC) ( $10^6 \text{ kg yr}^{-1}$ ) from Five Year Means for the Yukon River at Pilot Station (YRP), 2001–2005, with Coefficients of Variation (CV) from the LOADEST Results<sup>a</sup>**

season	FHg	CV	PHg	CV	THg	DOC <sup>b</sup>	CV <sup>b</sup>	POC <sup>b</sup>	CV <sup>b</sup>	TOC	[FHg]	[FMeHg]	[PHg]	[PMeHg]	[THg]	[DOC]
spring	198	-	1999	-	2205	826	-	345	-	1171	2.38	<0.04	18.1	0.05	20.5	11.3
summer	131	-	1955	-	2093	550	-	385	-	935	1.33	<0.04	18.5	0.05	19.9	5.7
winter	24.0	-	49.0	-	73.9	197	-	17.3	-	214	0.28	<0.04	0.75	<0.01	1.02	2.6
annual exp	353	9.2	4003	12.9	4372	1585	6.0	751	7.2	2318	-	-	-	-	-	-
annual avg <sup>c</sup>	-	-	-	-	-	-	-	-	-	-	0.98	<0.04	9.58	<0.05	10.6	5.08

<sup>a</sup> Average seasonal concentrations for this period for mercury, methylmercury, and DOC are in brackets. Mercury species: filtered mercury (FHg), filtered methylmercury (FMeHg), particulate mercury (PHg), particulate methylmercury (PMeHg), total mercury (THg). Organic carbon species: dissolved organic carbon (DOC), particulate organic carbon (POC), total organic carbon (TOC). Seasons: Spring, May 1 to June 30; Summer, July 1 to October 31; Winter, November 1 to April 30. <sup>b</sup> From Striegl et al.<sup>28</sup>, Table 2, the error, % reported, are CVs. <sup>c</sup> Annual averages are weighted by season.

concentration of PMeHg was  $0.05 \text{ ng L}^{-1}$  ( $n = 36$ ) with a MDL ranging from  $<0.01$  to  $<0.06 \text{ ng L}^{-1}$ . Thirty six of the 74 MeHg measurements were below the MDL resulting in a high uncertainty for use in export and yield calculations. Therefore, only concentrations of FMeHg and PMeHg are reported in Table 1. The median value for TMeHg/THg ratio was 1%, ranging from 0.1% to 9% ( $n = 34$ ). This value is much lower than what has been typically been reported in other studies (2–15%).<sup>32</sup> Despite the low relative abundance of MeHg in the YRB samples, the ranges and estimated exports of MeHg indicate that Hg methylation is occurring. Other studies in temperate systems have positively correlated the percent wetland cover in watersheds to the export of MeHg.<sup>33</sup> However, for the YRB, approximately 25% of which is classified as wetland, no clear relationship between percent wetland and TMeHg yields was observed from YRB subbasins (see Supporting Information, Figure S6). More thorough studies are needed to assess important Hg methylation sites in the YRB.

**Exports and Yields of Hg.** Annual THg export from the YRB averaged  $4400 \text{ kg yr}^{-1}$  (92% was in the particulate phase (PHg); Table 1) and yields were  $5.2 \mu\text{g m}^{-2} \text{ yr}^{-1}$ . Almost all the THg export (98%) occurred during the spring and summer (May 1 to Oct. 31). Hg exports estimated by LOADEST compared well with discretely measured exports (Figure 1). In addition, the coefficients of variation (CV), calculated as the standard error of prediction of the mean export, also suggest that Hg was generally modeled well for both the dissolved and particulate forms of Hg (Table 1). Overall, these results indicate that LOADEST was effective in estimating Hg exports and yields in the YRB.

**Correlation of Mercury, Organic Carbon, and Water Export.** The strong correlation of Hg to OC in surface waters is widely reported in the scientific literature. However, most study areas are orders of magnitude smaller<sup>3</sup> and are generally much less diverse ecosystems than the YRB. Hg concentrations from the YRB at the YRP were significantly correlated to concentrations of OC with DOC explaining 81% of the variability of FHg ( $p < 0.001$ ) and POC explaining 50% of the variability of PHg (still strongly significant,  $p < 0.001$ ) (Figure 2). Although exports and yields of OC are generally proportional to water yield<sup>24,28</sup> (see Supporting Information, Figure S4; DOC–Q correlation is weak but significant,  $R^2 = 0.52$ ,  $p < 0.001$ ), Hg concentrations from the YRB at YRP were weakly correlated to Q (see Supporting Information, Figure S5). LOADEST uses only Q as an input parameter and does not account for the strong positive correlation of OC and Hg. To assess the performance of LOADEST to estimate Hg exports based only on inputs of Hg concentrations and Q, linear regressions between DOC and FHg

and POC and PHg concentrations were compared to Hg exports estimated by LOADEST (Figure 3). There is disagreement in predicting PHg export during rare extreme flow events. Overall, however, there is good agreement between the two approaches, supporting the idea that both LOADEST and the Hg-OC correlation can be used as predictive tools for Hg export.

**Extrapolation of the Hg Export Record.** Although there are significant correlations among water, OC, and THg exports and good agreement between LOADEST and the linear regression approach (see Supporting Information), it is not yet possible to reconstruct or project annual Hg export from the YRB or other arctic and subarctic basins. Increased atmospheric deposition<sup>6</sup> will increase potential sources of Hg available for hydrologic transport from watershed surfaces. However, hydrologic trends throughout the YRB suggest increased infiltration and groundwater contribution to streamflow attributable to permafrost thaw, which will result in increased mineralization or adsorption of DOC<sup>17,18</sup> and potentially decreased FHg export. There is also evidence that increased DOC mineralization and soil respiration can lead to increased Hg vapor emissions from soils.<sup>34</sup> Conversely, there is evidence that DOC exports are increasing in Eurasian high latitudes experiencing increased precipitation in recent decades.<sup>35</sup> More relevant to the Hg export problem is quantification by our study that the vast majority (90%) of THg export is associated with particulates, most likely POC. POC data are sparse and difficult to measure accurately for large rivers, particularly for remote rivers, and the POC database for the Yukon<sup>28</sup> and other subarctic and arctic rivers<sup>36</sup> is small and mostly recent. Given the importance of POC to Hg transport and to other important biogeochemical processes, more emphasis needs to be placed on its measurement in large river studies.

**Comparison to Other Large Rivers.** The data required to estimate exports and yields of Hg from other large river basins are limited both spatially and temporally. Table 2 compares selected watershed characteristics, water yields, and the average annual concentrations, exports, and yields of FHg and PHg, suspended sediment, and TOC (calculated as the sum of DOC and POC) of the YRB to published results for eight major Northern hemisphere river basins (details and references for the development of Table 2 are in the Supporting Information). THg yields from the YRB (dominantly in the particulate phase) are up to 32 times greater than these other 8 major river basins suggesting five possibilities: (1) the YRB receives higher rates of atmospheric Hg deposition; (2) the YRB receives additional terrestrial Hg, such as from thawing permafrost; (3) all the other rivers in this comparison are significantly impacted by flow control structures



glacial meltwater sources are negligible and Hg export from the YRB is closer to the other rivers in this comparison (Table 1). If the climate continues to warm, Hg exports may initially increase in response to increased wasting of the glacial sources. However, as those glacial PHg sources become exhausted, Hg export from the Yukon River may more closely resemble Hg export from other large arctic rivers such as the Lena.

The percentage of permafrost cover across these nine watersheds is highly variable (Table 2) with the Yukon and the Lena having the greatest coverage (75–94%). Preliminary results from analyses of THg in a permafrost core from the YRB<sup>5</sup> indicate that permafrost soils contain a substantial reservoir of historically accumulated Hg (see Supporting Information for further details). Therefore, in response to a warming climate, northern watersheds with a high percentage of permafrost cover may experience an increase in THg export in the future. Unlike the glacial PHg source, Hg derived from thawing permafrost would likely have a much greater proportion of FHg due to its partitioning to DOC. The pristine setting of the YRB provides a unique opportunity to measure Hg concentrations, exports, and yields and evaluate terrestrial and atmospheric sources (natural and anthropogenic). The absence of Hg point sources, such as those at lower latitudes, greatly reduces complications associated with the study of Hg dynamics and the response to climate change in an ecosystem. These findings underscore the importance of a better understanding of Hg-OC interactions in large-scale northern ecosystems given the vast reservoirs of OC that exist in Arctic region wetlands and permafrost. Twenty percent of the Earth's land surface is covered by permafrost, which is thawing in the Arctic and Subarctic regions, thereby increasing the potential release of vast reserves of OC-bound Hg. This is particularly noteworthy because dissolved, OC-associated Hg is considered to be an important bioavailable Hg fraction that feeds the methylation process. Continued warming will likely promote or accelerate the mobilization of Hg from permafrost increasing concentrations, exports, yields, and potential Hg methylation in the YRB and other northern region river basins of similar character.

## ■ ASSOCIATED CONTENT

**S** Supporting Information. Detailed descriptions of the study area, experimental procedures, and analytical approaches. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## ■ DISCLOSURE

Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

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