1. Introduction

Ecosystem contamination by Hg remains a widespread and global concern and poses a health risk to wildlife and human consumers of fish [Selin, 2009], despite recent evidence of decreasing mercury (Hg) emissions and resulting decreases in atmospheric Hg deposition in North America and Europe [Sunderland et al., 2008; Pacyna et al., 2009]. Methylmercury is a potent neurotoxin and is readily bioaccumulated and biomagnified in aquatic and terrestrial food webs [Mergler et al., 2007]. Contamination of remote ecosystems by atmospheric Hg deposition is widespread due to several factors including the long residence time of elemental Hg (Hg₀) in the atmosphere, the reemission of previously deposited Hg from terrestrial and aquatic environments, the wide dispersal of emissions sources, and interconversions among different Hg forms with varying deposition properties [Lindberg et al., 2007]. Atmospheric Hg deposition to remote forested ecosystems occurs via wet and dry deposition [Lindberg et al., 2007]. Litterfall and throughfall transfer atmospherically deposited Hg to soils [St. Louis et al., 2001; Risck et al., 2012] where it may be reemitted [Lindberg et al., 2007], adsorbed to soil organic matter [Grigal, 2003], transformed to methyl Hg (MeHg) [Benoit et al., 2002], or transported to adjacent surface waters [St. Louis et al., 1994; Selvendaran et al., 2008].

Human activities such as coal burning and cement manufacturing are major sources of global Hg emissions, with natural sources including volcanoes and geothermal activity playing a comparatively minor role [Selin, 2009]. Due to past and current human activities, contemporary global atmospheric Hg deposition rates are about threefold to sevenfold greater than presumed natural background rates [Streets et al., 2011; Amos et al., 2013]. The legacy of past Hg deposition is evident as large multidecadal stores in soils and aquatic sediment [Grigal, 2003]. Quantifying and modeling the roles of soil and sediment as sources of MeHg to surface freshwaters and aquatic biota are important research goals with implications for the spatial and temporal variation of MeHg in aquatic ecosystems.

Hg concentrations and loads in aquatic ecosystems have been modeled through many varied approaches that range from simple spatial predictive models based on categorical statistical associations to process-based temporal models that explicitly represent the rates of most of the relevant physical and
biogeochemical processes [Roué-Legall et al., 2005; Knightes, 2008; Futter et al., 2012]. Some have argued for simpler Hg modeling approaches because of high uncertainties in scientific understanding of relevant transformation processes and associated rate estimates [Ether et al., 2008]. Others have emphasized the benefits of employing multiple approaches including process-based and empirical models in diverse geographic settings, arguing for a modeling dialog because no currently available model is capable of accurately simulating all aspects of the Hg cycle [Golden et al., 2012]. Models with diverse conceptualizations of hydrologic flow paths can often yield equally accurate simulations of Hg concentrations and loads [Golden et al., 2012], which poses a challenge to advancing our understanding of the role of hydrology as a control of the temporal and spatial variation of surface water concentrations and loads.

Here we demonstrate insights that can be derived from a simple, inverse empirical Hg modeling approach based on statistical associations evident in a time series of measurements of MeHg concentrations in a stream ecosystem. Our focus here is on better understanding the controls on temporal variation in filtered methylmercury (FMeHg) concentrations in Fishing Brook, a fourth-order stream with low to moderate FMeHg concentrations (range <0.04 to 0.5 ng/L) in the Adirondack region of New York State, located in the northeastern U.S. This region has previously been characterized as a "hot spot" of high levels of Hg bioaccumulation due to several interrelated factors that include extensive forest cover, abundant wetlands and surface waters, and a location downwasting of Hg emissions sources in the Ohio River Valley [Evers et al., 2007; Yu et al., 2013].

Previous work at Fishing Brook and the surrounding Upper Hudson River basin has quantified key aspects of the Hg cycle in this watershed: (1) THg and MeHg in stream water is dominated by the filtered fraction [Schelker et al., 2011; Burns et al., 2012], similar to other forested upland settings, (2) wetlands concentrated in near-stream riparian areas are strongly associated with spatial variation of MeHg and THg concentrations at this site and in the surrounding region [Bradley et al., 2011; Burns et al., 2012], (3) THg concentrations are strongly related to the connectivity of riparian wetland areas to the stream as simulated during high flow by TOPMODEL [Schelker et al., 2011], and (4) MeHg shows contrasting temporal patterns to that of THg including evidence of supply limitation during high flow such as the annual snowmelt [Schelker et al., 2011]. MeHg concentrations in Fishing Brook and surrounding streams are clearly highest during summer [Selvendiran et al., 2008; Bradley et al., 2011; Schelker et al., 2011; Burns et al., 2012], and these warm season concentrations are a strong predictor of Hg bioaccumulation in fish [Riva-Murray et al., 2013]. The current study and empirical modeling approach seeks to build on this past work by exploring the seasonally varying climatic and hydrologic factors that best explain temporal variation of FMeHg concentrations in Fishing Brook. We hypothesize that seasonally varying temperature can explain much of the variation in FMeHg concentrations, but that variation in hydrologic flow paths as they relate to the depth of the water table in the stream riparian area will also explain a significant fraction of temporal variation. To explore the role of hydrology, metrics were derived based on the simulated riparian water table from a recent application of TOPMODEL in the Fishing Brook watershed [Nystrom and Burns, 2011]. Unlike a previous application of TOPMODEL to describe aspects of the Hg cycle at this site [Schelker et al., 2011], the focus here is on FMeHg rather than THg and on controls of FMeHg concentrations during low flow conditions in summer rather than snowmelt processes because of the importance of the warm weather season to Hg bioaccumulation. Our hope in undertaking this work is that the empirical modeling approach applied at this site will have application in other watersheds in the Adirondacks [Driscoll et al., 1998; Selvendiran et al., 2008], as well as in other regions where riparian wetlands serve as a major source of MeHg to streams [Krobbenhoff et al., 1995; Lee et al., 1998; Branfireun and Roulet, 2002]. We also seek an ongoing dialog with those who apply explicit process-based models to improve our understanding of controls on the formation and transport of MeHg to stream ecosystems.

2. Conceptual Basis for MeHg Modeling Approach

The modeling approach described in this paper arose from a developing conceptual understanding of the sources and processes that control the cycling of Hg in the Upper Hudson River basin of which Fishing Brook is a western headwater. A companion site on the Atlantic Coastal Plain of South Carolina was part of the same investigation but is not described nor modeled here, though this watershed shows many patterns of Hg cycling that are similar to the Upper Hudson basin [Bradley et al., 2011].
This modeling approach arose from recognition of the hydrogeomorphic landscape elements that are most important in explaining spatial variation in MeHg concentrations in the stream network within the Upper Hudson basin, including (1) upland headwaters, (2) lowland riparian areas commonly occupied by wetlands, and (3) open/ponded water [Bradley et al., 2011; Burns et al., 2012]. Upland streams provide little to no MeHg to the drainage network and have concentrations that are typically at or just above the method detection limit (0.04 ng/L). Landscape metrics based on percent riparian area, percent wetland area, or inverse distance-weighted wetland area are all strongly related to MeHg concentrations and loads in the Upper Hudson basin [Burns et al., 2012], similar to results from other watersheds in the Adirondacks [Driscol et al., 1998] and in many regions [St. Louis et al., 1994; Lee et al., 1998; Hall et al., 2008]. The riparian landscape is believed to be the principal source of MeHg to the stream network [Bradley et al., 2011; Burns et al., 2012]. Riparian soils have greater MeHg concentrations and greater methylation production potential rates than those of either stream sediment or upland soils, and groundwater seeps emanating in the riparian area have MeHg concentrations that generally exceed those in adjacent stream water during the warm weather season [Bradley et al., 2011; Burns et al., 2014]. MeHg concentrations and stores in soils also vary as a function of depth, with the greatest values found in the topmost 30 cm associated with the largest stores of organic matter [Burns et al., 2014]. Additionally, MeHg concentrations in riparian wetlands were greater in shallow pore water (20–40 cm depth) than deeper pore water (80–100 cm depth) in a nearby watershed <10 km from Fishing Brook in similar terrain [Selvendiran et al., 2008]. Despite the strong riparian MeHg source, the majority (81.6%) of the Fishing Brook watershed consists of nonriparian landscape, much of which is upland area with steep slopes. Thus, the interaction of headwater streams with the lowland stream network provides an important control on the dynamics of MeHg concentrations at the watershed outlet through mixing and dilution, and these upland areas may be a significant source of Hg that is eventually methylated in lowland areas [Mitchell et al., 2008].

After entering the stream network, MeHg may be lost from solution through a variety of processes including photoreduction and degassing, bacterial demethylation, sedimentation of particulate MeHg, and biotic uptake [Sellers et al., 1996; Hines and Brezonik, 2007]. We observed an inverse correlation between MeHg concentrations and loads and the influence of open water bodies (ponds and lakes) in the Upper Hudson basin [Bradley et al., 2011; Burns et al., 2012], presumably the result of some combination of the processes described above and consistent with results of previous studies [St. Louis et al., 1994; Branfreun and Roulet, 2002; Selvendiran et al., 2009].

3. Study Site

Fishing Brook is a 65.6 km² watershed that forms the westernmost headwaters of the Upper Hudson River basin in the Adirondack region of New York (Figure 1). The watershed is located in the Eastern Forest–Boreal Transition Ecoregion [Olson et al., 2001] and has a mean annual temperature of 4.4°C and mean annual precipitation of 1080 mm (1970-2000 mean values, Newcomb, NY, http://climod.nrcc.cornell.edu/, accessed on 7 August 2013). Forest is the dominant watershed land cover (86.3%, National Land Cover Database [Homer et al., 2007]); northern hardwoods (Acer saccharum, Fagus grandifolia, and Betula alleghaniensis) are dominant below 980 m, and spruce-fir (Picea rubens and Abies balsamea) dominate at higher elevations and in wet areas adjacent to surface waters. The watershed consists of upland areas with steep hillslopes, lowland streams bounded by riparian floodplains, and several open water bodies. Soils are dominantly Spodosols developed on coarse glacial till in hillslope areas and Entisols or Histosols developed in fluvial and glaciofluvial sediment in riparian areas [Silverman and Krawiecki, 2006]. The underlying bedrock is Precambrian metamorphic, and granitic gneiss is the most common rock type [Bohlen et al., 1985].

The watershed consists of 18.4% riparian area (determined by an elevation above creek channel approach [Burns et al., 2012]), and wetlands occupy about one third of this riparian area. Wetlands occupy 8.2% of watershed area (National Wetlands Inventory approach [LaPoint et al., 2004]), and three fourth of these wetlands are located within the riparian area. Additionally, 2.7% of the watershed is open water of which County Line Flow, a 32.2 ha lake, is discussed in this paper. Less than 1% of watershed area is affected by human land use in this largely undisturbed setting.
4. Methods

4.1. Field Methods

Forty-three stream samples were collected at the Fishing Brook at County Line Flow site (Figure 1) between January 2007 and September 2009 for analysis of MeHg, SO\textsubscript{4}\textsuperscript{2-}, and dissolved organic carbon (DOC) concentrations. Data are available for particulate MeHg and FMeHg, but only data on the dominant FMeHg fraction are discussed here; the particulate MeHg fraction averaged only about 16% of total MeHg during 2007–2009 in this watershed. Stream stage was recorded every 15 min at this sampling site for conversion to discharge based on a stage-discharge rating developed using current meter measurements made at the time of each sample collection according to methods described in Rantz et al. [1982]. Water temperature was recorded every 15 min at this site by a thermistor probe. Additionally, stream water samples were collected and accompanying current meter measurements of streamflow were completed 7 times during this study at a site immediately upstream of County Line Flow and in its principal tributary (Figure 1), and these data are used in net mass balance calculations for FMeHg and SO\textsubscript{4}\textsuperscript{2-} in this lake.

Samples were collected using a trace metal technique similar to Environmental Protection Agency (EPA) Method 1669 [U.S. Environmental Protection Agency (U.S. EPA), 1996], employing wrist-length nitrile gloves over shoulder-length polyethylene gloves. Samples were chilled on ice and filtered on the same day; those for FMeHg analysis through 0.7 μm pore size prebaked quartz filters, those for SO\textsubscript{4}\textsuperscript{2-} analysis through 0.45 μm membrane filters, and those for DOC through 0.7 pore size prebaked glass fiber filters. All filtered aliquots were stored in the dark until analysis; MeHg aliquots were acidified to 1% with HCl and stored at room temperature, whereas those for SO\textsubscript{4}\textsuperscript{2-} and DOC were stored at 4°C.

4.2. Laboratory Methods

MeHg analyses were performed at the U.S. Geological Survey Mercury Research Laboratory in Middleton, WI. MeHg was determined after distillation by ethylation, gas chromatographic separation, pyrolysis, and Cold Vapor Atomic Fluorescence Spectrometry as described by DeWild et al. [2002], which is a slight modification of EPA Method 1630 [U.S. EPA, 2001]. The method detection limit for water samples is 0.04 ng/L, unless exceeded by a daily detection limit calculated from analyses of blanks, in which case the latter was reported for the applicable analytical run. Data quality objectives (DQO) were generally ±10% for precision and accuracy of all QA/QC processes. Failure to reach any of the DQOs in a given run resulted in reanalysis until
these objectives were met. Matrix spike recoveries reported by the Wisconsin lab for runs that included the samples analyzed during this study averaged 97.1% ± 21.1% (relative standard deviation, RSD) based on 61 spikes. Five filter blanks were processed coincident with collection of the samples for this study, and all five had MeHg values less than the 0.04 ng/L method detection limit. Additionally, two duplicate samples of Fishing Brook were collected during the study, and the mean standard deviation of these values was 0.028 ng/L (RSD = 16.7%).

Analysis of SO\textsubscript{4}\textsuperscript{2-} was by ion chromatography according to the method described in Fishman and Freidman [1989]. Analysis of DOC was by the heated persulfate method [Peltzer et al., 1996].

### 4.3. Statistical Approach

Multiple linear regression is the basis of the empirical model developed herein. Potential predictive variables that were explored represented the influence of seasonality (water temperature, air temperature, sine and cosine functions, and day length), streamflow, and riparian water table depth patterns (mean depth below surface and consecutive days above and below selected depths). The riparian water table metrics were developed based on the application of TOPMODEL [Wolock, 1993] to represent the hydrologic response in the study watershed. Metrics were derived from the best model run as determined by calibration to a multiobjective function that placed an equal weight on streamflow and riparian groundwater levels as described by Nystrom and Burns [2011]. The riparian water table is derived from the mean topographic index within the area defined as riparian, as determined by an approach that used an elevation of 0.65 m above creek cell, as previously discussed by Burns et al. [2012]. The riparian area was further constrained to represent the principal geographic MeHg source areas by selecting only riparian areas with slope <10% (Figure 1), a cutoff that effectively eliminated steeper upland areas believed to contribute little MeHg to the stream [Burns et al., 2012].

All potential model independent variables that could be designated in a time-varying manner were calculated as mean antecedent values for 1d, 3d, 7d, 10d, 15d, 30d, 45d, 60d, and 90d (Table 1). A series of systematic steps were followed to sequentially evaluate the independent variables that best explained the temporal variation in MeHg concentrations at Fishing Brook during 2007–2009:

1. The strength of correlations (Spearman Rank) of all potential variables with FMeHg concentrations was evaluated, and similar variables (e.g., water temperature and air temperature) with the weakest correlations were eliminated.
2. Bivariate linear regression was used to select, for each variable, the antecedent days with the strongest correlations to FMeHg concentrations. Only the five antecedent values for each variable that showed the strongest correlations with FMeHg concentrations were considered further.
3. Residuals of bivariate regressions with the group of variables selected in step #2 were used to select variables for further consideration.
4. Linear regression models for each permutation of these 16 variables was then calculated and evaluated by examining \textit{R}\textsuperscript{2} values, \textit{p} values, variance inflation factors (multicollinearity, using a cutoff value <5.0), Akaike’s Information Criteria (most parsimonious model with fewest independent variables), and residuals (bias).
5. A best model was selected based on the analyses above. Normality and equal variance assumptions of the residuals of this model were tested. The dependent variable was log transformed and the regression

<table>
<thead>
<tr>
<th>Variable Groups</th>
<th>Full Variable Set Explored</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seasonality</td>
<td>Sin, Cosine, Day length</td>
</tr>
<tr>
<td>Seasonality</td>
<td>Mean antecedent water temp in degree Celsius (days) = 1, 3, 7, 10, 15, 30, 45, 60, 90</td>
</tr>
<tr>
<td>Seasonality</td>
<td>Mean antecedent air temp in degree Celsius (days) = 1, 3, 7, 10, 15, 30, 45, 60, 90</td>
</tr>
<tr>
<td>Streamflow</td>
<td>Mean antecedent specific stream discharge in mm/d (days) = 1, 3, 7, 10, 15, 30, 45, 60, 90, overland flow</td>
</tr>
<tr>
<td>Riparian water table</td>
<td>Mean antecedent depth in millimeter (days) = 1, 3, 7, 10, 15, 30, 45, 60, 90</td>
</tr>
<tr>
<td>Riparian water table</td>
<td>Consecutive days above depth in millimeter = 100, 200, 300, 400, 500, 600, 700</td>
</tr>
<tr>
<td>Riparian water table</td>
<td>Consecutive days below depth in millimeter = 100, 300, 500, 700</td>
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</table>

\textsuperscript{a}Riparian variables were derived from results of the best fit TOPMODEL simulation as described by Nystrom and Burns [2011].
recalculated if the untransformed model did not pass these tests, and the resulting residuals were tested again for normality and equal variance. Predicted values derived from a log model were bias corrected before analysis and presentation using a smearing estimator [Duan, 1983].

6. The best model was recalculated using maximum likelihood estimation (MLE) regression as recommended by Helsel [2005] because there were six censored values in the FMeHg data set. A pseudo-$R^2$ value, which can be interpreted similarly to an $R^2$ value from least squares regression, was calculated for all models derived from MLE regression [Laitila, 1993].

In the final empirical model, a term was included to describe the loss rate of FMeHg due to in-lake processes. This loss term was not considered simultaneously with the other potential independent variables when developing the multiple regression models because few measurements (seven) were available to allow a rigorous statistical evaluation of FMeHg concentrations upstream and downstream of ponds and lakes. Rather, the loss term was added to the model later using guidance from the literature [Sellers et al., 1996; Hines and Brezonik, 2007] by exploring a range of typical loss rates in open waters (0.02/d to 0.25/d), and the loss term that resulted in the closest agreement to measured losses in FMeHg concentrations through the pond was selected. Because this empirical approach slightly changed the overall model fit to the FMeHg data, we adjusted the coefficient for the parameter representing water temperature upward by 15% to maximize the fit of the final model. This is discussed in greater detail later in the text.

Model uncertainty was evaluated using the estimated 5% and 95% prediction intervals of the MLE regression model according to the method described in Nowell et al. [2009]. This approach provides an expected range of uncertainty if the regression was used to make future predictions of FMeHg concentrations. Additional insight to model uncertainty and also to address the issue of model overfit to the data set, a cross-validation approach was used [Snee, 1977]. This approach is considered acceptable when the model cannot be readily applied to an independent data set [Shao, 1993], as in the case of this study. In this validation approach, 1000 data sets were created from the 43 samples by randomly selecting 35 samples to build the regression and eight samples to test the model fit. This approach was applied to examine variation in the fit and coefficients of the regression model and also to examine fit in the validation data set.

5. Results and Discussion

5.1. Seasonal and Annual Patterns in MeHg Concentrations and Related Variables

FMeHg concentrations showed a strong seasonal pattern in Fishing Brook with the highest concentrations during middle to late summer and the lowest values in late winter through early spring (Figure 2a). The majority of the lowest values (six samples <0.04 ng/L detection limit) were observed during peak spring
FMeHg concentrations are inversely related to stream discharge, but this relation is seasonal and evident only during the warm weather season (1 May to 31 October), with dormancy during all 3 years (Figure 2a). These patterns are consistent with the roles of $SO_4^{2-}$-reducing bacteria as a key driver of methylation [Gilmour et al., 1992] and DOC as a key agent for Hg binding and transport (with thiol groups, the key binding sites). Similar patterns among MeHg, DOC, and $SO_4^{2-}$ have been observed in the Adirondacks and in other settings [Branfireun and Roulet, 2002; Selvendiran et al., 2008] and are believed to reflect temperature-driven seasonal patterns in $SO_4^{2-}$ reduction [DeVito and Hill, 1997; Inamdar and Mitchell, 2008], in the rates of DOC release from soil organic matter degradation [Christ and David, 1996; Clark et al., 2009], and consequently Hg methylation and mobilization. The seasonal increase in FMeHg concentrations is also correlated with an increase in stream Fe concentrations ($r = 0.74$, $p < 0.001$; data not shown), and because Fe-reducing bacteria are also capable of methylating Hg [Fleming et al., 2006], a role for Fe-reducers cannot be ruled out.

Interannual variation in FMeHg concentrations is evident, especially during the summer of 2007, when the peak values were less than half those observed during the summers of 2008 and 2009 (Figure 2a). The peak DOC concentration in summer 2007 (8.7 mg/L) was less than the peak values observed in 2008 (11.3 mg/L) and 2009 (11.7 mg/L), whereas the seasonal decline and minimum $SO_4^{2-}$ concentrations varied little among the three summers. This is reinforced by an observed strong inverse relation between FMeHg concentrations and those of $SO_4^{2-}$ during 2008 ($r = -0.62$, $p = 0.004$) and 2009 ($r = -0.80$, $p = 0.006$), but no significant relation in 2007 ($r = -0.28$, $p = 0.33$), whereas FMeHg concentrations were strongly related to those of DOC during all 3 years ($r = 0.58$, $p = 0.03$; $r = 0.73$, $p < 0.001$; and $r = 0.71$, $p = 0.02$ during 2007, 2008, and 2009, respectively). The similar seasonal decline in stream $SO_4^{2-}$ concentrations is consistent with a similar influence of seasonal $SO_4^{2-}$ reduction occurring in Fishing Brook riparian soils/groundwater during all 3 years. This is consistent with observations from other studies in the Adirondacks and in the boreal of Canada that $SO_4^{2-}$ reduction in riparian soils is the principal mechanism that lowers stream $SO_4^{2-}$ concentrations during the warm weather season [Branfireun and Roulet, 2002; Selvendiran et al., 2008]. The lower DOC and FMeHg concentrations during 2007 than in 2008 and 2009 are consistent with the discharge of riparian groundwater to the stream from a greater depth in riparian soils, where there is less soil organic matter and lower MeHg concentrations in soil [Burns et al., 2014].

FMeHg concentrations are inversely related to stream discharge, but this relation is seasonal and evident only during the dormant season (1 November to 30 April; Figure 3). Growing season concentrations are widely scattered with no apparent relation to discharge and reflect a narrower flow range than those of the dormant season, which are strongly influenced by snowmelt samples (Figure 3). The inverse relation of MeHg concentrations with dormant season discharge was first reported at this site by Schelker et al. [2011] and was attributed to supply-limited flushing behavior [Burns, 2005], suggesting a limited supply of MeHg relative to the flux of water through the subsurface during high flow conditions when soil temperatures are cold, implying that the rate of $SO_4^{2-}$ reduction and Hg methylation is temperature limited. A similar inverse relation of MeHg and streamflow has been observed previously in many other streams [Bishop et al., 1995a;
However, published studies show a range of MeHg-flow relations that include increases, no relation, and more complex patterns [Balogh et al., 2006; Brigham et al., 2009], which likely reflect varying interactions of seasonal temperatures, hydrology, and the juxtaposition and influence of different landscape types (termed the “hydrologic cascade”) [Branfrenun et al., 1998; Branfrenun and Roulet, 2002]. Reflecting the complex interaction of streamflow with these other factors, an inverse exponential regression explains only 40% of the variation in dormant season FMeHg concentrations at Fishing Brook (Figure 3), and when considered together with the lack of a significant relation of MeHg and flow during the growing season, indicates that no simple, dominant, year-round relation to hydrologic patterns is apparent at this site.

The effect of open water on diminishing stream FMeHg concentrations is an additional facet of these data that are consistent with our spatial conceptualization of this system. This pattern is illustrated by an analysis of the net mass balance of FMeHg for County Line Flow during the seven periods when samples were collected upstream, downstream, and at the principal lake tributary. These samples were generally collected within a 24 h period at relatively similar flow conditions with one exception in March 2007 during snowmelt. Snapshot mass fluxes of FMeHg and SO$_4^{2-}$ were calculated for each of these sites by combining concentration data with streamflow measurements collected simultaneously with the samples to calculate a net mass balance for County Line Flow during each sampling period. This analysis generally shows strong losses of FMeHg during six of the seven sampling periods that ranged from about 20% to >80% of the load immediately upstream of the lake (Figure 4). Mean FMeHg concentrations downstream of County Line Flow were about half the mean value upstream of the pond for the eight sampling periods. The March 2007 sample was an exception to this pattern. This sample reflects different conditions than the others and was collected during snowmelt when FMeHg concentrations were low, streamflow was changing sharply with time, and the lake was ice covered. The mass balance for this sampling period has high uncertainty, which may partly explain why FMeHg loads appear to be increasing on this date. Data for SO$_4^{2-}$ loads in County Line Flow are shown for comparison to those of FMeHg. These values indicate little net gain or loss of SO$_4^{2-}$ during transport through County Line Flow (except for the snowmelt samples with high uncertainty), suggesting conservative behavior and providing further confidence of large in-pond losses of FMeHg.

5.2. Development of Model

The conceptual understanding of the principal sources and sinks of FMeHg and the processes responsible for these observed patterns summarized above suggests an approach to modeling FMeHg concentrations in this stream that employs variables that reflect the combined influence of seasonal temperature, streamflow, transport from riparian areas to the stream, and open water. Our approach was not to develop a comprehensive model of all the processes and fluxes that affect the Hg cycle in a watershed. For example, we do not include gas fluxes, methylation and demethylation rates, numerous open water processes, particulate fluxes, atmospheric deposition, and others, focusing instead on key physical environmental variables that can be calculated from observed and modeled data and that are likely to influence stream FMeHg concentrations. These physically based predictor variables are believed to represent the influence of the dominant factors that control the rates of key biogeochemical (e.g., methylation) and hydrological (e.g., discharge of riparian groundwater) processes that affect the availability and transport of MeHg to the stream. Furthermore, we did not attempt to model MeHg using stream chemistry variables such as SO$_4^{2-}$ and DOC.

**Figure 4.** Net mass balance of FMeHg and SO$_4^{2-}$ in County Line Flow expressed as a percent of the load upstream of the lake for seven sampling dates during 2007–2009.
concentrations as others have done [Dittman et al., 2009]. Nonetheless, observations of the relation of FMeHg concentrations to those of SO$_4^{2-}$ and DOC concentrations informed our interpretation of processes and likely landscape-based sources and sinks.

The group of variables that were most highly correlated with FMeHg concentrations were those intended to represent seasonality, and among these seasonal variables, water temperature showed the strongest correlations ($r = 0.60$ to $0.69$, $p < 0.001$), though correlations with air temperature were only slightly weaker. Among the water temperature variables, the 10d, 30d, and 60d antecedent variables were most strongly correlated with FMeHg concentrations ($r = 0.69$, 0.67, and 0.68, respectively). These results indicate that metrics based on water temperature alone can explain a little less than 50% of the variation in these FMeHg data. The antecedent periods represented by these variables suggest that FMeHg concentrations measured in the stream reflect an integration of many prior days, which is consistent with stream MeHg originating in riparian soils near the stream channel with a lag governed by subsurface transport of shallow groundwater to the stream as well as downstream transport to the sampling site. The 60 day antecedent water temperature variable (WTemp60d) was ultimately selected for inclusion in the model based on an improved fit when other variables were included (Table 2). Seasonal temperature variation alone reasonably reproduces the annual patterns in FMeHg concentrations in Fishing Brook, especially the winter period of low concentrations (Figure 5a). However, seasonal temperature as the sole driver does not well represent the peak FMeHg concentrations in summer, overpredicting these values in 2007 and substantially underpredicting these values in 2008 and 2009. When streamflow (Q7d) is added to the WTemp60d variable in a multiple regression model, the ability to account for annual variation in FMeHg concentrations improves slightly (Figure 5a; $R^2 = 0.57$), but this model does not substantially improve the predictions in summer.

Only when the additional three TOPMODEL-based variables (WTable10d, Gt600mm, and Gt400mm; Table 2 and Figure 5b) that simulate the history and depth of the riparian water table are added to the model is there substantial improvement in accounting for patterns of FMeHg concentrations during June through September across all 3 years ($r = -0.71$, $p = 0.002$). For samples collected when the simulated riparian water table depth was $<600$ mm, mean FMeHg concentration was 0.27 ng/L, and when this depth was $>600$ mm, the mean value was 0.14 ng/L. The addition of the three TOPMODEL-derived variables in the MeHg model and the ability of these variables to improve predictions of FMeHg concentrations...
during the growing season point to the importance of the interaction of shallow groundwater with the principal source of MeHg in the uppermost riparian soil. Stream FMeHg concentrations decreased as the mean simulated riparian water table (WTable10d) moved deeper in the profile. A simulated water table depth of 600 mm appeared to be a threshold, and as the number of consecutive days the water table remained above 600 mm (Gt600mm) increased, FMeHg concentrations were greater as well. The significance of these two variables in the statistical model indicate that connection of the water table with the principal MeHg source in the shallow riparian floodplain soils is the key to understanding transport in the subsurface, especially during the growing season. These two variables explain an additional 22% of the variation in these data (Table 2) and help explain why FMeHg concentrations during the summer of 2007 were much less than those measured in the summers of 2008 and 2009. The final TOPMODEL-derived variable (Gt400mm) indicates a tendency for FMeHg concentrations to decrease slightly as the length of time the riparian water table remains above 400 mm increases. The significance of this metric is consistent with a buildup/washoff conceptualization of MeHg behavior in the warm weather season. A similar approach has been applied to describe the buildup and flushing behavior of DOC in soils in an effort to model stream DOC concentrations in the Rocky Mountains of Colorado [Boyer et al., 1996]. The significance of these terms suggests that stream FMeHg concentrations reflect, in part, a balance of (1) riparian water table connection to the MeHg source, but tempered by (2) limitation in the MeHg supply if the connection persists for too long.

The final empirical model includes a variable that accounts for the effects of County Line Flow, the open water body immediately upstream of the sampling site, on diminishing stream FMeHg concentrations (Table 2). The fit of this
model to the data is similar to the fit of the regression model, and the model was not developed using an MLE approach. However, we believe that a model that considers the net effects of open water on FMeHg concentrations is warranted by the data shown in Figure 4 and as discussed in many previous studies in the Adirondacks and elsewhere [Sellers et al., 1996; Branfireun and Roulet, 2002; Hines and Brezonik, 2007; Burns et al., 2012]. As part of fitting the final empirical model, the coefficient of the WTemp60d term was adjusted upward from 0.0252 in the five variable regression model to 0.029 in the final empirical model to improve the overall fit to the data after adding the chosen open water loss term of 0.04/day. County Line Flow has a slight warming effect (mean for seven samples shown in Figure 4 = +1.7°C) on stream water, and since the lake is modeled as a FMeHg sink, the model has to be adjusted to slightly increase the temperature sensitivity to FMeHg sources (presumably riparian soils) to maximize the final model fit.

5.3. Model Diagnostics and Uncertainty

The regression model predictions show good fit and little bias (slope = 0.90, y intercept = −0.076) across the range of FMeHg concentrations that were measured in Fishing Brook (Figure 7a). The mean bias of the observations from model predictions was −0.006 ng/L (min = −0.17, max = 0.002), and the mean relative bias was −8.6% (min = −92.1%, max = −1.2%). Additionally, all observations fall within the estimated 5% and 95% prediction intervals of the MLE regression (Figure 7b). The uncertainty of the model-predicted values as reflected by deviation from the upper (95%) and lower (5%) estimated prediction intervals is substantial, as expected of a regression model that despite an $R^2$ value of 0.81 is based on a log-transformed-dependent variable. Mean relative deviation of predictions from the lower interval (5%) was 0.07 ng/L, equivalent to a mean of 52.6% of the predicted concentration, and the mean relative deviation of predictions from the upper interval (95%) was 0.22 ng/L, equivalent to 77.5% of the predicted concentration. These prediction intervals indicate that the regression model developed at Fishing Brook would be expected to make predictions (within a confidence range of 90%) of FMeHg concentrations to within an accuracy range of about 50% to 80% of the real value for samples collected outside of the period of the current study.

Cross validation of the regression model reveals a generally robust identification of the independent variables as shown by variation in the coefficients and significance of these variables (Table 3). Coefficients generally ranged by about 10–20% of the median value for the 5th and 95th percentile of the 1000 model runs, with the exception of the Gt400mm variable that ranged more widely by about 40% from the median value. Furthermore, this variable had a median $p$ value of 0.053 and was significant ($p < 0.05$) in only about
47% of the model runs. This finding is not surprising given that the Gt400mm variable was only marginally statistically significant ($p = 0.044$) and explained little of the variation in FMeHg concentrations. This variable was included in the full model, because it met the criteria applied in the model development approach that was followed in this study. However, the cross-validation process further highlights the marginal nature of this variable.

The cross-validation predictions for the eight samples held out of each model run generally show good fit to the data (Table 4). Mean bias was low (median = 0.0009 ng/L) and had a fairly even distribution of positively biased ($\sim 51\%$) and negatively biased ($\sim 49\%$) fits. Nash-Sutcliffe efficiency of these model fits, though less than that of the full five-parameter model, are still generally strong with a median value of 0.72. A small proportion of the model runs showed somewhat weak fits, but in 85% of these runs, more than half the variation among the eight samples could be explained by the cross-validation regression models.

### 5.4. Relative Roles of Temperature and Hydrologic Variation

The model developed herein is based on data collected in a single watershed over a 33 month period, so caution is warranted in deriving generalizations from these results. However, the Hg cycle in the Fishing Brook watershed is believed to show similar behavior to other forested watersheds that are dominated by a MeHg source to the stream from riparian wetland areas such as those located throughout the Adirondacks, in the U.S. Coastal Plain, in the Upper Midwestern U.S., and in the boreal region of Canada and Scandinavia [Driscol et al., 1998; Bradley et al., 2011; Krabbenhoft et al., 1995; St. Louis et al., 1994; Bishop et al., 1995b]. The predictive ability of a variable that represents temperature and the improved predictive ability when the four variables are added that represent aspects of hydrology suggests that FMeHg concentrations in stream water in this and similar settings are sensitive to climate variation.

The important roles identified in this empirical model for water temperature, stream discharge, and riparian water table depth can provide useful feedback to existing process-based models that might guide future application of such models in a setting similar to Fishing Brook. First, the primacy of water temperature as a predictive variable suggests that net methylation is sensitive to seasonal variation in riparian soils. The coefficient of the WTemp60d variable of 0.029 in the final empirical model equates to a Q10 value of 1.95, close to the value of 2 often reported for Hg methylation [Rodgers et al., 1995] and similar to values used in some Hg models [Carroll and Warwick, 2001]. Although it is difficult to equate the coefficient for WTemp60d exactly to a Q10 value, the temperature sensitivity of FMeHg concentrations at Fishing Brook appears to exceed that observed and modeled for a stream in the Coastal Plain of South Carolina [Knightes et al., 2014] with similar riparian

### Table 3. Cross-Validation Results of the Five Parameter Multiple Regression Model Applied to Explain Controls on Temporal Variation in FMeHg Concentrations at Fishing Brook

<table>
<thead>
<tr>
<th>Variable</th>
<th>Median Coefficient</th>
<th>5% Coefficient</th>
<th>95% Coefficient</th>
<th>p Value</th>
<th>5% p Value</th>
<th>95% p Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>-0.668</td>
<td>-0.787</td>
<td>-0.556</td>
<td>$&lt;0.001$</td>
<td>$&lt;0.001$</td>
<td>$&lt;0.001$</td>
</tr>
<tr>
<td>WTemp60d</td>
<td>0.0252</td>
<td>0.0223</td>
<td>0.0278</td>
<td>$&lt;0.001$</td>
<td>$&lt;0.001$</td>
<td>$&lt;0.001$</td>
</tr>
<tr>
<td>Q7d</td>
<td>-0.0849</td>
<td>-0.103</td>
<td>-0.0745</td>
<td>$&lt;0.001$</td>
<td>$&lt;0.001$</td>
<td>$&lt;0.001$</td>
</tr>
<tr>
<td>WTable10d</td>
<td>-0.00099</td>
<td>-0.00116</td>
<td>-0.00076</td>
<td>$&lt;0.001$</td>
<td>$&lt;0.001$</td>
<td>0.007</td>
</tr>
<tr>
<td>Gt600mm</td>
<td>0.00074</td>
<td>0.00059</td>
<td>0.00089</td>
<td>0.002</td>
<td>$&lt;0.001$</td>
<td>0.019</td>
</tr>
<tr>
<td>Gt400mm</td>
<td>-0.00231</td>
<td>-0.00328</td>
<td>-0.00144</td>
<td>0.053</td>
<td>0.014</td>
<td>0.26</td>
</tr>
</tbody>
</table>

*The median, 5th percentile, and 95th percentile are shown for the regression model coefficients, and the p value of each coefficient based on 1000 multiple regression models developed from randomly selected subsets of 35 samples.

### Table 4. Measures of Fit Based on Cross Validation of the Five-Parameter Multiple Regression Model Applied to Explain Controls on Temporal Variation in FMeHg Concentrations at Fishing Brook

<table>
<thead>
<tr>
<th>Model Fit Measures</th>
<th>Median</th>
<th>5%</th>
<th>95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard error of estimate</td>
<td>0.143</td>
<td>0.095</td>
<td>0.187</td>
</tr>
<tr>
<td>Mean bias</td>
<td>0.0009</td>
<td>-0.088</td>
<td>0.10</td>
</tr>
<tr>
<td>Mean absolute bias</td>
<td>0.121</td>
<td>0.079</td>
<td>0.167</td>
</tr>
<tr>
<td>Nash-Sutcliffe coefficient</td>
<td>0.72</td>
<td>0.28</td>
<td>0.88</td>
</tr>
</tbody>
</table>

*Each of 1000 models was developed from randomly selected subsets of 35 samples, and predictions were made for the remaining eight samples. The median, 5th percentile, and 95th percentile are shown for these 1000 models fit to the eight samples.
control of MeHg delivery to the stream but with a sharply warmer dormant season and soils that are more sandy than those of Fishing Brook.

The empirical model developed here also indicates strong sensitivity to the simulated depth of the riparian water table. These model results await further confirmation by detailed measurements of FMeHg concentrations and fluxes in riparian groundwater in this setting. However, this model suggests strong depth sensitivity to the net methylation rate at Fishing Brook. This depth sensitivity could be simulated in models such as Visualizing Ecosystems for Land Management Assessment [Golden et al., 2012; Knightes et al., 2014] by setting the methylation rate to the highest value in soil layer 1 and decreasing this rate sequentially through layers 2–4 of the model. This empirical model also suggests that approaches that apply a depth partitioning of subsurface flow and Hg loads such as in the recently developed TOPOLOAD model [Golden et al., 2012] are likely to yield more accurate fluxes of MeHg to streams in settings similar to that of Fishing Brook.

6. Conclusions

The model developed in this study indicates seasonal and annual patterns in FMeHg concentrations in Fishing Brook are controlled by four factors: (1) seasonal surface water temperature variation, (2) streamflow, (3) riparian water table depth, and (4) presence of open water. As water temperature increases during the growing season, the net methylation rate and the rate of decomposition of soil organic matter are believed to increase in parallel resulting in peak FMeHg concentrations during summer and minimum concentrations during late winter and spring snowmelt. Increasing streamflow has a dilution effect on FMeHg concentrations, especially during the 1 November to 30 April dormant season when soil temperatures are cold and the rates of these biogeochemical processes are low. The modeled depth of the riparian water table provides contact of the saturated zone with the principal source of MeHg in the shallow riparian soils, which is then transported to the stream. Therefore, the water table depth acts as a principal control on FMeHg concentrations during the growing season, which can vary by more than twofold during dry summers relative to wet summers. This modeling approach highlights the potential interaction of key biogeochemical and hydrological processes as principal controls on the temporal patterns of FMeHg concentrations and reinforces the conceptual model previously developed for this watershed that transport from riparian soils to the adjacent stream is a dominant control on MeHg.

Acknowledgments

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References


