

## Landscape controls on total and methyl Hg in the upper Hudson River basin, New York, USA

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[1] Approaches are needed to better predict spatial variation in riverine Hg concentrations across heterogeneous landscapes that include mountains, wetlands, and open waters. We applied multivariate linear regression to determine the landscape factors and chemical variables that best account for the spatial variation of total Hg (THg) and methyl Hg (MeHg) concentrations in 27 sub-basins across the 493 km<sup>2</sup> upper Hudson River basin in the Adirondack Mountains of New York. THg concentrations varied by sixfold, and those of MeHg by 40-fold in synoptic samples collected at low-to-moderate flow, during spring and summer of 2006 and 2008. Bivariate linear regression relations of THg and MeHg concentrations with either percent wetland area or DOC concentrations were significant but could account for only about 1/3 of the variation in these Hg forms in summer. In contrast, multivariate linear regression relations that included metrics of (1) hydrogeomorphology, (2) riparian/wetland area, and (3) open water, explained about 66% to >90% of spatial variation in each Hg form in spring and summer samples. These metrics reflect the influence of basin morphometry and riparian soils on Hg source and transport, and the role of open water as a Hg sink. Multivariate models based solely on these landscape metrics generally accounted for as much or more of the variation in Hg concentrations than models based on chemical and physical metrics, and show great promise for identifying waters with expected high Hg concentrations in the Adirondack region and similar glaciated riverine ecosystems.

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### 1. Introduction

[2] Elevated mercury (Hg) concentrations in fresh water fish are ubiquitous in North America and globally, and are of concern because of potential neurological effects in humans that can result from high exposures to methylmercury (MeHg) [Selin, 2009]. In the U.S., for example, all 50 states have issued fish consumption advisories for one or more surface fresh water bodies, and many states have issued blanket advisories for all surface waters within a given state or region [U.S. Environmental Protection Agency (U.S. EPA), 2009]. Additionally, high levels of Hg in tissue and blood are associated with neurological impairment and weakened reproductive success in numerous bird, mammal,

and amphibian species, and these effects may extend down to mid-trophic levels in some aquatic and terrestrial ecosystems [Scheuhammer *et al.*, 2007]. Atmospheric deposition is believed to be the principal source of Hg to most aquatic ecosystems, and a broad relation between Hg deposition loads and concentrations in fish has been identified across the U.S. [Hammerschmidt and Fitzgerald, 2006], with some exceptions in areas with large point sources such as heavily mined regions, and near industrial/urban emissions sources [Waldron *et al.*, 2000; Evers *et al.*, 2007]. Within given regions with similar atmospheric Hg deposition levels, however, wide spatial variation in Hg concentrations in waters and biota is common, and investigations have revealed a host of local factors such as wetland area, vegetation cover, food web structure, and others that promote spatial variation [Wiener *et al.*, 2006; Driscoll *et al.*, 2007; Evers *et al.*, 2007]. MeHg in particular is the focus of much attention because this form bioaccumulates and biomagnifies in food webs and is the source of neurotoxicological effects; therefore, the factors that control MeHg formation, transport, and uptake are of greatest interest and concern.

[3] Because of the dual problems of widespread Hg contamination of remote aquatic ecosystems and the large range in MeHg concentrations among waters and biota that receive

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similar Hg deposition, a need exists for spatial modeling approaches that can identify Hg “hot spots” in landscapes and help focus sampling, remediation, and health risk assessments where they are most needed. While food web trophic structure plays an important role in controlling Hg levels observed in top predators, past studies [Sorensen *et al.*, 1990] as well as recent work [Simonin *et al.*, 2008; Chasar *et al.*, 2009] has shown that Hg concentrations in biota are commonly strongly correlated to MeHg or total Hg (THg) concentrations in resident water bodies, suggesting that assessments of Hg concentrations in surface waters may indicate expected levels in local biota. However, there are exceptions to this generalization, most commonly related to the factors that control trophic transfer in aquatic food webs [Driscoll *et al.*, 2007].

[4] Research over the past three decades has resulted in improved understanding of the transport of atmospherically deposited Hg to surface waters, and the processes and factors that control its speciation (ionic, elemental, methyl), physical partitioning (dissolved, particulate), and fate (volatile loss, sedimentation, fluvial export, and bioaccumulation to apical predators). Landscape factors such as the presence and extent of wetlands, the extent of forest cover, aspects of catchment geomorphology, and land use are often strongly correlated with THg and MeHg concentrations in surface waters [St. Louis *et al.*, 1996; Grigal, 2002; Munthe *et al.*, 2007]. In contrast, the presence and size of open water bodies, steepness of slopes, and aquatic productivity are often inversely correlated with Hg concentrations, particularly MeHg [St. Louis *et al.*, 1994; Pickhardt *et al.*, 2002].

[5] Much past research has focused on studying Hg behavior and transport in lakes [Sorensen *et al.*, 1990; Bodaly *et al.*, 1993; Driscoll *et al.*, 1995], with less effort focused on Hg behavior in riverine ecosystems [Brigham *et al.*, 2009]. The factors that affect Hg concentrations in rivers and lakes show some similarities such as the pivotal role of wetlands [Driscoll *et al.*, 1995; Wiener *et al.*, 2006; Brigham *et al.*, 2009], but also some differences that reflect the greater role of direct deposition, interactions with bottom sediment, and potential for various loss processes in lakes [Shanley *et al.*, 2005]. Although lake and river watersheds are often studied separately, many river basins consist of linked networks of lakes and ponds, most commonly of small to medium size (surface area <50 km<sup>2</sup>); these networks are common globally, particularly in glaciated regions between 40° and 70°N [Lehner and Döll, 2004]. Man-made impoundments occur commonly in river networks, and evidence indicates that this category of open water generally acts as a source rather than a sink for MeHg, and that function may change with age [Montgomery *et al.*, 2000]. Despite the widespread geographic distribution of linked river-lake networks and their importance in modeling the behavior of other solutes such as nitrogen [Wollheim *et al.*, 2008], little research has focused on modeling Hg transport in these linked networks over moderate to large spatial scales.

[6] The various forms of Hg present in surface waters often show different behavior and controls. Hg associated with particulate transport is generally responsive to factors such as land disturbance that increases erosion and suspended sediment loads [Balogh *et al.*, 1998]. In forested landscapes with minimal human land use, however, Hg is

generally dominated by dissolved and filter-passing forms (defined herein as filtered), which are associated with dissolved organic matter [Babiarz *et al.*, 2003; Brigham *et al.*, 2009]. Filtered THg and MeHg are often strongly positively correlated within regions resulting from common mobilization factors such as dissolved organic carbon (DOC) concentrations, but divergent behavior has been observed as well, resulting from divergent mobilization factors such as the association of MeHg but not THg with microbial sulfate reduction [Kelly *et al.*, 1995]. This observation of varying behavior of MeHg and THg provides justification for efforts to model the mobilization of these two Hg forms separately, and a benefit from comparing differences and similarities in results. Non-methyl forms of Hg are worthy of separate attention because of the potential for methylation downstream as well as some uptake of non-methylated Hg in lower life forms such as algae [Mason *et al.*, 1996].

[7] Multivariate approaches have been applied in several previous investigations to model spatial variations in Hg concentrations in surface waters across small catchment, large basin, and regional landscape scales [Sorensen *et al.*, 1990; Hurley *et al.*, 1995; Yin and Balogh, 2002; Roué-LeGall *et al.*, 2005; Shanley *et al.*, 2005; Simonin *et al.*, 2008]. Most of these types of investigations have focused on lakes, and many have also included measurements of Hg in aquatic biota, soils, and atmospheric deposition. Among landscape factors, wetland area, is typically the strongest correlate of THg and MeHg concentrations and loads, presumably because wetlands are a major source of DOC to surface waters, and DOC is the dominant Hg binding and transport agent in most natural waters. Other biogeochemical factors such as the presence of anoxic soils where sulfate (SO<sub>4</sub><sup>2-</sup>) and iron (Fe) reduction may occur, favor MeHg formation, and physical factors such as the proximity of wetlands to surface waters and shallow flow paths favor the transport of MeHg and THg to adjacent waters [Krabbenhoft *et al.*, 1995; Bishop and Lee, 1997]. Many studies of the landscape measures that most greatly affect Hg concentrations and loads in surface waters have identified important secondary factors that include forested land cover [Sorensen *et al.*, 1990; Hurley *et al.*, 1995], land use and/or disturbance history [Hurley *et al.*, 1995; Yin and Balogh, 2002; Porvari *et al.*, 2003], open water [Sorensen *et al.*, 1990; St. Louis *et al.*, 1994], drainage area [Grigal, 2002], and basin slope [Dennis *et al.*, 2005]. Other studies have focused on the relationship of Hg to related solutes, with DOC/TOC generally the constituent that is most strongly related to Hg concentrations [Yin and Balogh, 2002; Grigal, 2002; Dennis *et al.*, 2005; Wiener *et al.*, 2006]. Additional constituents that are commonly related to Hg concentrations across regions include pH [Wiener *et al.*, 2006; Simonin *et al.*, 2008] and SO<sub>4</sub><sup>2-</sup> [Wiener *et al.*, 2006]. DOC is often assumed to be a surrogate for the combined effects of wetland area and connectivity [Dennis *et al.*, 2005; Wiener *et al.*, 2006], and recently DOC concentrations (or related absorbance properties) have been used as a direct surrogate for Hg [Dittman *et al.*, 2009], although DOC-Hg concentrations are only weakly related in some surface waters [Schelker *et al.*, 2011].

[8] The Adirondack Mountains of New York have been deemed a “hot spot” for Hg based on high levels found in

fish and in piscivorous birds such as the common loon (*Gavia immer*) in this region [Evers et al., 2007]. Several of the factors discussed above are likely to promote high rates of Hg mobilization, methylation, and bioaccumulation in the Adirondacks including abundant wetlands, predominantly forested land cover, low pH waters, and a location downwind from the concentration of coal-fired power plants in the Ohio River valley [Driscoll et al., 1994; Simonin et al., 2008]. The upper Hudson River basin in the central Adirondacks is of concern because high MeHg concentrations have been measured in streams, lakes, and aquatic biota within this basin [Selvendiran et al., 2008; Bradley et al., 2011; Riva-Murray et al., 2011]. Additionally, high Hg concentrations have been reported in sediment, fish, and the angling community downstream in the lower Hudson River basin, and atmospherically deposited Hg transported from upstream sources is a major contributor to Hg contamination in the Hudson Estuary [Gobeille et al., 2006; Balcom et al., 2008].

[9] In this study, we use landscape, hydrologic, and chemical metrics to develop empirical multivariate linear regression models of THg and MeHg concentrations in the upper Hudson River basin of New York based on synoptic surface water samples collected in 2006 and 2008. Here, we emphasize the role of landscape measures that have not often been applied in previous studies as controls on THg and MeHg concentrations, and work across basin scales from <1 km<sup>2</sup> to about 500 km<sup>2</sup> to better identify the factors that promote Hg source and sink behavior.

## 2. Study Area

[10] The upper Hudson River basin is defined here as the 492.8 km<sup>2</sup> basin upstream of the USGS gage near Newcomb, NY (Figure 1). The basin is generally underlain by metamorphic bedrock of middle Proterozoic age [Chiarenzelli and McLelland, 1993]. Elevations range from 424 m at the stream gage to 1624 m on Mt. Marcy, the highest summit in NY State. Median slope is 15.9%. Mountainous uplands dominate the northern part of the basin and near most divides, and valley bottoms are nearly flat and often overlain by wetlands. Surface deposits consist of sandy or rocky till in upland areas and outwash and alluvium in floodplains, with peat deposits intermixed and overlying sand and loam [Schelker et al., 2011]. The basin consists of 6.7% wetland area; forested evergreen and broad-leaved deciduous scrub/shrub are the two most common wetland types in the basin [LaPoint et al., 2004]. Schelker et al. [2011] demonstrated that 2/3 of the wetland area in a western sub-basin of the upper Hudson is within the riparian area, indicating that wetlands contiguous to stream channels are dominant in the basin. About 3.6% of the basin is open water (excluding wetland area), and 325 distinct open water bodies are delineated in the 1:24,000 National Hydrography Data set [<http://nhd.usgs.gov/data.html>; accessed 10/24/11], of which Catlin Lake (2.61 km<sup>2</sup> surface area) is the largest. The basin is largely forested (92%) [1992 National Land Cover Data set; <http://landcover.usgs.gov/natlndcover.php>; accessed 10/24/11], with <1% developed land. The basin is in the southernmost part of the Eastern forest – boreal transition ecoregion [Olson et al., 2001], and is dominated by northern hardwood forest (*Acer saccharum*, *Fagus grandifolia*, *Betula*

*alleghaniensis*) below 1000 m and spruce-fir (*Picea rubens*, *Abies balsamea*) at higher elevations and in wet areas adjacent to surface waters.

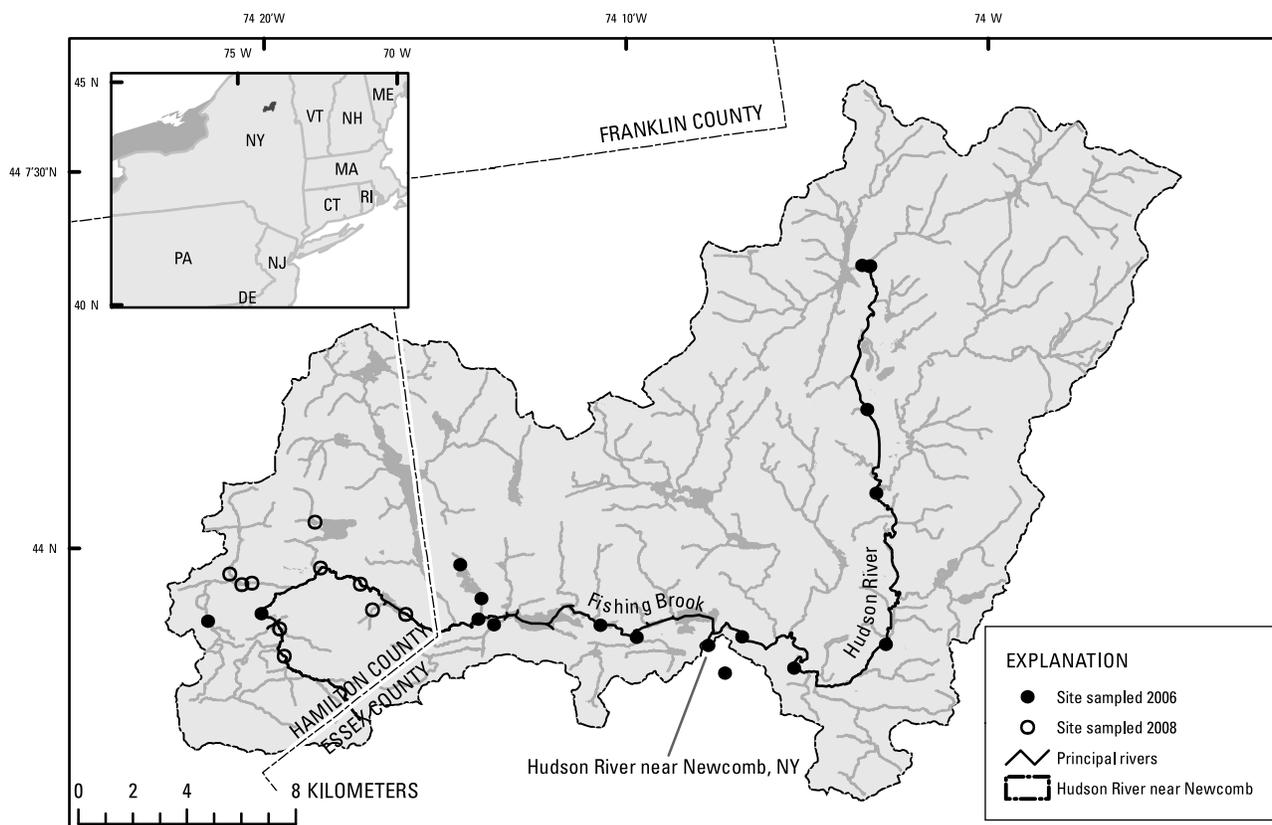
## 3. Methods

[11] Data from 27 surface water sampling sites are presented in this paper (Figure 1); however, only 25 of these sites were sampled during each of the seasons. These sites were sampled in spring and summer of 2006 and 2008, and were chosen to represent a range of landscape conditions and basin areas as well as easy accessibility from nearby roadways. These sites were generally sampled during low-to-moderate and relatively stable flow conditions over two to four day periods; thus concentration patterns are assumed to represent quasi steady state patterns. Eighteen sites were sampled in 2006 and nine in 2008, but in 2006 two of the sites were not sampled during each of the seasons. The resulting spring and summer data sets represent 23 coincident sites, and two unique sites in each of the seasons. Sampled catchments ranged from small, headwater catchments with no open water or wetlands, to catchments with open water >10% of drainage area, to catchments with wetland area >10% of drainage area. Median drainage area of the catchments sampled is 21.4 km<sup>2</sup> (range 0.4–492.8), and median percent open water area and wetland area are 2.1% (range 0–14.1) and 6.1% (range 0–13.8) of drainage area, respectively.

### 3.1. Field Sampling and Processing

[12] Most stream sites were sampled by wading into the mid-point of flow and filling several bottles. A few sites were too deep for wading and were sampled either from the mid-point of a bridge (if available) or by sampling from the stream bank. Each bottle was rinsed three times with stream water before filling. A trace metal sampling technique similar to EPA Method 1669 [U.S. EPA, 1996] was used for Hg samples that employed wrist-length nitrile gloves over shoulder-length polyethylene gloves. Samples collected during 2006 were not filtered, and THg and MeHg concentrations reflect a whole water analysis. Samples collected during 2008 were filtered at a field laboratory through 0.7- $\mu$ m nominal pore size, prebaked (550°C) quartz-fiber filters, acidified to approximately 1% with hydrochloric acid, and stored in the dark until analysis. The quartz fiber filters were placed on dry ice and stored frozen until analysis. All analyses reported in this paper are for total Hg and total MeHg concentrations; however, the data from the 2006 samples originated from a whole water analysis that included dissolved and suspended Hg, whereas the data from the 2008 samples originated by summing the filtered and particulate fractions obtained by separate analyses.

[13] In situ measurements of pH, water temperature, and air temperature were performed at the time of sampling with a portable system (Hydrolab Surveyor with MS-5 Sonde; note brand names here and throughout the text are provided for identification purposes only and do not imply endorsement) that was calibrated daily. Streamflow was measured by wading with a current meter according to standard USGS practices [Rantz et al., 1982]. Water samples were immediately placed on ice and transported to a field lab for processing. Samples for DOC and Abs<sub>254</sub> were pressure-filtered



**Figure 1.** Map of the upper Hudson River basin as defined by the gage near Newcomb, NY with the Hudson River and Fishing Brook shown with darker lines. The 27 surface water sampling sites discussed in this paper are shown as dots. The largest lakes and ponds in the basin are shown in dark gray shading.

through baked glass fiber  $0.7 \mu\text{m}$  filters and stored at  $4^\circ\text{C}$  until analysis. Samples for Fe analysis were filtered through  $0.45 \mu\text{m}$  membrane filters and stored at  $4^\circ\text{C}$  until analysis.

### 3.2. Laboratory Analysis

[14] Mercury analyses were performed at the USGS Wisconsin Mercury Research Laboratory. All samples with visible color were first treated by exposure to ultraviolet radiation until the color disappeared. These samples were later treated with  $\text{BrCl}$  at  $50^\circ\text{C}$  to insure complete oxidation and conversion of all Hg forms to  $\text{Hg}^{2+}$ . THg was determined by cold vapor atomic fluorescence spectrometry (CVAFS) according to the method described by *Olson and DeWild* [1999], which is a slight modification of EPA Method 1631 [U.S. EPA, 2002]. MeHg was determined after distillation by ethylation, gas chromatographic separation, pyrolysis, and CVAFS as described by *DeWild et al.* [2002], which is a slight modification of EPA Method 1630 [U.S. EPA, 2001]. The method detection limit (MDL) of both of these procedures is  $0.04 \text{ ng/L}$  for water samples, unless exceeded by a daily detection limit calculated from analyses of blanks, in which case the latter was reported for the applicable analytical run. For PTHg and PMeHg analysis, solids from filters were digested/extracted according to methods described by *Olund et al.* [2004] and *DeWild et al.* [2004], respectively. Based on a one liter sample passed through each filter as was generally followed in this study,

MDL values were  $0.059 \text{ ng/L}$  for PTHg and  $0.01 \text{ ng/L}$  for PMeHg, but these values varied with sample volume filtered.

[15] In addition to analyses of method blanks, duplicate analysis of all THg samples, matrix spikes, and check samples insured data quality. Data quality objectives (DQO) were generally  $\pm 10\%$  for precision and accuracy for all of these QA/QC processes, and failure to reach any of these in a given run resulted in re-analysis until all DQO passed. Matrix spike recoveries reported by the Wisconsin lab for runs that included the filtered samples analyzed in this study averaged  $99.0\% \pm 7.3\%$  (relative std. dev. of mean (RSD);  $n = 132$ ) for THg and  $97.1\% \pm 21.6\%$  ( $n = 61$ ) for MeHg. Field duplicate samples were collected from the upper Hudson for Hg analysis on 3 occasions during 2006–08. Mean standard deviation values of these duplicates were  $0.08 \text{ ng/L}$  for FTHg (RSD = 5.4%),  $0.02 \text{ ng/L}$  for FMeHg (RSD = 20.2%),  $0.02 \text{ ng/L}$  for PTHg (RSD = 7.4%), and  $0.008 \text{ ng/L}$  for PMeHg (RSD = 26.3%). Six field blanks were collected for Hg analysis during the study period. One of these was below the MDL for FTHg, and the mean value for the other five was  $0.06 \text{ ng/L}$ . All values were below the MDL for FMeHg. For the particulate Hg fractions, all measurements were below the detection limit, which averaged  $0.08 \text{ ng/L}$  for PTHg and  $0.01 \text{ ng/L}$  for PMeHg.

[16] DOC concentrations were determined by persulfate oxidation and  $\text{Abs}_{254}$  was measured in a spectrophotometer at 254 nm. Specific ultraviolet absorbance (SUVA) values

were determined by dividing  $Abs_{254}$  by the DOC concentration and are reported in units of L/mg C/m [Weishaar et al., 2003]. Analysis of 4 sets of field duplicate samples during this study resulted in mean standard deviations of 0.3 mg/L for DOC (RSD = 4.6%) and 0.1 L/mg/m for SUVA (RSD = 3.1%). Field blanks averaged 0.5 mg/L for DOC and 0.001 for  $UV_{254}$ .

[17] Total Fe concentrations were measured colorimetrically using a phenanthroline reagent. These values were measured in the field for samples collected in 2006 with a portable spectrophotometer according to Hach method 8008, an approved U.S. Environmental Protection Agency method (see [http://cfpub.epa.gov/npdes/npdesreg.cfm?program\\_id=45](http://cfpub.epa.gov/npdes/npdesreg.cfm?program_id=45), accessed 10/24/11). In 2008, Fe concentrations were determined by a similar colorimetric method using phenanthroline, but samples were analyzed at the U.S. Geological Survey Water Quality Laboratory in Denver, Colorado. Three sets of field duplicates had a mean standard deviation of 71  $\mu\text{g/L}$  (RSD = 15.0%) and four field blanks averaged 7  $\mu\text{g/L}$  during the study.

### 3.3. Statistical Analysis Approach

[18] Multivariate linear regression was applied to spring and summer data to develop and select parsimonious models of THg and MeHg spatial patterns during each season. Three types of models were developed using different sets of predictive metrics. The first modeling approach used landscape metrics, and the second used chemical and physical metrics as predictors of Hg concentrations. The results of these approaches were compared to determine whether landscape or chemical metrics were better predictors of spatial variation in THg and MeHg concentrations in this Adirondack basin. A third approach applied both landscape and chemical metrics to develop hybrid models to explore whether stronger predictive ability could be obtained than with either of the landscape or chemical metric approaches individually. SigmaStat (version 4) and SAS software (version 9.2) were used to develop multivariate linear regression models and for other statistical analyses. The following approach was used to develop and evaluate the “best” multivariate regression models that are presented in this paper:

[19] 1. A best subsets of regressions approach explored models that included successively one through six independent variables. The best three to five of these models for each number of independent variables and with the greatest  $R^2$  values were further evaluated with several diagnostic tests to determine consistency with the assumptions of regression analysis. Only models for which each independent variable had a  $p$  value for inclusion  $<0.10$  were considered further.

[20] 2. Variance Inflation Factors (VIF) were examined to eliminate models in which the independent variables showed unacceptably high multicollinearity. Any model with a VIF value  $>10$  for any of the independent variables was deemed to have high multicollinearity [Menard, 2002] and was not further considered. For models with similar  $R^2$  values, the VIF values were used to aid in the decision as to the “best” models, and ultimately, all of the models selected had VIF values  $<4$ . This approach eliminated most models with more than four independent variables due to high multicollinearity.

[21] 3. Variables and model residuals were examined for adherence to assumptions of linear regression. Normality was examined with the Shapiro-Wilk test [Shapiro and Wilk, 1965]

and a test for constant variance was applied by measuring the significance of a linear regression between the Spearman Ranks of the absolute values of the residuals and the observed dependent variable. Most models for THg passed these tests ( $p < 0.05$ ), but most for MeHg failed these tests. This limitation was overcome by a  $\log_{10}$  transformation of MeHg values, and most models then passed the diagnostic tests on the residuals. Residuals were further examined visually for any models that failed the normality test. If any patterns in residuals were evident indicating systematic bias, the model was discarded, but if the normality test failure was largely driven by one or two outliers only, the model was further considered in steps 4–5. Additionally, influential outliers were evaluated using the Cook’s Distance measure [Cook and Weisburg, 1982]. Any points with a Cook’s Distance value  $>1$  were further evaluated by recalculating the regression with the outlier removed.

[22] 4. Any models that did not pass the diagnostic steps outlined in 2 and 3 were discarded and are not presented or discussed in the paper. For those models that passed these diagnostic steps, the best fit model of each type (landscape, chemical/physical, and hybrid) with the highest adjusted  $R^2$  value was selected for each analysis data set, THg spring, THg summer, MeHg spring, and MeHg summer, and for each of 1, 2, 3, and 4 independent variables. In many cases, models with  $>2$  independent variables failed one of these diagnostic tests. The THg summer data set had no censored values and multivariate models based on least squares linear regression are presented and evaluated. For the other three data sets, censored concentration values were substituted by half the value defined by the range derived from the laboratory detection limit. Once several of the best models were selected for each successive number of independent variables, these models were further evaluated and finalized using maximum likelihood regression analysis with the censoring level included without substitution using SAS PROC LIFEREG, considered an appropriate approach for data analysis with censored values [Helsel, 2005]. A likelihood  $R^2$  (sometimes termed a generalized  $R^2$ ) was calculated for each model as described by Helsel [2005, p. 187]. Note that a generalized  $R^2$  value cannot be adjusted as in ordinary least squares regression.

[23] 5. Akaike’s Information Criteria (AIC) [Akaike, 1974] was employed to assess the relative contribution of each additional independent variable to each model. The model with the lowest AIC statistic was chosen as best representing the data in a parsimonious manner.

[24] 6. Data that show high spatial autocorrelation violate the assumption of statistical independence [LeGendre, 1993]. Spatial autocorrelation was evaluated by examining the correlation of the residuals of each of the best selected models as a function of: (1) basin nesting, the extent to which the basins draining every possible sampling site pair coincide (scale of 0–1), and (2) distance, the Euclidean distance between each site pair. Pearson Product Moment correlation was applied when assumptions of normality and equal variance (as described above) were met, and Spearman Rank correlation when these conditions were not met.

### 3.4. Landscape, Chemical, and Physical Metrics

[25] Several landscape variables were derived that represent the potential influence of wetlands, open water, topography/

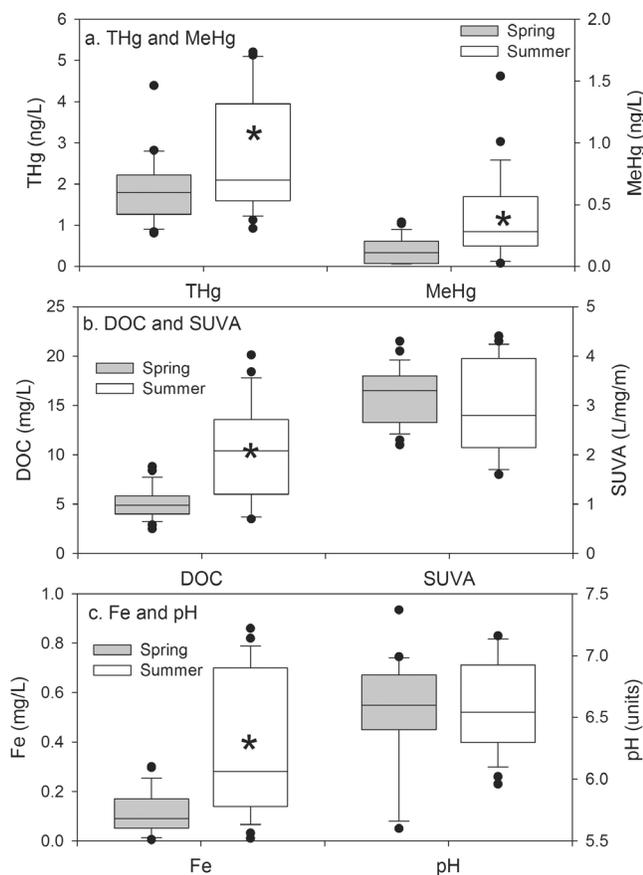
**Table 1.** Landscape and Chemical/Physical Metrics Used in Multivariate Linear Regression Models to Account for Spatial Variation in THg and MeHg Concentrations at 27 Sampling Sites in the Upper Hudson River Basin That Were Sampled in the Spring and Summer of 2006 and 2008

Metric (symbol)	Representation	Calculation	Units	Data Source
Slope (slope)	Mean for basin	$\Sigma$ slope for each basin cell	Percent	10 m DEM
Topographic Wetness Index (TWI)	Mean for basin	$\ln(a/\tan \beta)$	ln m	10 m DEM
Overland Flow Distance (OFD)	Mean for basin	Flow path distance on land surface to nearest stream cell	m	10 m DEM, SAGA stream network
Riparian Area (ripct)	Proportion of total basin area	Area within 0.65 m elevation of each stream cell excluding open water	Unitless	10 m DEM, SAGA stream network
Riparian Width (ripwidth)	Mean for basin	Width across riparian area adjacent to each stream cell	m	10 m DEM, SAGA stream network
Wetland Area (wetpct)	Proportion of total basin area	All area classified as wetland excluding open water	Unitless	<i>LaPoint et al.</i> [2004]
Inverse Distance Weighted Wetland Area (idwet)	Proportion of total basin area	$\Sigma$ (wetland area/OFD) for each wetland cell	Unitless	10 m DEM, SAGA stream network; <i>LaPoint et al.</i> [2004]
Percent Open Water (owpct)	Proportion of total basin area	All area defined as open water	Unitless	<i>LaPoint et al.</i> [2004]
Open Water Index (OWI)	Total surface area for basin	$\Sigma$ outlet drainage area/sampling site drainage area for each open water body (53 largest)	m <sup>2</sup>	10 m DEM; <i>LaPoint et al.</i> [2004]
Small Open Water Bodies (small ow)	Total surface area for basin	All open water surface area not included in OWI calculation	m <sup>2</sup>	10 m DEM; <i>LaPoint et al.</i> [2004]
DOC concentration	Each sample	Chemical analysis	mg/L	Measured
SUVA	Each sample	Chemical analysis	L/mg/m	Measured
Fe concentration	Each sample	Chemical analysis	mg/L	Measured
Flow	Each sample	Field measurements	mm/day	Measured

slope, and landscape heterogeneity on Hg concentrations. Similarly, several chemical and physical metrics were explored that included measures of Hg transport capability and indicators of biogeochemical processes or conditions believed to be associated with Hg mobilization or methylation. A notably absent chemical metric in this analysis is  $\text{SO}_4^{2-}$  concentrations, a common indicator of  $\text{SO}_4^{2-}$  reduction dynamics that are associated with Hg methylation, because these values were not available for all samples.

[26] Discharge was one of the physical metrics explored for inclusion in models, but note that these synoptic samples generally represent low-to-moderate flow conditions, and the analysis here is not intended to explore Hg behavior over the full range of flow conditions. Such analyses have been done previously at individual stream sites in the upper Hudson [*Dittman et al.*, 2010; *Schelker et al.*, 2011]. Streamflow data from the USGS gage at Fishing Brook at County Line Flow, a mid-sized sub-basin (65.6 km<sup>2</sup>) that was also one of the synoptic sites in the upper Hudson, provides a good index of the relative flow conditions at the time that each set of synoptic samples was collected. On a percent exceedance basis (the percent of days with higher flow), the mean flow at Fishing Brook for the days when synoptic samples were collected in spring of 2006 had an exceedance value of 42.7% and those collected in spring of 2008 had a value of 44.7% indicating moderate flow on an annual basis. The comparable exceedance values for samples collected in the summers of 2006 and 2008 were 90.5% and 22.7%, respectively, indicating more widely varying flow conditions from low to moderately high among these samples. Landscape metrics (Table 1) were compiled for each sub-basin by Geographic Information System (GIS) analyses using Arc GIS software. Slope, the Topographic Wetness Index, and Overland Flow Distance were calculated for each

sub-basin by terrain analysis of the 10-m National Elevation Data set (<http://seamless.usgs.gov>, accessed 10/24/11) using the System for Automated Geoscientific Analyses (SAGA, <http://www.saga-gis.org/en/index.html>, accessed 10/24/11) [*Cimmery*, 2007]. The relations of THg and MeHg concentrations to mean values and the coefficient of variation of these landscape metrics were derived to determine whether typical values or heterogeneity were stronger predictors of Hg; the mean values of landscape metrics were stronger predictors than the coefficient of variation. The Topographic Wetness Index (TWI), first defined by *Beven and Kirkby* [1979], was calculated as  $\ln(a/\tan \beta)$ , where  $a$  is accumulated area per unit contour length and  $\beta$  is the local slope angle. In the calculations of TWI presented here, the D8 multidirection flow algorithm was used [*O'Callaghan and Mark*, 1984]. This metric captures the combined influence of slope on transport and the subsurface contributing area on source strength of Hg. The Overland Flow Distance (OFD) was calculated as the distance (horizontal and vertical) over the land surface to the nearest stream cell for each non-stream cell according to the flow accumulation algorithm. This metric was selected to quantify the typical distance of overland flow and shallow subsurface flow to the nearest stream channel. A final landscape metric derived from SAGA, riparian area (expressed as proportion of total basin area and termed ripct), was calculated by including all cells contributing to a given stream cell within an elevation <0.65 m above the stream cell to define the extent of the riparian area [*Shoutis et al.*, 2010; *Schelker et al.*, 2011]. An elevation of 0.65 m was chosen because this value best identified the break in slope between the near-flat riparian area and adjacent hillslopes. SAGA requires that a channel network be defined for calculations that involve stream cells (OFD and ripct in this study). This network was



**Figure 2.** Bar charts of chemical constituents in the upper Hudson River basin for samples collected during spring and summer. (a) THg and MeHg, (b) DOC and SUVA, and (c) Fe and pH. An asterisk placed within the bar indicates that there is a significant difference in concentrations ( $p < 0.05$ ) among the seasons as determined by a Mann-Whitney Rank Sum test or t-test depending on whether data passed a test for normality and equal variance.

defined through visual comparison to the 1:24,000 National Hydrography Data set (NHD) by selecting an accumulated area threshold that created a stream network that appeared closest to that of the NHD network.

[27] Wetland land cover was derived from the Adirondack Park Agency Wetlands map, in which wetlands were delineated from 1:40,000 color infrared aerial photographs according to the approach used in the National Wetlands Inventory [LaPoint *et al.*, 2004]. An inverse distance weighted wetland area (idwet) was calculated by multiplying each wetland cell by  $1/\text{OFD}$  to more strongly weight wetland area closest to the stream channel, similar to an approach used in a recent report on land use/land cover influences on Hg in fish across the U.S. [Scudder *et al.*, 2009], except in the current study a flow path length was used in contrast to Euclidean distance in the aforementioned study.

[28] A common open water metric applied in studies of spatial controls on Hg cycling is the percent open water area in a basin [Hurley *et al.*, 1995; Shanley *et al.*, 2005], a quantity easily obtained from NHD and other sources. However, in river systems that include linked networks of

streams and lakes such as the upper Hudson River basin, a simple calculation of the percent of basin area that consists of open water or open water surface area fails to account for the position of the lake in the basin and how much of total basin flow passes through a given lake. To better account for the location of open water in a given basin, the surface area of each open water body  $>0.025 \text{ km}^2$  within a basin was multiplied by the drainage area at the pond outlet divided by the drainage area at the sampling location to create an open water index (OWI). Preliminary analysis (not shown) indicated that open water considered in this manner showed a stronger inverse relation to THg and MeHg concentrations than that obtained with percent open water, consistent with the net effects of physical and biogeochemical processes known to occur in open water that act to decrease Hg concentrations. The calculation of OWI was performed for the 53 largest open water bodies of the 325 identified in the 1:24,000 NHD coverage, 83.4% of the total open water surface area in the upper Hudson basin. The remaining small open water bodies ( $<0.025 \text{ km}^2$  each) were compiled into a separate small open water body surface area metric (small ow) for each sub-basin.

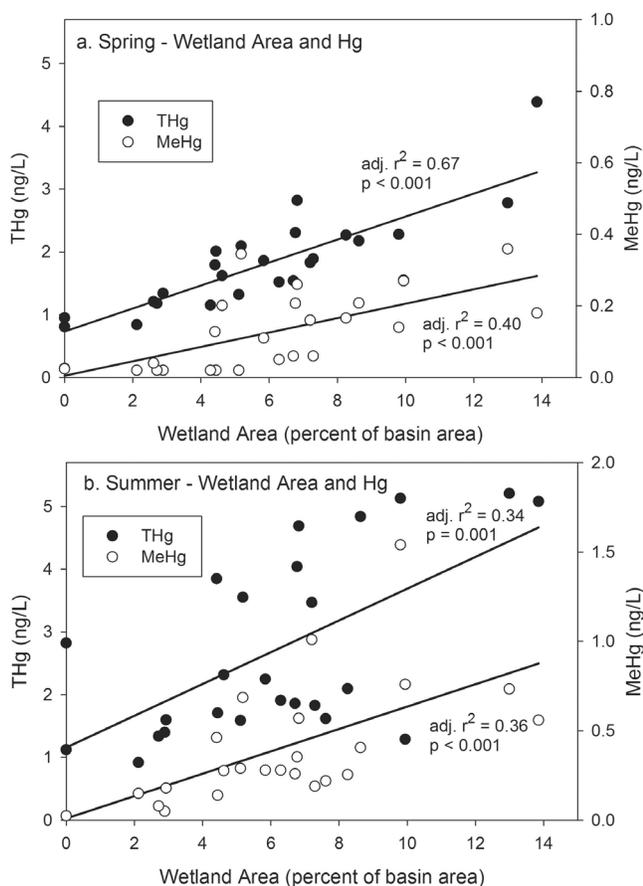
## 4. Results

[29] Prior to presentation of the multivariate regression model results, general characteristics of the chemical data sets and seasonal differences are presented followed by bivariate regression relations of THg and MeHg concentrations as a function of wetland area and DOC concentrations, two variables shown previously to be strong controls on Hg behavior. The data reported on total concentrations includes the filtered plus suspended particulate concentrations of each Hg form; however we believe that these data largely represent filtered concentrations. The particulate fraction represented only 16.6% of THg for samples collected in 2008 and presented here, and only 13.8% of MeHg for these same samples. These data are consistent with the dominance by filtered Hg concentrations shown for a sub-basin of the upper Hudson River by Schelker *et al.* [2011], and are generally consistent with the mostly forested, undisturbed conditions in this basin and the low-to-moderate flow conditions that prevailed during sample collection.

### 4.1. General Characteristics and Seasonal Differences in Hg and Related Solute Concentrations

[30] Median THg concentrations in spring samples (1.8 ng/L) were significantly different ( $p < 0.05$ ) than in those collected in summer (2.1 ng/L; Figure 2a). Median MeHg concentrations were more than  $2\times$  greater in summer (0.28 ng/L) than in spring (0.11 ng/L;  $p < 0.001$ ). Additionally, eight samples had MeHg concentrations below the detection limit in spring, but only two in summer.

[31] Among the other chemical constituents measured in these samples, median DOC and Fe concentrations in summer were significantly greater and more than double those in spring samples (Figures 2b and 2c). In contrast, SUVA and pH values did not differ significantly between the two seasons. Greater spatial variation in DOC, SUVA, and Fe in summer than in spring was noted as well. These differences in Hg and related solute concentrations warrant separate multivariate regression models for each season.



**Figure 3.** THg and MeHg concentrations as a function of percent wetland area for samples collected in the Upper Hudson River basin during (a) spring and (b) summer. Least squares linear regression lines with corresponding adjusted  $r^2$  and  $p$  values are shown for each.

#### 4.2. Bivariate Linear Regressions of Hg Concentrations With Wetland Area and DOC Concentrations

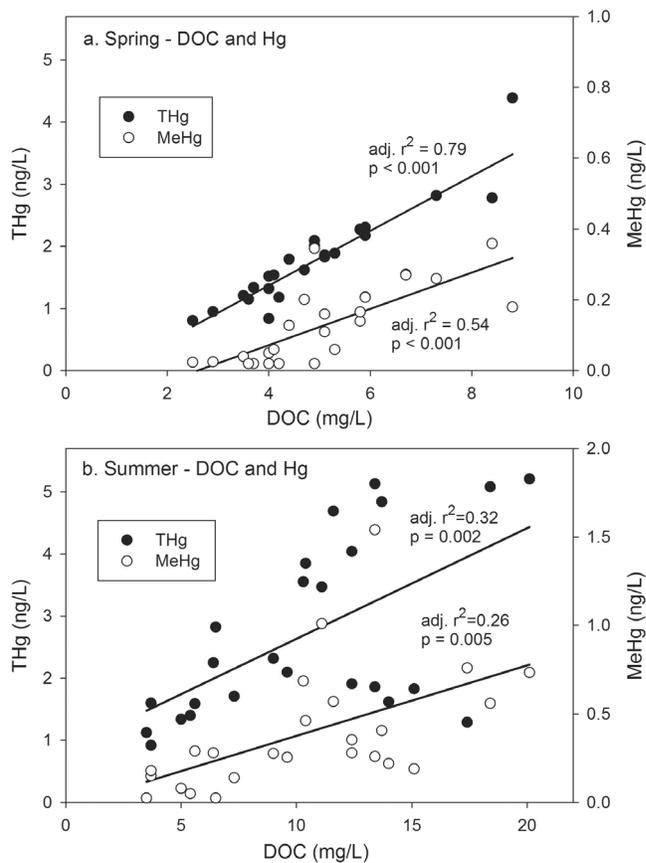
[32] Previous investigations have shown that THg and MeHg concentrations are strongly related to wetland area (expressed as percent of basin area) and DOC concentrations. These relations are often so strong in some regions that metrics derived from wetland area or DOC have been suggested as surrogate indicators of THg and MeHg concentrations or loads [Grigal, 2002; Dittman *et al.*, 2009]. If these variables were strongly related to Hg concentrations across the upper Hudson River basin, then perhaps multivariate regression would be unnecessary to develop strong spatial predictive models.

[33] Significant bivariate linear regressions ( $p < 0.05$ ) were evident for both THg and MeHg concentrations and each of these two independent variables (Figures 3 and 4). Wetland area accounted for about 2/3 of the variation (adj.  $r^2 = 0.67$ ) in THg concentrations and <1/2 of the variation (adj.  $r^2 = 0.40$ ) in MeHg concentrations in spring (Figure 3a). In contrast, these regressions were weaker in summer, particularly for THg (adj.  $r^2 = 0.34$ ; Figure 3b). DOC concentrations were also a stronger predictor of THg concentrations (adj.  $r^2 = 0.79$ ) and MeHg concentrations

(adj.  $r^2 = 0.54$ ) in spring than in summer, when adjusted  $r^2$  values declined to 0.32, and 0.26, respectively (Figure 4). In summary, these relations of Hg concentrations with wetland area and DOC concentrations were generally stronger for THg than for MeHg, and were weaker in summer than in spring; neither independent variable accounted for much more than one-third of the variation in Hg concentrations during summer.

#### 4.3. Multivariate Linear Regression Models

[34] Spatial autocorrelation was not high in these data, and the basin nesting and distance metrics explained <5% of the variation in the residuals of the best models; variation explained was <1% in 75% of these models. Residuals in 6 of 24 best models were significantly inversely correlated ( $p < 0.05$ ) with one of the spatial metrics; 4 of these were with basin nesting, and 2 with distance between sites. Because little variation was explained by either basin nesting or distance between sites, we concluded that spatial autocorrelation did not greatly affect model results; therefore, spatial autocorrelation was not considered further in analyses of these data. Additionally, there were few influential outliers in the best models as determined by the Cook's Distance measure; only 3 of the 12 best models presented here



**Figure 4.** THg and MeHg concentrations as a function of DOC concentrations for samples collected in the Upper Hudson River basin during (a) spring and (b) summer. Least squares linear regression lines with corresponding adjusted  $r^2$  and  $p$  values are shown for each.

**Table 2.** Linear Regression Models That Best Predicted THg During Spring and Summer for Each of 1, 2, 3, and 4 Independent Variables for Sites Sampled in the Upper Hudson River Basin<sup>a</sup>

Dependent Variable	Model Type	Season	n <sup>b</sup>	r <sup>2</sup> or R <sup>2</sup>	Independent Variables	AIC
THg	Landscape	Spring	25(2)	0.72	-slope	42.02
	Landscape			0.80	-slope, -small ow	35.47
	Landscape			0.87	-slope, +wtpct, -log small ow	26.81
	<i>Landscape</i>			<i>0.92</i>	<i>-owpct, -small ow, +TWI, -OFD</i>	<i>17.60</i>
	Chemical			0.80	+DOC	33.83
	<i>Chemical</i>			<i>0.84</i>	<i>+DOC, +SUVA</i>	<i>30.29</i>
	<i>Hybrid</i>			<i>0.87</i>	<i>-small ow, +DOC</i>	<i>25.98</i>
THg <sup>c</sup>	Landscape	Summer	25(0)	0.34	+wtpct	82.44
	Landscape			0.59	-slope, -owpct	71.52
	Landscape			0.63	-slope, -owpct, -OWI	70.02
	<i>Landscape</i>			<i>0.70</i>	<i>-slope, -owpct, -small ow, +ripwidth</i>	<i>65.72</i>
	Chemical			0.42	+SUVA	79.33
	<i>Chemical</i>			<i>0.68</i>	<i>+DOC, +SUVA</i>	<i>65.27</i>
	Hybrid			0.64	+wtpct, +SUVA	68.59
	Hybrid			0.82	-small ow, +DOC, +SUVA	51.58
	<i>Hybrid</i>			<i>0.86</i>	<i>-OWI, -small ow, +DOC, +SUVA</i>	<i>47.20</i>

<sup>a</sup>The model type selected as best for each set of spring and summer samples is given in italics.

<sup>b</sup>The number in parentheses in the column marked n is the number of censored THg values.

<sup>c</sup>R<sup>2</sup> values for THg in summer were adjusted for the number of explanatory variables in each model.

showed values >1. For these three models, the regression equations were re-calculated after removing the influential outliers; however, there was no change in the significance of the independent variables, little change in the coefficients for these variables, and a marginal improvement in the R<sup>2</sup> values for the models. Based on this analysis, these influential outliers were not removed from the models, but points with Cook's Distance values >1 are indicated in each pertinent figure panel in which the multivariate regression model results are presented. Results are presented below for the best multivariate models for THg and MeHg concentrations in spring and summer samples.

#### 4.3.1. THg Concentrations

[35] The spatial landscape models that accounted for the most variation in THg concentrations included four independent variables (Table 2). These model variables were different for each of the seasons, and none included percent wetland area. Instead, the best models included hydrogeomorphic metrics such as the TWI and OFD in spring, and slope and riparian width in summer. Additionally, each seasonal model included two open water metrics (owpct, small ow) that were inversely related to THg concentrations indicating an association with a loss of Hg from the water column. Overall, these landscape models accounted for 92% of the variation in THg concentrations among these sites in spring, and 75% of the variation in summer (adj. R<sup>2</sup> = 0.70), with no apparent bias or strong leveraging (Figures 5a and 6a).

[36] The best spatial models for THg concentrations based on chemical-physical metrics included DOC concentrations and SUVA (Table 2). Model R<sup>2</sup> values were 0.84 in spring and 0.68 (adj. R<sup>2</sup>) in summer, similar though with slightly lower predictive strength than those based on landscape metrics (Figures 5b and 6b). Overall, SUVA was a stronger predictor in summer than in spring. The best single variable model for summer includes SUVA and has an adjusted r<sup>2</sup> of 0.42, whereas the best single variable model in spring includes DOC and has an r<sup>2</sup> of 0.80. Adding DOC to the

summer model resulted in a greater increase (0.27) than addition of SUVA to the spring model (0.04).

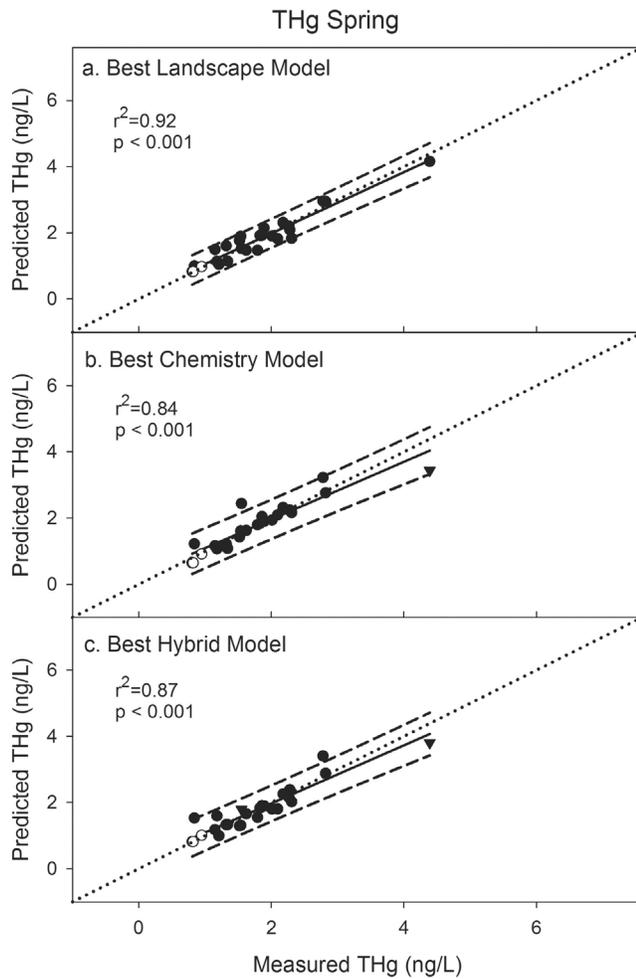
[37] The best hybrid models, showed similar predictive strength to those based on a single metric type, although the R<sup>2</sup> (0.86) of the best hybrid model in summer was greater than either of the other modeling approaches with little change in predictive ability for spring or summer data (Table 2 and Figures 5c and 6c). The best spring model included an open water metric (small ow) and DOC concentrations, whereas the best summer model included four independent variables, two representing the influence of open water (OWI, small ow) and two representing carbon (DOC concentrations, SUVA).

#### 4.3.2. MeHg Concentrations

[38] The multivariate landscape models that accounted for the most spatial variation in MeHg concentrations at these sites included measures of riparian/wetland influence (ripct, idwet, ripwidth), hydrogeomorphology (slope, OFD) and open water (OWI; Table 3). During spring, the best model included slope, OWI, OFD, and ripct as independent variables and has an R<sup>2</sup> value of 0.80, whereas during summer, the best model included idwet, OWI, and ripwidth, and has an R<sup>2</sup> value of 0.81 (Figures 7a and 8a).

[39] The best chemical-physical models included SUVA, Fe concentrations, and runoff during spring (R<sup>2</sup> = 0.79), and SUVA, DOC concentrations, and runoff during summer (R<sup>2</sup> = 0.66; Table 3 and Figures 7b and 8b). Stream runoff was inversely related to log<sub>10</sub> MeHg concentrations in both seasonal models, whereas the other chemical variables were positively related to log<sub>10</sub> MeHg concentrations. The chemical and landscape models in spring explained about the same amount of the variation in log<sub>10</sub> MeHg concentrations, whereas the best chemical model in summer explained about 15% less of the data variation than that of the best landscape model.

[40] The best hybrid models for MeHg each included two independent variables, idwet and runoff in spring (R<sup>2</sup> = 0.76), and Fe concentrations and ripwidth during summer



**Figure 5.** Predicted and measured values based on the best multivariate linear regression models for THg concentrations in samples collected during spring in the upper Hudson River basin using (a) Landscape metrics, (b) Chemistry/Physical metrics, and (c) Hybrid metrics. Solid circles represent uncensored data, and open circles represent interval censored data shown as the mid-point of the interval. The best fit least squares linear regression is shown as a solid line, the 1:1 line is shown as a dotted line, and the 95% prediction intervals are shown as dashed lines. An inverse triangle symbol indicates a Cook's Distance measure  $> 1$ .

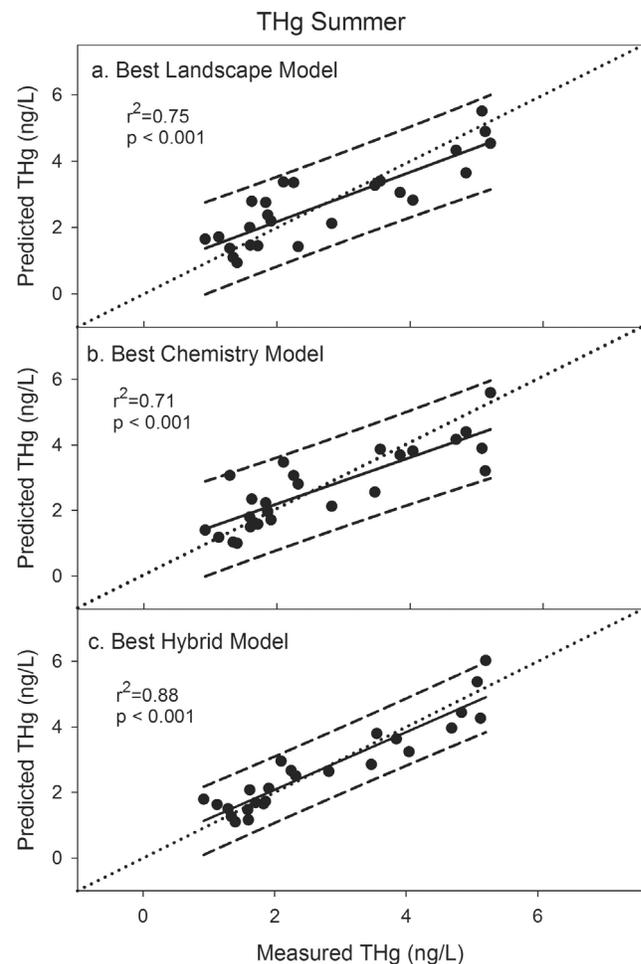
( $R^2 = 0.69$ ; Table 3 and Figures 7c and 8c). These two-variable hybrid models accounted for about the same amount of the variability in these data as did the three-variable models based on chemical-physical variables.

## 5. Discussion

### 5.1. General Concentration Patterns

[41] The data presented show a basin with moderately high THg concentrations of about 2 ng/L, and values as high as 5 to 6 ng/L in summer. MeHg concentrations were also moderately high in the basin, with median values of 0.1 to about 0.3 ng/L and values  $> 1$  ng/L at two sites during summer. These sites are broadly consistent with previous compilations of Hg data in surface water across eastern

North America, the northeastern U.S., New York State, and the Adirondacks. For example, *Shanley et al.* [2005] report a median THg concentration of 2.15 ng/L for nearly 500 stream samples collected across the northeastern U.S., and *Dennis et al.* [2005] report a median value of 2.09 ng/L for a data set that overlaps with that of *Shanley et al.* [2005] and includes 831 samples of lakes and streams across the northeastern U.S. and southeastern Canada, including the Adirondacks. *Simonin et al.* [2008] report a lower median value of 0.98 ng/L for 131 lakes across New York State that includes the Adirondacks. All of these data sets indicate wide spatial variation in THg concentrations that span a greater than 10 fold range, slightly greater than the sixfold spatial variation found in the current study. Several other studies of narrower geographic scope, including within the same upper Hudson Basin, also report THg concentrations in the same range of about 1 to 6 ng/L [*Driscoll et al.*, 1995; *Selvendiran et al.*, 2008; *Bradley et al.*, 2011], with some



**Figure 6.** Predicted and measured values based on the best multivariate linear regression models for THg concentrations in samples collected during summer in the upper Hudson River basin using (a) Landscape metrics, (b) Chemistry/Physical metrics, and (c) Hybrid metrics. The best fit least squares linear regression is shown as a solid line, the 1:1 line is shown as a dotted line, and the 95% prediction intervals are shown as dashed lines.

**Table 3.** Linear Regression Models That Best Predicted MeHg During Spring and Summer for Each of 1, 2, 3, and 4 Independent Variables for Sites Sampled in the Upper Hudson River Basin<sup>a</sup>

Dependent Variable	Model Type	Season	n <sup>b</sup>	r <sup>2</sup> or R <sup>2</sup>	Independent Variables	AIC
Log <sub>10</sub> MeHg	Landscape	Spring	25(8)	0.54	+id wet	24.08
	Landscape			0.65	-slope, +ripct	19.06
	Landscape			0.73	-slope, -OWI, +ripct	14.76
	Landscape			0.80	-slope, -OWI, -OFD, +ripct	8.90
	Chemical			0.67	+SUVA	15.56
	Chemical			0.72	+Fe, -flow	13.96
	Chemical			0.79	+SUVA, +Fe, -flow	8.24
	Hybrid			0.76	+id wet, -flow	9.92
	Hybrid			0.72	+id wet, -flow	9.92
Log <sub>10</sub> MeHg	Landscape	Summer	25(2)	0.69	+id wet	7.75
	Landscape			0.74	+id wet, -OWI	5.64
	Landscape			0.81	+id wet, -OWI, +ripwidth	-0.46
	Chemical			0.46	+Fe	21.52
	Chemical			0.55	+DOC, +SUVA	19.10
	Chemical			0.66	+DOC, +SUVA, -flow	13.95
	Hybrid			0.69	+Fe, +ripwidth	9.66
	Hybrid			0.72	-OWI, +ripwidth, +DOC	9.43

<sup>a</sup>The model type selected as best for each set of spring and summer samples is highlighted in gray shading.

<sup>b</sup>The number in parentheses in the column marked n is the number of censored MeHg values.

upland, low DOC catchments showing even lower THg concentrations <0.5 ng/L [Dittman *et al.*, 2009; Demers *et al.*, 2010]. Even greater spatial heterogeneity was evident in MeHg concentrations across the upper Hudson basin with values ranging from less than the detection limit (0.04 ng/L) to greater than 1.5 ng/L, about a 40 fold variation among sites. Similarly, MeHg concentrations reported in other studies in the region range from 0.01 ng/L in surface waters with little wetland area and low DOC concentrations to ranges of 1 to >3 ng/L in waters where these variables have high values [Dennis *et al.*, 2005; Selvendiran *et al.*, 2008; Bradley *et al.*, 2011].

## 5.2. Seasonality

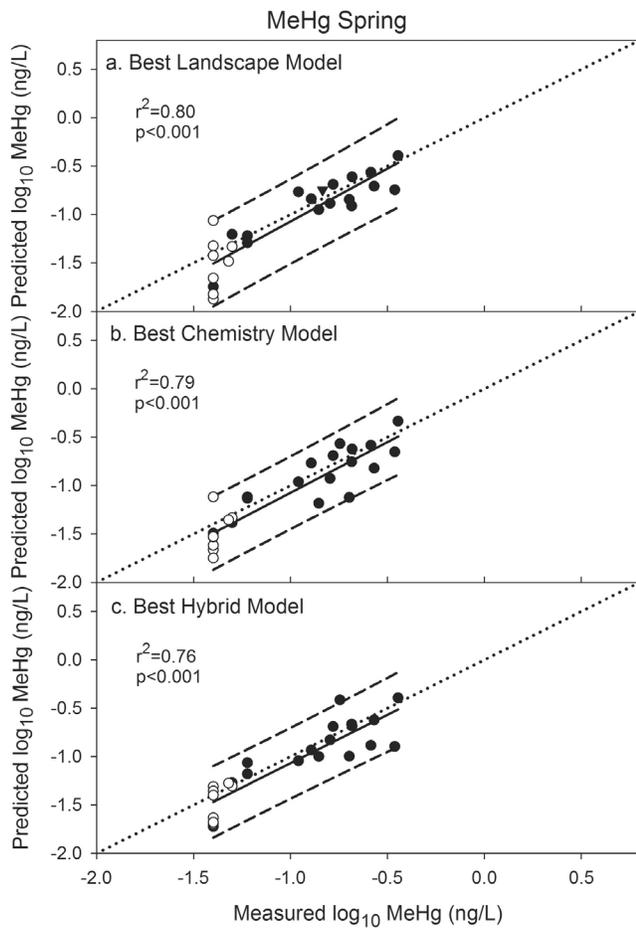
[42] The seasonality evident in these data show greater THg, MeHg, and DOC concentrations during summer than spring samples, consistent with similar patterns reported for wetland-influenced sites in the Adirondacks, Upper Midwest, Canada, and Europe [Branfireun and Roulet, 2002; Yin and Balogh, 2002; Selvendiran *et al.*, 2008]. This seasonal pattern is generally stronger for MeHg than THg and DOC concentrations since the latter two solutes often also show increases with flow during snowmelt and rain storms, whereas MeHg often does not show this pattern [Bishop and Lee, 1997; Schelker *et al.*, 2011]. These seasonal differences are presumably driven in part by a greater influence of wetland areas on stream chemistry in summer, when flows tend to be lower. Soil temperature can also play an important role in seasonality because biogeochemical processes such as decomposition of soil organic matter [Yin, 1999] and Hg methylation increase with temperature [Ullrich *et al.*, 2001]. Seasonal differences are especially evident at sites where wetlands are located in riparian areas immediately adjacent to the stream channel [Bishop *et al.*, 1995]. Uplands with little wetland area tend to show less seasonality for Hg and DOC concentrations [Selvendiran *et al.*, 2008], and these uplands often show waning influence in larger basins during summer (so-called “seasonal disconnection”). This general statement is borne out by linear regression analysis of this data set that indicates the relative seasonal difference

(summer conc. – spring conc./mean) is significantly positively related to wetpct for THg ( $r^2 = 0.34$ ,  $p = 0.004$ ), MeHg ( $r^2 = 0.36$ ,  $p = 0.003$ ) and especially for DOC ( $r^2 = 0.79$ ,  $p < 0.001$ ).

[43] Past studies in the upper Hudson basin and at other sites in eastern North America also generally show that THg and DOC concentrations increase with flow, and MeHg can show either increases or decreases with flow [Branfireun and Roulet, 2002; Brigham *et al.*, 2009; Schelker *et al.*, 2011]. A previous study at one of the sites sampled in the current study (Fishing Brook at County Line Flow) indicates that THg shows a significant positive relation with flow that varies with season, DOC shows no relation with flow, and MeHg is inversely related to flow [Schelker *et al.*, 2011]. Relations with flow could not be evaluated with the current data set that provides only short-term snapshots in time; however, flow was a significant inverse variable in several of the MeHg models in both spring and summer as summarized in Table 3, consistent with the conclusions of Schelker *et al.* [2011] that MeHg shows supply limited flushing behavior.

## 5.3. Bivariate Linear Regression Models

[44] The bivariate linear regression results show significant positive relations for THg and MeHg concentrations with percent wetland area and DOC concentrations consistent with previous studies [St. Louis *et al.*, 1994; Driscoll *et al.*, 1995; Hurley *et al.*, 1995; Krabbenhoft *et al.*, 1995; Grigal, 2002; Selvendiran *et al.*, 2008; Brigham *et al.*, 2009; Dittman *et al.*, 2009; Demers *et al.*, 2010]. These relations were generally stronger for THg concentrations than those of MeHg, and stronger in the spring samples than those collected in summer. Other investigations have also noted that DOC concentrations are more strongly related to THg concentrations than to MeHg concentrations [Lee *et al.*, 2000; Brigham *et al.*, 2009], suggesting that factors beyond the role of DOC as a complexing and transporting agent such as those that affect the conditions favorable for methylation and the rate of methylation are of increasing importance for MeHg.

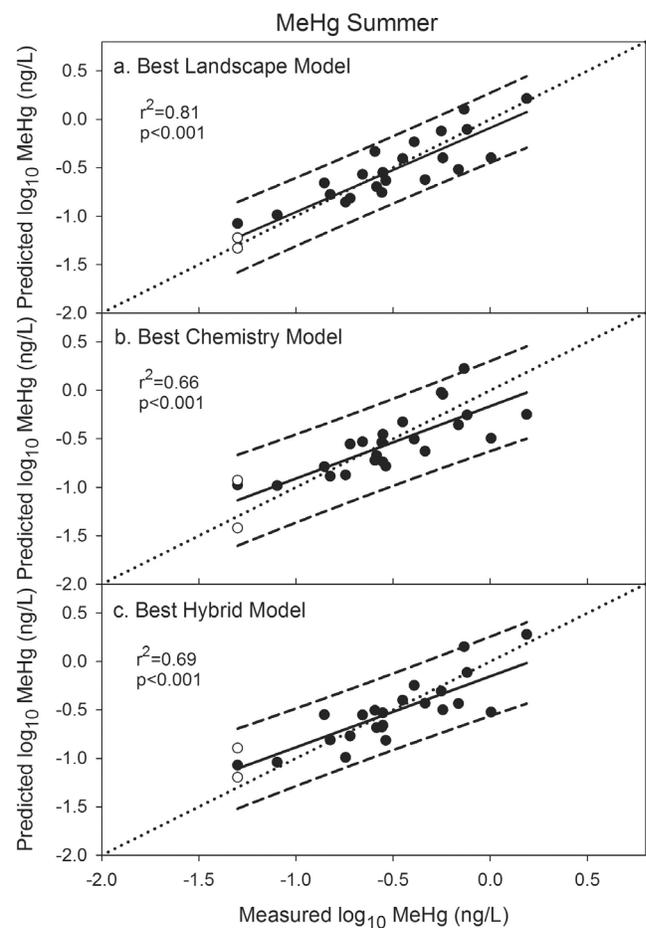


**Figure 7.** Predicted and measured values based on the best multivariate linear regression models for MeHg concentrations in samples collected during spring in the upper Hudson River basin using (a) Landscape metrics, (b) Chemistry/Physical metrics, and (c) Hybrid metrics. Solid circles represent uncensored data, and open circles represent interval censored data shown as the mid-point of the interval. The best fit least squares linear regression is shown as a solid line, the 1:1 line is shown as a dotted line, and the 95% prediction intervals are shown as dashed lines. An inverse triangle symbol indicates a Cook's Distance measure  $>1$ .

[45] A surprising aspect of these bivariate regression results is that simple metrics such as percent wetland area and DOC concentrations, proven powerful predictors of THg and MeHg concentrations in some settings, cannot explain the majority of variation in these data collected within a single  $<500$  km<sup>2</sup> drainage area basin. This finding is also consistent with the lack of a significant temporal relation between THg and DOC concentrations as reported by *Schelker et al.* [2011] in Fishing Brook, a sub-basin of the upper Hudson. These findings are in contrast to others that indicate a strong temporal relation between DOC and THg concentrations in the Archer Creek and Arbutus Lake catchments, also within the upper Hudson basin, and sampled as part of the current study [*Selvendiran et al.*, 2009; *Dittman et al.*, 2009].

#### 5.4. Multivariate Linear Regression Models

[46] The inability of simple bivariate linear regressions to account for the majority of variation in THg and MeHg concentrations in the upper Hudson basin, argues for a multivariate approach to explore more widely the factors that can explain the majority of variation. This is especially relevant during summer when the highest THg and MeHg concentrations were observed, and when the simple bivariate linear regressions were weakest. Overall, the best multivariate models developed here explain most of the variation in THg and MeHg concentrations and the significant independent variables that appear in the best models can provide some insight into the dominant processes operating across this basin. These multivariate results indicate that spatial models based on just landscape metrics are generally as good, or better at accounting for variation in Hg concentrations at



**Figure 8.** Predicted and measured values based on the best multivariate linear regression models for MeHg concentrations in samples collected during summer in the upper Hudson River basin using (a) Landscape metrics, (b) Chemistry/Physical metrics, and (c) Hybrid metrics. Solid circles represent uncensored data, and open circles represent interval censored data shown as the mid-point of the interval. The best fit least squares linear regression is shown as a solid line, the 1:1 line is shown as a dotted line, and the 95% prediction intervals are shown as dashed lines.

low-to-moderate flow conditions in the upper Hudson basin than common chemical metrics or a hybrid approach that uses both types of metrics.

### 5.5. Role of Open Water

[47] The lack of a strong relation between THg and DOC concentrations in the upper Hudson basin, especially during summer, has previously been suggested to originate from the effects of open water [Schelker *et al.*, 2011]. Several different physical and biogeochemical processes have been identified that can affect Hg and DOC concentrations including photo-reduction and volatile loss, photo-oxidation, settling of particulate matter, biological uptake and later settling, and demethylation originating in bottom sediment [Seller *et al.*, 1996; Hintelmann *et al.*, 2000; Selvendiran *et al.*, 2009]. The net effect of these processes results in open waters often but not always acting as a sink for downstream transport of Hg and DOC as observed in previous studies [St. Louis *et al.*, 1994; Branfireun and Roulet, 2002; Selvendiran *et al.*, 2009]. Schelker *et al.* [2011] show that the net effect of these processes can affect THg and DOC concentrations differently in some open water bodies such as County Line Flow in the upper Hudson basin, resulting in a “smearing” of the relation between THg and DOC concentrations that was evident upstream of the pond.

[48] The importance of open water as a predictor of THg and MeHg concentrations across the upper Hudson basin was confirmed by the significance of various open water metrics in many of the best multivariate models developed during both spring and summer. All significant open water metrics included in spatial models were inversely related to THg and MeHg concentrations consistent with the role of ponded water as a sink for Hg in this basin. The metric that reflects small open waters (with surface area  $<0.025 \text{ km}^2$ , 16.6% of total open water surface area) was significant in many models, and points to the importance of these numerous (272 in upper Hudson basin) small ponds to Hg transport. The predictive ability of this small open water metric was explored because many of these small ponds showed evidence of past or current beaver activity, and previous studies have indicated that beaver ponds can serve as sources of Hg, especially MeHg [Driscoll *et al.*, 1998; Roy *et al.*, 2009]. Source behavior that would be indicated by a positive relation with MeHg concentrations was not evident, perhaps because most of the small water bodies were not beaver ponds (not evaluated quantitatively), or that many may have been older beaver ponds, which have been shown to diminish as a Hg source with time [Roy *et al.*, 2009].

[49] The percent open water metric (owpct) appeared more commonly in the models for THg concentrations, whereas the open water index (OWI) that accounts for the proportion of the basin that drains through the pond as well as surface area appeared more commonly in models for MeHg concentrations. The strength of OWI as a predictor of MeHg concentrations and not those of THg may point to the dominance of different in-pond processes affecting the concentrations of these two Hg forms. These findings are consistent with a greater role of photo-reduction on MeHg concentrations, which should depend to a greater extent on the gross flux of water across total open water surface area as captured by the OWI metric. In contrast, the percent open

water metric that appeared in many THg models does not necessarily reflect the total surface area of ponded water but only the area relative to total basin area. This latter metric may better capture the processes that depend on settling and interaction with bottom sediment as opposed to surface-oriented photo-reduction that in the absence of re-oxidation results in permanent loss of MeHg from solution [Seller *et al.*, 1996].

### 5.6. Role of Wetlands and Related Metrics

[50] The simple percent wetland metric (wtpct) did not appear in many of the models shown in Tables 2 and 3, and in none of the best models for either Hg form in spring or summer. Instead, many of these models included a hydrogeomorphic metric such as slope, TWI, ripwidth, or OFD and/or one of the alternative wetland metrics such as ripct or idwet. The hydrogeomorphic metrics are likely better general indicators of sources of Hg and reflect the influence of low slope (slope), and high accumulated area (TWI), which are likely surrogate indicators for the occurrence tendency and extent of area with a high water table. Areas with a high water table are more likely to intersect shallow organic-rich soils with abundant Hg and organic matter, and are also more likely to have reducing conditions that favor methylation. Other hydrogeomorphic metrics may reflect the influence of transport distance of Hg such as OFD, a metric that Riva-Murray *et al.* [2011] found was strongly related to slope and drainage density and inversely related to spatial variation in Hg concentrations in invertebrates and fish in part of the upper Hudson basin. The significance of these hydrogeomorphic metrics in many of the models suggest that aspects of landscape morphology relevant to THg and MeHg concentrations are not captured by a simple wetland area metric in this basin.

[51] Some of the other wetland-related metrics such as idwet, ripct, and ripwidth appeared more commonly in landscape and hybrid models than did percent wetland area. Notably, these metrics appear more often in models for MeHg and not THg suggesting that riparian area and wetlands located in these near-stream zones are relatively more important as sources of MeHg than THg. These riparian-focused metrics seem to better reflect the influence of source and transport distance on Hg concentrations than a simple measure of total wetland area. The idwet metric may better predict solutes originating primarily from riparian areas [King *et al.*, 2005]. Similarly, ripct also includes near-stream areas not classified as wetlands, but that represent relatively flatter terrain likely to have a high water table and organic rich soil that would favor higher Hg concentrations. Ripwidth also appeared as a significant positive variable in the best landscape and hybrid models for MeHg and the best landscape model for THg. These results suggest that higher Hg concentrations are associated with broader riparian areas.

## 6. Conclusions

[52] The data presented here show wide spatial variation in THg and MeHg concentrations that during low-to-moderate flow are generally greater in summer than in spring across the upper Hudson River basin. Observed variation is well explained by multivariate models that include metrics

reflecting basin geomorphology, riparian/wetland areas, and open water, consistent with the findings of previous investigations of the importance of these factors in explaining Hg source, speciation, and transport. Models based solely on landscape characteristics were comparable or stronger at accounting for variation in THg and MeHg concentrations than models based on chemical metrics such as DOC concentrations and SUVA. These results await confirmation by additional sampling in the upper Hudson basin as well as possible application in other similar landscapes, but the strength of the models obtained here suggest that landscapes similar to the upper Hudson can be screened for Hg hot spots solely by GIS-based landscape approaches prior to resource-intensive sampling and analysis of Hg or Hg surrogates such as DOC and SUVA.

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