Environmental Science & Technology

pubs.acs.org/est

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Mercury Export from Arctic Great Rivers

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Cite This: https://dx.doi.org/10.1021/acs.est.9b07145

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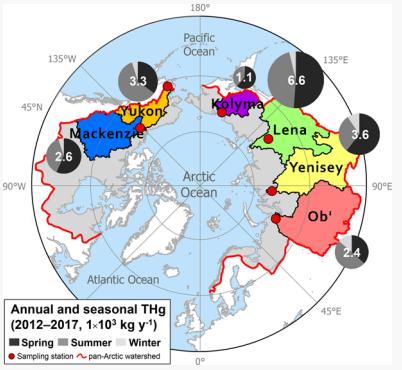
ABSTRACT: Land−ocean linkages are strong across the circumpolar north, where the Arctic Ocean accounts for 1% of the global ocean volume and receives more than 10% of the global river discharge. Yet estimates of Arctic riverine mercury (Hg) export constrained from direct Hg measurements remain sparse. Here, we report results from a coordinated, year-round sampling program that focused on the six major Arctic rivers to establish a contemporary (2012−2017) benchmark of riverine Hg export. We determine that the six major Arctic rivers exported an average of 20 000 kg y^{-1} of total Hg (THg, all forms of Hg). Upscaled to the pan-Arctic, we estimate THg flux of 37 000 kg y^{-1}. More than 90% of THg flux occurred during peak river discharge in spring and summer. Normalizing fluxes to watershed area (yield) reveals higher THg yields in regions where greater denudation likely enhances Hg mobilization. River discharge, suspended sediment, and dissolved organic carbon predicted THg concentration with moderate fidelity, while suspended sediment and water yields predicted THg yield with high fidelity. These findings establish a benchmark in the face of rapid Arctic warming and an intensifying hydrologic cycle, which will likely accelerate Hg cycling in tandem with changing inputs from thawing permafrost and industrial activity.



INTRODUCTION

Mercury (Hg) is of broad public interest because it is transported between air, water, and soils,[1] and its neurotoxic form, methylmercury (MeHg), bioaccumulates in organisms and biomagnifies in food webs.[2] From a biogeochemical perspective, large rivers integrate across broad and ecologically diverse watersheds, and are a primary source of Hg to the coastal ocean.[3] Land−ocean linkages are strong across the circumpolar north, where the Arctic Ocean accounts for 1% of the global ocean volume but receives more than 10% of the global river discharge.[4] While much of the river-borne Hg is thought to be resequestered in sediments in the Arctic coastal margin,[3,5] the magnitude and fate of Arctic riverine Hg is of particular concern because traditional northern diets include marine biota which can exceed Hg toxicity thresholds for safe consumption.[6]

Most of the annual Arctic river discharge coincides with periods of enhanced marine primary production during the spring and summer,[7] suggesting that greater riverine Hg export during this time could increase the amount of Hg available for transformation and uptake into marine ecosystems. Further, Arctic warming[8] and intensifying hydrologic cycles[9,10] are strengthening land−freshwater−ocean linkages,[11−13] with unknown implications for the magnitude, timing, and species of Hg exported by Arctic rivers. Contemporary measurements of annual riverine Hg fluxes made from direct, coordinated measurements enable a benchmark against which to measure future change, yet these measurements do not currently exist for the pan-Arctic.

A growing interest in Arctic Hg cycling has inspired numerous estimates of riverine Hg fluxes, often made by extrapolating measurements from a single site and/or via correlations with other constituents, or using mass balance models.[3,5,14−23] Early estimates of total Hg (THg, all forms of Hg) fluxes in Arctic rivers were limited to spring and summertime measurements of THg concentrations, yet they provided a baseline which showed regional variability in THg fluxes in the Ob', Yenisey, Lena, and Mackenzie rivers (1350, 720, 4050, and 2200 kg y^{-1} respectively).[14,15] This early research showed a strong association between THg concentration and discharge, suggesting that hydrologic mobilization is a key driver of regional Hg cycling.[14] Paired with river discharge and suspended sediment flux data, these early estimates facilitated upscaling to the first estimate of pan-Arctic riverine THg flux (12 500 kg y^{-1}).[16]

While the majority of river discharge to the Arctic Ocean occurs in the Eurasian Arctic,[24] a considerable proportion of

Received: November 25, 2019
Revised: February 28, 2020
Accepted: March 2, 2020
Published: March 2, 2020

the subsequent research on riverine Hg drivers and fluxes occurred in North America (e.g., refs 17−19, and 25). More recent studies on pan-Arctic riverine THg fluxes have generated varying estimates (20 000 to 80 000 kg y^{-1}) using biogeochemical models.[3,5,23] In comparison, recent flux estimates extrapolated from direct measurements using THg−dissolved organic carbon (DOC) relationships from a subset of North American and Eurasian Arctic rivers are converging toward similar magnitudes of Hg export (44 000 to 50 000 kg y^{-1}).[20,21] As these studies indicate, river discharge, DOC, and suspended sediments all show promise as proxies for estimating Hg concentrations in Arctic rivers. Predictive models of THg concentration and flux could be particularly useful in northern regions, where natural and anthropogenic Hg loadings are changing[26−29] concurrent with widespread permafrost thaw[30] and the mobilization of Hg from permafrost and active layer soils,[29] an intensifying hydrologic cycle,[9] increasing river discharge,[31] and variable fluvial DOC[11,32] and sediment regimes.[33]

Research on Arctic riverine Hg reveals two overarching themes: first, North American rivers have been studied more directly and intensively. Second, river discharge drives DOC and suspended sediment concentrations, which in turn affect the dissolved and particulate phases of Hg (e.g., refs 17, 25). Yet to-date there have been few coordinated assessments of riverine THg fluxes[20] or of the utility of predictive THg models for the pan-Arctic domain. Here, we calculate pan-Arctic riverine THg fluxes using a multiyear (2012−2017) data set of THg, DOC, and total suspended sediments (TSS) samples (n = 178) encompassing the hydrograph for the six major Arctic rivers (Ob', Yenisey, Lena, Kolyma, Yukon, and Mackenzie). Together, these rivers account for nearly 60% of the river discharge to the Arctic Ocean.[34] Additionally, we evaluate the seasonality and regional variability of THg export, and assess the utility of regression models for predicting THg concentrations and yields from our measurements of discharge, DOC, and TSS. Our objectives were to (i) determine annual and seasonal THg fluxes for the six major Arctic rivers and the pan-Arctic watershed, using the coordinated sampling and analytical framework of the Arctic Great Rivers Observatory (Arctic-GRO, https://arcticgreatrivers.org); (ii) assess the degree to which discharge, DOC, and TSS concentrations can be used to predict bulk THg concentrations and yields across disparate regions and watersheds; and (iii) better constrain contemporary riverine Hg fluxes to the Arctic Ocean, to aid efforts to monitor future change in Arctic and global Hg cycling.

METHODS

Sample Collection and Chemical Analyses. River water samples for chemical analyses were collected at Salekhard (Ob'), Dudinka (Yenisey), Zhigansk (Lena), Cherskiy (Kolyma), Pilot Station (Yukon), and Tsiigehtchic (Mackenzie) (Table S1 of the Supporting Information, SI). Field sampling for the Arctic-GRO program occurred every two months at each river from 2012 to 2017, targeting alternate months in alternate years. Sampling occurred throughout the year, to capture variability in river discharge from low flow in the winter (November−April), higher flow in the spring (May−June), and intermediate flow during the summer (July−October). Sample collection and processing was identical across the six rivers. Bulk (unfiltered) water samples for total mercury (THg) were processed following ref 35. Briefly, samples were collected directly into 100 mL polyethylene terephthalate glycol (PETG) bottles from immediately below the surface at midchannel, using the clean hands-dirty hands technique, and stored chilled until analysis at the U.S. Geological Survey (USGS) Mercury Research Laboratory (Middleton, WI). THg was measured by cold vapor atomic fluorescence spectroscopy (Brooks Rand MERX-T) following U.S. Environmental Protection Agency Method 1631 and USGS Mercury Research Laboratory standard operating procedures for quality assurance and control (https://wi.water.usgs.gov/mercury-lab/quality.html). These procedures include the analysis of analytical blanks, sample replicates, and standard reference materials. THg concentrations for all samples measured above the detection limit (0.04 ng L^{-1}).

Ancillary Parameters. Samples for DOC and TSS concentrations were acquired on the same day as THg and following established Arctic-GRO protocols.[36] Surface water was collected from immediately below the surface from the midchannel and opposite sides of the river and composited for DOC, and collected from the midchannel only for TSS. DOC samples were filtered (0.45 μm) on the day of collection and stored frozen until analysis by Shimadzu TOC/TN Analyzer within one year at the Woods Hole Research Center using established protocols.[37] TSS was stored chilled until processing. Briefly, water was filtered through ashed (450 °C, 4 h) and preweighed 0.7 μm glass fiber filters, dried (60 °C, 24 h), and measured by gravimetric analysis following USGS Method I-3765.

Discharge Measurements and THg Flux Estimates. River discharge (Q) was obtained from the Federal Service for Hydrometeorology and Environmental Monitoring, Ministry of Natural Resources and Environment, Russian Federation (Roshydromet), the United States (USGS), and Canada (Water Survey of Canada).[38] Discharge data were obtained from the downstream-most monitoring stations on the Ob', Yukon, and Mackenzie rivers, and coincided with the water sampling locations at Salekhard, Pilot Station, and Tsiigetchic, respectively (Table S1). For the Yenisey, Lena, and Kolyma rivers, discharge data were obtained from the monitoring stations located closest to the water sampling locations, at Igarka, Kyusyur, and Kolymskoye, respectively. Prior to all data analyses, spatiotemporal offsets in sampling and discharge monitoring locations for the Yenisey, Lena, and Kolyma rivers were corrected following ref 24. Daily THg fluxes were modeled with measurements of THg and Q using LoadRunner software, which automates runs of the USGS constituent-load modeling software LOADEST.[39] LOADEST uses paired measurements of concentration and Q to build calibration regressions, which are applied to daily measurements of river Q to obtain daily constituent fluxes. Calibration regressions were derived using the Adjusted Maximum Likelihood Estimator (AMLE) and default model (Model = 0), to allow for automated model selection based on Akaike Information Criterion (AIC). We used the model with the lowest AIC and without variables for long-term change during the calibration period (Model 1, 2, 4, or 6). Models were nested within:

$$\ln \text{load} = a_0 + a_1 \ln Q + a_2 \ln Q^2 + a_3 \sin(2\pi \text{dtime}) + a_4 \cos(2\pi \text{dtime}) \quad (1)$$

where a_i is the i^{th} model coefficient; ln Q is the ln Q minus the center of ln$Q$; dtime is the decimal time minus the center of decimal time; Q was converted to ft^3 s^{-1}; and THg, DOC, and TSS flux = kg d^{-1}.[39] Total annual yields were obtained by

https://dx.doi.org/10.1021/acs.est.9b07145
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Table 1. Mean (Standard Deviation) of Annual and Seasonal Total Mercury (THg) Fluxes (kg y^{-1}) Modeled Using LOADEST and the Corresponding Yields (g km^{-2} y^{-1}) for the Six Major Arctic Rivers (2012−2017)

constituent	Ob'	Yenisey	Lena	Kolyma	Yukon	Mackenzie	sum	Pan-Arctic
fluxes[a]								
annual	2421 (647)	3642 (567)	6591 (406)	1107 (565)	3282 (425)	2610 (700)	19 652 (610)	37 079 (1529)
spring (May−June)	887 (174)	2204 (349)	3375 (309)	679 (394)	1143 (151)	1482 (559)	9769 (501)	18 432 (945)
summer (July−October)	1200 (449)	1090 (214)	2968 (451)	415 (190)	1981 (318)	997 (155)	8651 (463)	16 323 (874)
winter (November−April)	333 (82)	348 (36)	248 (32)	13 (4)	158 (2)	132 (10)	1232 (69)	2324 (131)
yields								
annual	0.8 (0.2)	1.5 (0.2)	2.7 (0.2)	2.1 (1.1)	4.0 (0.5)	1.6 (0.4)		

[a]Fluxes were extrapolated to the pan-Arctic following ref 24.

summing daily THg fluxes for each calendar year and standardizing to the respective watershed areas reported in ref 24. To evaluate THg seasonality, we calculated seasonal fluxes by summing daily THg fluxes from LOADEST for the spring, summer, and winter, following previous studies on large Arctic rivers.[24,40] LOADEST output diagnostics were inspected to evaluate model suitability and model coefficients and fits are provided in the SI (Table S2). For each river, we report annual and seasonal fluxes as means and the uncertainty as standard deviation for 2012−2017. For the six major Arctic rivers combined, we report the means and standard deviations of total annual and seasonal fluxes. We additionally report the mean daily fluxes on a monthly basis during the study period for each river with 95% confidence intervals, accounting for both the LOADEST model parameter uncertainty (standard error) and unexplained variability in the model (random error).[39] Our calculated Hg fluxes for the six major Arctic rivers—which span 53% of the pan-Arctic watershed, including the Yukon and Hudson Bay—were scaled up to the unsampled portion of the pan-Arctic following ref 24, assuming that export in the sampled and unsampled portions scale proportionally. To provide context for these results, we compare our estimates of THg yields in the six major Arctic rivers with a compilation of published riverine Hg yield values from diverse locations and environments.

To compare THg concentrations between rivers while controlling for the effects of flow on concentration in our temporally distributed measurements, we further calculated annual flow-weighted (FW) concentrations of THg for each river from daily observations of river flow and LOADEST-calculated THg following ref 41:

$$\text{FW concentration} = \sum (c \times t \times Q) / \sum (t \times Q) \quad (2)$$

where c, t, and Q are the concentration (ng L^{-1}), time window (daily), and flow (ft^3 s^{-1}) for each sample.

Statistical Analyses. To assess the capability of regression models to estimate riverine THg from parameters commonly associated with Hg (DOC, TSS, and Q) across diverse pan-Arctic catchments, we developed predictive models of Hg concentration and yield:

$$\text{THg} = a_0 + a_1\text{DOC} + a_2\text{TSS} + a_3Q \quad (3)$$

The concentration models used the direct measurements of DOC and TSS concentration and Q, while the yield models used DOC, TSS, and water yield (runoff). The multiple linear regressions were first trimmed using the *step* function in the R package *lmerTest*[42] to eliminate nonsignificant covariates. Variance Inflation Factors (VIF) were then used to identify collinear covariates (VIF > 3),[43] which were removed from the trimmed models. We used an analysis of variance (ANOVA) to compare flow-weighted THg concentrations between rivers. Model fits were inspected visually with residual plots and covariates were transformed as needed to meet assumptions of residual independence and homoscedasticity.[44] Throughout, we report the F statistic from ANOVA and from multiple linear regressions with the numerator and denominator degrees of freedom as $F_{df1,df2}$. All statistics were performed in the R programming environment,[45] and significance was interpreted at $\alpha = 0.05$.

RESULTS AND DISCUSSION

Annual Mercury Export from Arctic Great Rivers. Our coordinated, multiyear measurements of THg across the hydrograph for the six major Arctic rivers paired with LOADEST modeling establishes a rigorous baseline of annual and seasonal pan-Arctic riverine Hg export. From 2012 to 2017, mean annual THg flux from the six major Arctic rivers was 19 700 kg y^{-1} (Table 1). Scaled up to the pan-Arctic (following ref 24), our estimate of mean riverine THg flux (37 000 kg y^{-1}) is three times higher than some earlier estimates[16] and is consistent with more recent estimates[5,20] (Table S3). While not directly measured, THg flux via bed load sediment transport was likely minor, as bed loads are thought to comprise a relatively small proportion of sediment fluxes in Arctic rivers (<3%, e.g., refs 46,47). The good correspondence between our estimates of Arctic riverine THg flux and estimates from other recent studies (40 000 to 50 000 kg y^{-1})[5,20,22,48] shows that efforts to constrain the magnitude of Hg exported by rivers to the Arctic Ocean are converging toward similar values (Table S3). Together, these studies confirm Arctic riverine Hg as an important component of the Arctic Ocean Hg budget.[22] These estimates of riverine THg flux are comparable to Hg inputs from coastal erosion (30 000 to 47 000 kg y^{-1}) and ocean currents (i.e., Atlantic and Pacific Ocean inflows; 48 000 to 53 000 kg y^{-1}),[22,49] and equivalent to roughly half of atmosphere deposition directly to the ocean and via meltwater from sea ice and snow (76 000 to 108 000 kg y^{-1}).[22,48,49]

Seasonal and Regional Variability in Mercury. Flow-weighted annual concentration of THg (mean FW-THg = 5.6−14.9 ng L^{-1}) varied significantly between rivers (ANOVA: $F_{5,30} = 40.4$, $p < 0.001$) (Figure 1) and was highest in the Yukon and lowest in the Ob' and Yenisey (*posthoc* Tukey HSD) with the Lena, Kolyma and Mackenzie exhibiting intermediate values (Table 2). These results are consistent with previous measurements in the Yukon and Mackenzie rivers[17,19] and reveal notable variability in THg across the six major Arctic rivers, most of which have few measurements historically and/or samples which mainly reflect the spring and summer seasons.[15,17,19]

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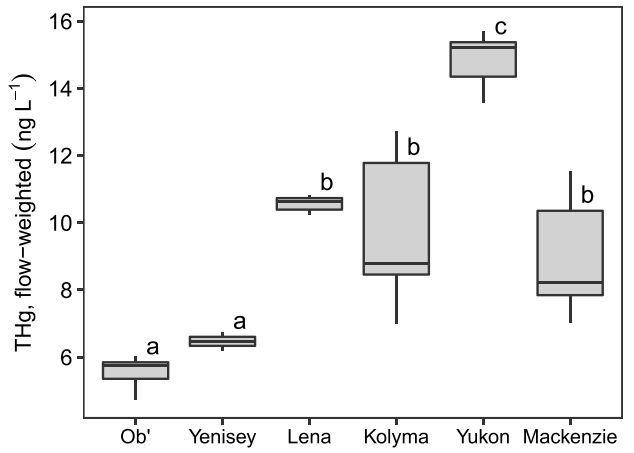

Figure 1. Annual flow-weighted concentrations (2012−2017) of total mercury (THg) by river. Boxes with different letters have significantly different flow-weighted Hg concentrations, determined by analysis of variance. Horizontal line within each box represents the median. Horizontal lines below and above the median represent the first and third quartiles, respectively. Lower and upper whiskers extend from the first or third quartile to the smallest or greatest value, respectively, to no more than 1.5 times the interquartile range. Outliers beyond this range are shown as individual points, where applicable.

The hydrology of high latitude northern rivers and thus fluvial transport of most chemical constituents is strongly seasonal.[24,50−52] For instance, biological uptake and dilution reduce summertime nitrate concentrations, while DOC fluxes are typically highest during spring freshet, when snowmelt and flushing of organic rich surface litter and soil layers intensify the hydrologic export of carbon.[24,51] Across rivers, there was significant seasonal variability in THg flow-weighted concentrations ($F_{2,105}$ = 93.9, p < 0.001) and fluxes ($F_{2,105}$ = 67.6, p < 0.001). Flow-weighted THg concentrations were significantly higher in the spring than in summer (FW-THg = 12.6 and 8.8 ng L^{-1}, respectively) (p < 0.001, Tukey HSD), and significantly lower in the winter than during the rest of the year (FW-THg = 3.3 ng L^{-1}) (p < 0.001, Tukey HSD) (Table 2). THg fluxes were significantly lower in winter (THg = 1200 kg) (p < 0.001, Tukey HSD), but not significantly different between spring (THg = 9800 kg) and summer (THg = 8700 kg) (Table 1), despite the fact that our spring period is only half the length of the four-month summer season. Thus, more than 90% of the annual THg flux occurred during half of the year (spring and summer) and in conjunction with the majority of Q (Figure 2). These seasonal trends (Figure 3, S1) suggest that riverine Hg transport to the Arctic Ocean is strongly coupled with hydrology and coincides with periods of greater marine primary production.[7]

To constrain annual Hg fluxes, previous studies in the Mackenzie and Yukon rivers sampled Hg at a relatively high temporal resolution (roughly biweekly) during the spring freshet and summertime falling limb, when flow is variable.[17,19] Our annual THg flux estimates for the Mackenzie River (2610 ± 700 kg y^{-1}, mean ± sd) (Table 1) correspond well with these previous estimates from 2007 to 2010 (2766 ± 647 kg y^{-1}),[19] while our estimates for the Yukon River (3282 ± 425) were lower than estimates from a decade earlier (4372 kg y^{-1}).[17] As Yukon River discharge did not change significantly over the 2001−2014 period,[12] this discrepancy may reflect changes in THg concentration over the intervening decade (2001−2005 versus 2012−2017) and/or variability captured via higher-resolution sampling by ref 17. The latter indicates that high-frequency sampling targeted around periods of variable discharge during the thaw season may help to constrain future estimates of riverine Hg flux.

To better understand the regional variability of Hg fluxes, we controlled for potential effects from Q by evaluating the relationship between annual THg yields (flux normalized to watershed area) and annual water yields (runoff). Annual THg yields in the six major Arctic rivers (range of means = 0.8−4.0 g km^{-2} y^{-1}) were in the lower range of values reported for large rivers in other regions of the world (Table S4). When comparing between rivers, annual THg yields varied significantly ($F_{5,30}$ = 24.6, p < 0.001; Table 1) and did not increase in equal proportion to runoff. THg yields per unit of runoff were considerably higher in the Mackenzie, Yukon, and Kolyma (Table S5, Figure 4), where greater TSS yields[50] are associated with surficial geology consisting of relatively more erodible material within loosely consolidated alluvium (Yukon, Mackenzie) and Quaternary sediments containing interstratified layers of ice (Kolyma).[53] Coupling between Hg and sediments is well documented[15,17,26] and reflected by the positive association between THg yields and TSS in the six major Arctic rivers (Table 3). These findings indicate that variability in the magnitude of soil Hg stores,[54] intensification of the Arctic hydrologic cycle,[9] and the degree to which Hg and sediments are mobilized from soils into fluvial networks[29] are likely to drive future trends in riverine Hg export to the Arctic Ocean.[55]

Utility of Regression Models for Estimating Riverine Mercury. The strong relationship between THg yields and runoff (above) and previously documented associations between Hg, TSS, and DOC in freshwaters[17,20,25] suggests that there is potential for estimating pan-Arctic riverine Hg from geochemical constituents that are analytically more straightforward and less expensive to measure than Hg, or which can be estimated indirectly (e.g., from remote sensing).[56,57] We developed multiple linear regression models for THg concentration and yield to better understand the suitability of Q, TSS, and DOC for predicting Hg in the six major Arctic rivers together (eq 3). While the regression model for THg concentration was significant ($F_{3,174}$ = 41.8, p < 0.001), it explained only a modest proportion of the variance

Table 2. Mean (Standard Deviation) of Annual and Seasonal Flow-Weighted Concentrations of Total Mercury (THg, ng L^{-1}) in the six major Arctic rivers (2012-2017)

season	Ob'	Yenisey	Lena	Kolyma	Yukon	Mackenzie
annual	5.6 (0.5)	6.5 (0.2)	10.6 (0.2)	9.7 (2.4)	14.9 (0.8)	9.0 (1.8)
spring (May−June)	6.5 (0.4)	8.3 (0.1)	13.1 (0.4)	13.8 (3.6)	17.9 (1.3)	15.8 (4.5)
summer (July−October)	5.8 (0.7)	6.3 (0.2)	9.6 (0.4)	6.9 (1.5)	16.4 (1.1)	7.5 (0.7)
winter (November−April)	3.6 (0.2)	2.8 (0.1)	4.4 (0.2)	2.5 (0.1)	4.3 (0.2)	2.1 (0.1)

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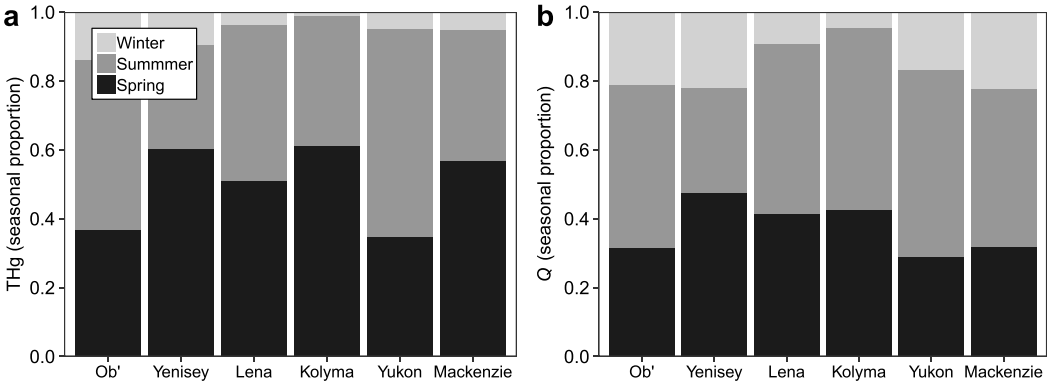

Figure 2. Mean proportions of (a) total mercury (THg) flux modeled using LOADEST and (b) discharge (Q) by season (2012−2017). Spring = May−June, summer = July−October, winter = November—April.

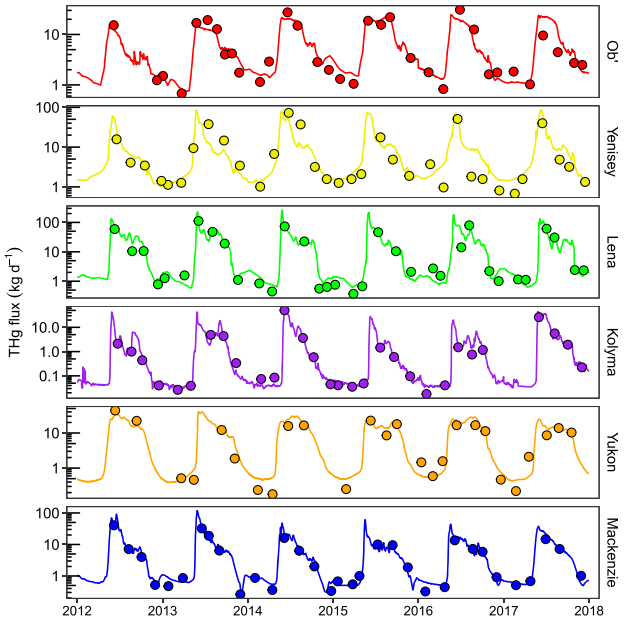

Figure 3. Fluxes of total mercury (THg) during the study period (points = measured, lines = modeled using LOADEST).

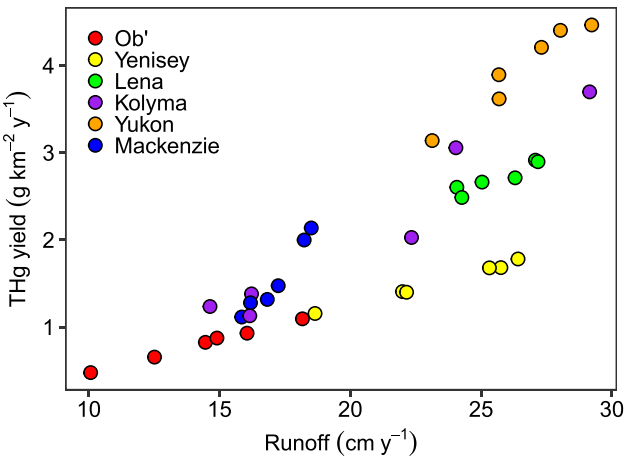

Figure 4. Relationship between annual yields of LOADEST-calculated total mercury (THg) (g km^{-2} y^{-1}) and annual runoff (cm y^{-1}). Regression statistics are presented in Table S5.

in fluvial THg (R^2 = 0.41) (Table 3). The relatively weak predictive power of the model and the variation in residuals (Figure S2) reveals that complexity underlying the relationship between these metrics and Hg makes it challenging to predict THg concentrations in the six major Arctic rivers. In comparison, the model of THg yields had strong predictive power ($F_{2,33}$ = 503, p < 0.001, R^2 = 0.97) (Table 3, Figure S3). Runoff and TSS yield were significant predictors of THg yield, demonstrating that regional variability in hydrology and TSS regimes are key controls on pan-Arctic riverine Hg export.

Implications for the Arctic Hg Cycle and Monitoring. Warming,[8] intensifying hydrologic regimes,[9] and changing anthropogenic Hg inputs in northern environments from industrial activity[49] will likely reshape the strong relationships that we observed between Hg yields, runoff, TSS, and DOC. In regions where permafrost thaw[30] is sufficiently intense to mobilize Hg from permafrost soils into aquatic networks, increasing fluvial Hg export[29] may strengthen linkages between the large Hg stores in permafrost[54] and aquatic and marine ecosystems. Changes in hydrology and nutrient cycling may alter the methylation capacity of freshwaters by creating environments favorable to MeHg production.[58] Estimates of pan-Arctic riverine total MeHg (TMeHg) flux remain scarce and variable (Table S3). Recent work estimated riverine TMeHg flux of 2500 kg y^{-1}, using an estimated THg flux of 50 000 kg y^{-1} and TMeHg:THg of 5%.[22] In comparison, ref 20 estimated a pan-Arctic THg flux of 44 000 kg y^{-1} and TMeHg flux of 800 kg y^{-1}, using relatively high estimates of dissolved MeHg yields in the Severnaya Dvina River to upscale TMeHg flux across the Eurasian basin. Constraining pan-Arctic riverine MeHg export and its fate in marine environments is a priority for resolving Hg uptake in northern foodwebs and ecosystems.[59]

While riverine DOC fluxes are increasing in some regions,[11] permafrost thaw may also deepen flow paths and increase DOC mineralization in soils[32] or promote DOC adsorption to thawed permafrost sediments.[60] Such effects, which are not captured in our models, are likely to change the interactions between Hg, DOC, TSS, and hydrology in the future. From a contaminants perspective, ample evidence suggests that freshwater ecosystems in the Eurasian Arctic are recovering from distant historical atmospheric Hg emissions and deposition.[27,28] In large major Russian rivers in recent decades, decreasing Hg concentrations in burbot (*Lota lota*) tissues are thought to reflect more recent historical declines in

https://dx.doi.org/10.1021/acs.est.9b07145
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Table 3. Summary of Models Predicting Observed Concentrations and LOADEST Yields of Total Mercury (THg)[a]

metric	model (see eq 3 for full model)	t_{df}	$F_{df1,df2}$	p	R^2
concentration	log THg = 0.00001Q + 0.214 log TSS + 0.0303DOC + 0.688		$41.8_{3,174}$	< 0.001	0.41
	DOC	1.7_{174}		0.09	
	TSS	7.8_{174}		< 0.001	
	Q	3.1_{174}		< 0.001	
yield	log THg = 0.082runoff + 0.169 log TSS − 2.682		$503_{2,33}$	< 0.001	0.97
	TSS	13.2_{33}		< 0.001	
	runoff	23.2_{33}		< 0.001	

[a]Metrics for individual covariates included beneath full model summaries. DOC = dissolved organic carbon, TSS = total suspended sediments, Q = discharge. log indicates data were natural log-transformed. df1 and df2 = numerator and denominator degrees of freedom (df), respectively.

atmospheric Hg from decreased industrial activity and also an offset in bioaccumulation from increasing growth rates driven by warming river temperatures.[27,28] In contrast, Hg in burbot is increasing in the Mackenzie River watershed,[27] where the weathering of sulfide minerals, erosion of coal deposits, and Hg release from thawing permafrost are among the primary sources of Hg in regional freshwaters.[26,29] At this time, it remains difficult to predict how these complex, interacting factors will reshape aquatic Hg cycling in northern environments.

While some riverine Hg may ultimately re-emit to the atmosphere,[20] its fate within marine ecosystems remains poorly constrained.[59,61] A small number of observations suggest that a substantial proportion of riverine Hg is deposited in coastal sediments via settling of particulate Hg and flocculation of Hg−DOC complexes upon entering saline environments.[3,18] Yet, in some regions (e.g., the Beaufort Sea), Hg in marine biota can exceed toxicity thresholds.[49,59,62] Constraining the drivers and fate of Arctic riverine Hg is a clear priority for understanding Hg cycling in marine ecosystems, which are an important natural resource for northern communities.[59] Together, the regional diversity in riverine Hg sources and drivers suggest a nonuniform response of the Arctic Hg cycle to future environmental change, which cannot be constrained by models alone.

Our estimates set a robust contemporary baseline of riverine THg export from the six major Arctic rivers and our models predicted THg yields with high fidelity. As this work demonstrates, coordinated river chemistry and discharge measurements show promise for enabling future studies to develop models to assess changes in Hg export using Q, TSS, and DOC.[20,62] The utility of these parameters for reliably extrapolating Hg concentrations across the pan-Arctic in the future will depend on the degree to which environmental change continues to reshape northern carbon and Hg cycles. Continuing to make direct and frequent measurements of Hg in Arctic rivers is thus critical for establishing long-term trends and resolving the effects of changing northern environments on the Arctic Hg cycle.[27−29,54]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.9b07145.

Table S1, Document containing locations of water sampling and discharge monitoring stations; Table S2, models and coefficients from LOADEST; Table S3, compilation of flux values reported in the literature for total mercury and total methylmercury; Table S4, compilation of annual total mercury yields reported in the literature; Table S5, slopes, confidence intervals, and adjusted R^2 values from the linear regressions between yields of total mercury and runoff; Figure S1, LOADEST estimates of mean daily total mercury flux with 95% confidence intervals for each month during the study period; Figure S2, the relationship between measured and predicted concentrations of total mercury, and the residuals of the predictive models; and Figure S3, the relationships between LOADEST-calculated and predicted yields of total mercury, and the residuals of the predictive models (PDF)

Raw data for measurements of total mercury, dissolved organic carbon, total suspended sediments, and discharge made in the field and modeled by LOADEST (XLSX)

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https://dx.doi.org/10.1021/acs.est.9b07145
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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Mikhail Suslov, Martin Kelly, community members from Tsiigehtchic, the Gwichya Gwich'in RRC, the Aurora Research Institute, and the many other field scientists and collaborators for their assistance in collecting samples. We acknowledge support for the Arctic Great Rivers Observatory from the National Science Foundation (grants 1602615, 1602680, 1603149, and 1602879) and the USGS Toxic Substances Hydrology Program. The processing of discharge data for Russian Arctic rivers was partly supported by the Russian Foundation for Basic Research (grant 18-05-60192). All data are available in the manuscript text or in the Arctic-GRO database online (https://arcticgreatrivers.org/data/). Any use of trade, product, or firm names in this publication is for descriptive purposes only and does not imply endorsement by the U.S. Government.

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https://dx.doi.org/10.1021/acs.est.9b07145
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Supporting Information:

Mercury Export from Arctic Great Rivers

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Number of pages: 12

Number of figures: 3

Number of tables: 5

Table S1. Locations of water sampling and discharge monitoring stations. "–" indicates that discharge monitoring station and water sampling locations are identical. Latitude and longitude are provided in decimal degrees.

	Water chemistry			Discharge				
River	Sampling location	Lat (DD)	Long (DD)	Monitoring station	Station ID	Lat (DD)	Long (DD)	Data source*
Ob'	Salehard	66.63	66.60	–	11808	–	–	Roshydromet
Yenisey	Dudinka	69.38	86.15	Igarka	9803	67.43	86.48	Roshydromet
Lena	Zhigansk	66.77	127.37	Kyusyur	3821	70.68	127.39	Roshydromet
Kolyma	Cherskiy	68.75	161.30	Kolymskoye / Kolymsk-1	1802 / 1803	68.73	158.72	Roshydromet
Yukon	Pilot Station	61.93	-162.88	–	15565447	–	–	USGS
Mackenzie	Tsiigehtchic	67.45	-133.74	–	10LC014	–	–	WSC

*Roshydromet = Federal Service for Hydrometeorology and Environmental Monitoring, Ministry of Natural Resources and Environment, Russian Federation; USGS = United States Geological Survey; WSC = Water Survey of Canada.

Table S2. Models and coefficients from LOADEST. The standard deviation of model coefficients is included in parentheses. Models were nested within: ln Load = $a_0 + a_1 \ln Q + a_2 \ln Q^2 + a_3 \sin(2\pi dtime) + a_4 \cos(2\pi dtime)$. THg = total mercury. Q and $dtime$ are centered estimates as described in the main text; THg, DOC, TSS flux = kg d^{-1}.

River	Constituent	Model	R^2	a0	a1	a2	a3	a4
Ob'	THg	1	87.0	15.3243 (0.074)	1.3797 (0.0942)	–	–	–
Ob'	DOC	2	95.6	16.1921 (0.071)	1.3461 (0.0529)	-0.1333 (0.0929)	–	–
Ob'	TSS	1	72.0	16.2913 (0.1294)	1.4891 (0.1641)	–	–	–
Yenisey	THg	4	77.2	15.6931 (0.1656)	1.1374 (0.2558)	–	0.5441 (0.2342)	-0.2702 (0.1875)
Yenisey	DOC	4	96.0	16.1053 (0.0581)	1.5416 (0.0892)	–	-0.0978 (0.0816)	-0.1377 (0.0658)
Yenisey	TSS	4	67.3	15.4744 (0.2097)	2.0433 (0.3221)	–	-0.8896 (0.2947)	-0.0167 (0.2375)
Lena	THg	1	92.2	15.6651 (0.0906)	1.369 (0.0705)	–	–	–
Lena	DOC	4	96.2	15.9728 (0.0615)	1.3996 (0.0925)	–	-0.4085 (0.16)	0.2913 (0.0997)
Lena	TSS	4	93.7	15.7618 (0.1342)	1.8269 (0.2022)	–	0.5206 (0.2855)	0.0675 (0.289)
Kolyma	THg	2	96.9	12.5921 (0.1164)	1.2984 (0.0455)	0.1369 (0.0351)	–	–
Kolyma	DOC	4	99.1	13.0588 (0.0374)	1.2924 (0.0408)	–	-0.1155 (0.066)	0.2926 (0.0853)
Kolyma	TSS	6	93.8	11.2833 (0.4133)	1.0396 (0.256)	0.6069 (0.1346)	-0.3582 (0.3198)	-1.5895 (0.5656)
Yukon	THg	4	90.0	14.7739 (0.1219)	1.3453 (0.2711)	–	0.6012 (0.2524)	-0.2637 (0.3158)
Yukon	DOC	1	97.3	14.2849 (0.0424)	1.3847 (0.0432)	–	–	–
Yukon	TSS	4	87.7	16.7491 (0.1676)	1.144 (0.3842)	–	0.0246 (0.2999)	-1.5304 (0.4812)
Mackenzie	THg	2	95.5	14.6424 (0.1203)	2.1374 (0.085)	0.3264 (0.2158)	–	–
Mackenzie	DOC	2	96.2	14.756 (0.0558)	1.1883 (0.0423)	0.3506 (0.092)	–	–
Mackenzie	TSS	1	89.3	16.7894 (0.1412)	3.235 (0.1979)	–	–	–

Table S3. Compilation of flux values (kg y^{-1}) reported in the literature for total mercury (THg) and total methylmercury (TMeHg).

Parameter	Year	Ob'	Yenisey	Lena	Kolyma	Yukon	Mackenzie	Sum	pan-Arctic	Reference
THg	2017	2614	4030	6042	1960	2605	2477	19727	37220	This study
	2016	2467	3359	7038	599	3706	2213	19381	36569	This study
	2015	3273	4036	6326	655	3002	1874	19166	36163	This study
	2014	2781	4274	6470	1620	3493	2148	20786	39219	This study
	2013	1961	3376	7081	1075	3232	3590	20313	38327	This study
	2012	1429	2774	6589	732	3654	3358	18536	34974	This study
	2012-2016	3051	5826	4891	952	–	2207	–	44000	1
	2004-2014	–	–	–	–	–	–	–	50000	2
	Various*	–	–	–	–	–	–	–	46136	3
	2005-2009	–	–	–	–	–	–	–	50200	4
	Various (see reference)	–	–	–	–	–	–	–	15044	5
	2010	–	–	–	–	–	1858	–	–	6
	2009	–	–	–	–	–	3382	–	–	6
	2008	–	–	–	–	–	2847	–	–	6
	2007	–	–	–	–	–	2976	–	–	6
	~2008	–	–	–	–	–	–	–	80000	7
	2001-2005	–	–	–	–	4372	–	–	–	8
	2004	–	–	–	–	–	1208	–	–	9
	Various**	–	–	–	–	–	–	–	12485	10
	2005	–	–	–	–	–	2400	–	–	11
	2004	–	–	–	–	–	1200	–	–	11
	2003	–	–	–	–	–	2900	–	–	11
	1991/1993	1350	720	4050	–	–	–	–	–	12
TMeHg	2012-2016	108	109	105	27	–	72	–	800	1
	2004-2014	–	–	–	–	–	–	–	2500	2
	2010	–	–	–	–	–	13	–	–	6
	2009	–	–	–	–	–	20	–	–	6

2008	–	–	–	–	–	18	–	–	6
2007	–	–	–	–	–	18	–	–	6
2004	–	–	–	–	–	8	–	–	9
2004	–	–	–	–	–	7	–	–	11
2003	–	–	–	–	–	22	–	–	11

*Based on fluxes from ref 5.

**Scaled to pan-Arctic using data from refs 11 and 12.

Table S4. Compilation of annual total mercury (THg) yields reported in the literature. Yields and errors for this study are reported in Table 1 in the main text. THg concentrations from the literature were converted to fluxes in kg y^{-1}, as required, and normalized by watershed area to obtain yields.

River	Region	Country	Flux (kg y^{-1})	Watershed area (km^2)	Yield (g km^{-2} y^{-1})	Reference
Ob'	Arctic	Russia	2421	3.0×10^6	0.8	This study
Yenisey	Arctic	Russia	3642	2.4×10^6	1.5	This study
Lena	Arctic	Russia	6591	2.4×10^6	2.7	This study
Kolyma	Arctic	Russia	1107	5.3×10^5	2.1	This study
Yukon	Arctic	USA	3282	8.3×10^5	4.0	This study
Mackenzie	Arctic	Canada	2610	1.7×10^6	1.6	This study
St. Lawrence	North Atlantic	Canada	1189	1.3×10^6	0.9	8
Hudson	North Atlantic	USA	188	4.2×10^4	4.5	13
Mississippi	South Atlantic	USA	2117	3.2×10^6	0.7	8
Songhua	North Pacific	China	1674	5.5×10^5	3.1	14
Pearl	Pacific	China	5717	4.5×10^5	12.7	15
Mekong	Pacific	Vietnam	3913	7.5×10^5	5.2	16
Rhone	Mediterranean	France	319	9.5×10^4	3.4	17,18
Nile	Mediterranean	Africa	241	3.1×10^6	0.1	17,18

Rhone watershed area from ref 19; Nile watershed area from ref 20.

Table S5. Slopes, confidence intervals (CI, ±95%), and adjusted R^2 values from the linear regressions between yields of total mercury (THg) and runoff. For all, $p < 0.01$. Data are presented in Figure 4. THg values were log-transformed for the model containing data for all six of the rivers. Sediment yield data from ref 21.

River	Slope	95% CI	Adjusted R^2	Sediment yield (t km^{-2} y^{-1})
Ob'	0.08	0.005	0.995	6.4
Yenisey	0.08	0.006	0.992	1.9
Lena	0.11	0.042	0.846	8.5
Kolyma	0.18	0.045	0.925	19
Yukon	0.23	0.053	0.935	72
Mackenzie	0.38	0.085	0.938	74
All	0.10	0.016	0.795	–

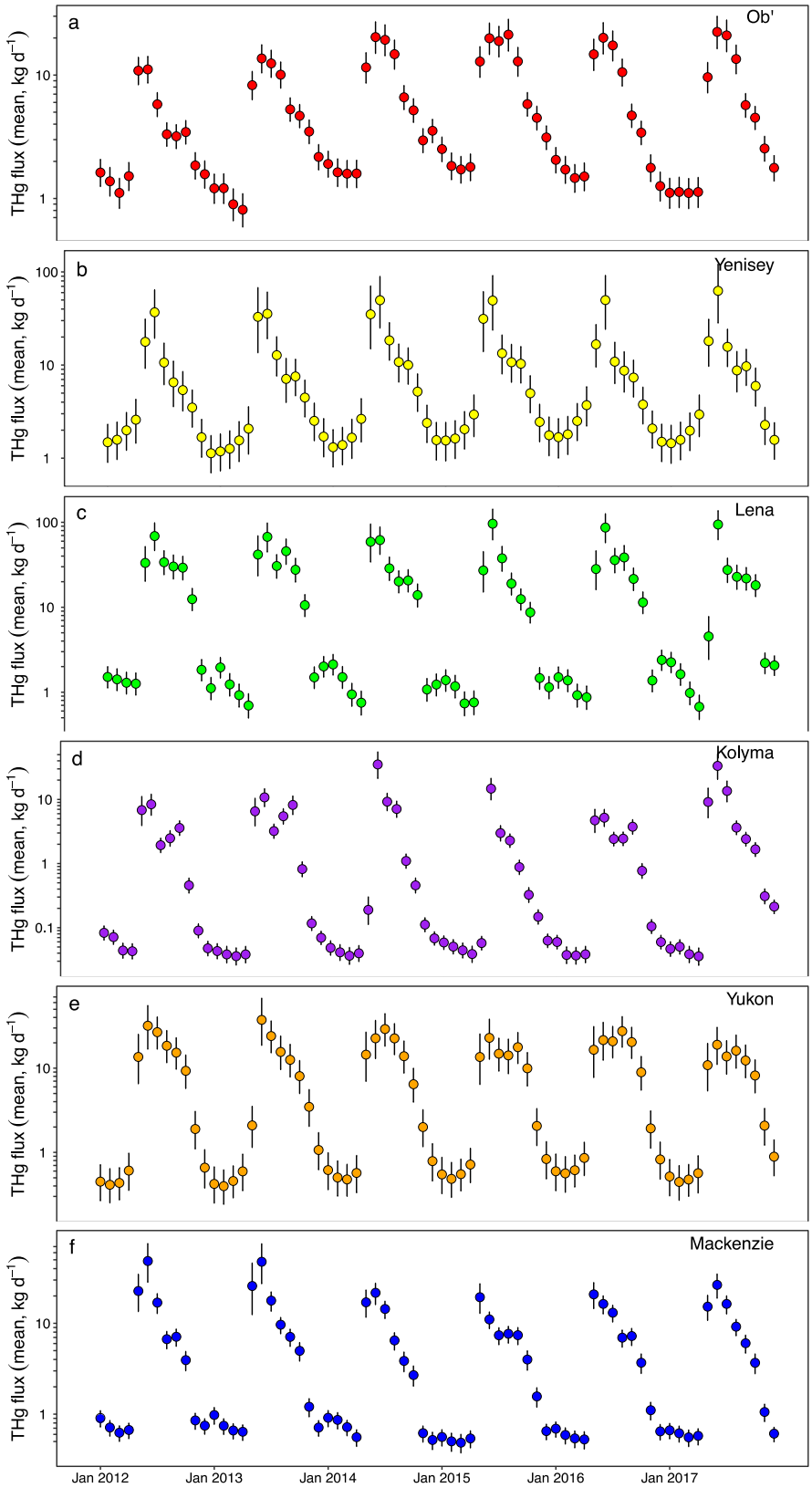

Figure S1. LOADEST estimates of mean daily THg flux (kg d^{-1}) with 95% confidence intervals for each month during the study period (2012–2017).

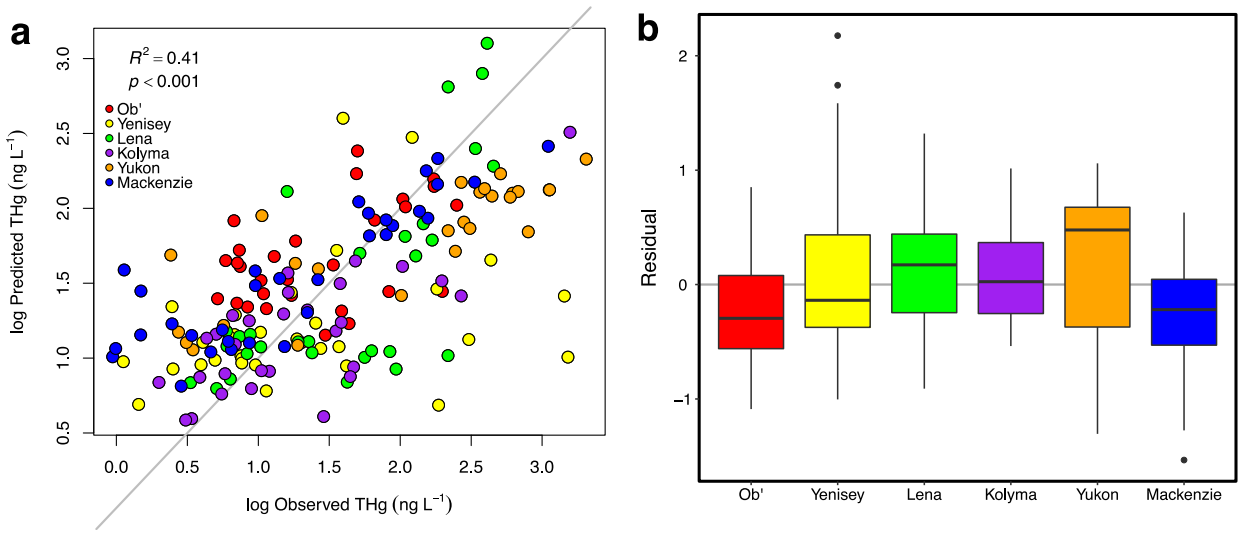

Figure S2. (a) The relationship between measured and predicted concentrations of total mercury (THg) (ng L^{-1}). (b) The residuals of the predictive models. Horizontal line within each box represents the median. Horizontal lines below and above the median represent the first and third quartiles, respectively. Lower and upper whiskers extend from the first or third quartile to the smallest or greatest value, respectively, to no more than 1.5 times the interquartile range. Outliers beyond this range are shown as individual points, where applicable.

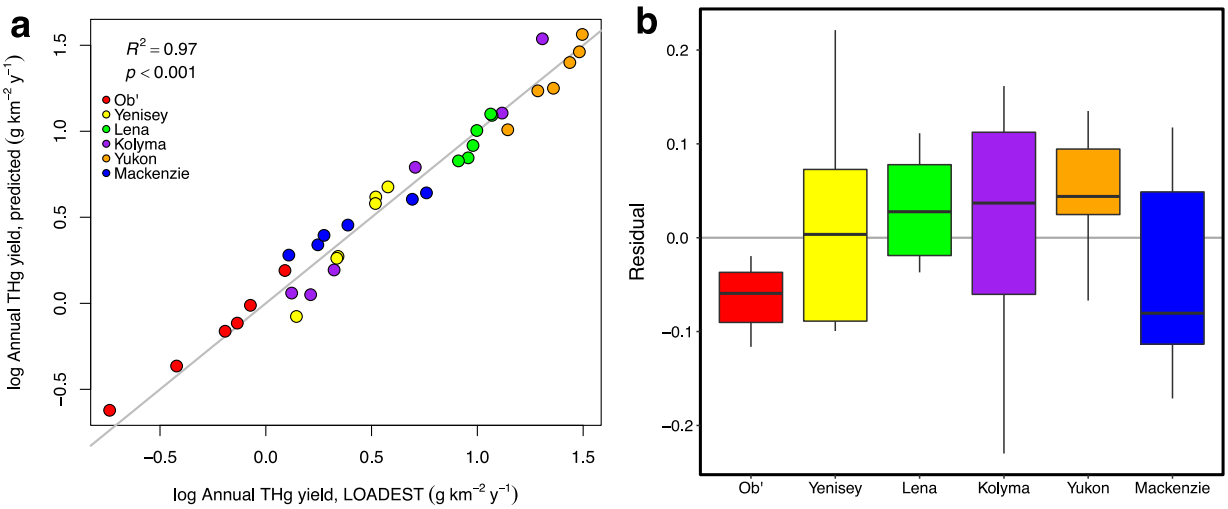

Figure S3. (a) The relationships between LOADEST-calculated and predicted yields of total mercury (THg) (g km^{-2} y^{-1}). (b) The residuals of the predictive models. Horizontal line within each box represents the median. Horizontal lines below and above the median represent the first and third quartiles, respectively. Lower and upper whiskers extend from the first or third quartile to the smallest or greatest value, respectively, to no more than 1.5 times the interquartile range. Outliers beyond this range are shown as individual points, where applicable.

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