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## Using River Distance and Existing Hydrography Data Can Improve the Geostatistical Estimation of Fish Tissue Mercury at Unsampld Locations

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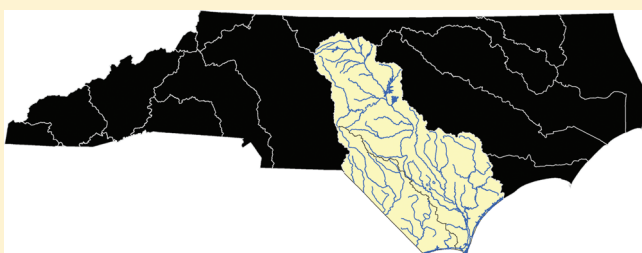
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**S** Supporting Information

**ABSTRACT:** Mercury in fish tissue is a major human health concern. Consumption of mercury-contaminated fish poses risks to the general population, including potentially serious developmental defects and neurological damage in young children. Therefore, it is important to accurately identify areas that have the potential for high levels of bioaccumulated mercury. However, due to time and resource constraints, it is difficult to adequately assess fish tissue mercury on a basin wide scale. We hypothesized that, given the nature of fish movement along streams, an analytical approach that takes into account distance traveled along these streams would improve the estimation accuracy for fish tissue mercury in unsampled streams. Therefore, we used a river-based Bayesian Maximum Entropy framework (river-BME) for modern space/time geostatistics to estimate fish tissue mercury at unsampled locations in the Cape Fear and Lumber Basins in eastern North Carolina. We also compared the space/time geostatistical estimation using river-BME to the more traditional Euclidean-based BME approach, with and without the inclusion of a secondary variable. Results showed that this river-based approach reduced the estimation error of fish tissue mercury by more than 13% and that the median estimate of fish tissue mercury exceeded the EPA action level of 0.3 ppm in more than 90% of river miles for the study domain.



### INTRODUCTION

**Mercury in the Environment.** Mercury (Hg) is an extremely reactive element that is present in air, water, and sediments because of both anthropogenic and natural sources.<sup>1</sup> Mercury is emitted into the atmosphere primarily by combustion of fossil fuels, various industrial processes, and natural sources including volcanic activity and emissions from geological deposits.<sup>2,3</sup> Atmospheric mercury undergoes photochemical oxidation and settles on land and water through wet and dry deposition. In an aquatic system, inorganic mercury can be transformed into methylmercury by bacteria in the water and sediment.<sup>4–6</sup> Methylmercury is the organic, neurotoxic form that is bioaccumulated by aquatic organisms, makes up the majority of total mercury in fish tissue (95–99%), and poses a significant risk to human health. Fish consumption is the primary vector for mercury movement from the environment into human populations.<sup>7</sup> Methylmercury can penetrate mammalian cells and alter cell division, which poses significant risk to developing fetuses and young children. Although methylmercury is primarily a neurotoxin, in high doses, it can also affect the kidneys and cardiovascular system.<sup>8,9</sup>

Many state and local agencies monitor fish tissue mercury (*FishHg*) and use this information to issue consumption advisories for particular areas and species of fish. As of 2008, in the United States alone, 43% of total lake acreage and 39% of all river miles were subject to fish consumption advisories.<sup>10</sup> However, assessing the spatiotemporal trends of *FishHg* in rivers on a larger scale, particularly when based on monitoring data, is a difficult task. The high variability in biotic (e.g., fish size, age, and trophic position) and abiotic (e.g., pH, dissolved organic carbon, sulfate) drivers of mercury movement in riverine systems further complicates the development of site- and species-specific consumption advisories.<sup>11–13</sup> Given these complexities, a robust method for estimating fish tissue mercury across broad spatial scales is necessary.

**Geostatistical Estimation Methods.** Geostatistical techniques, such as kriging, rely on the fact that many natural phenomenon exhibit spatial autocorrelation. Kriging methods

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construct a regional model of correlation to estimate variables at unsampled locations based on data from sampled locations.<sup>14–16</sup> Cokriging uses not only the spatial correlation of a single variable but also the correlations associated with other environmental variables. There have been numerous examples of cokriging for estimation of environmental variables ranging from soil salinity, suspended sediment, and rainfall to regional stream quality.<sup>17–20</sup> It is most beneficial where the primary variable is under-sampled with respect to the secondary variable. Generally, the inclusion of secondary information (i.e., secondary variables) results in more accurate local predictions than when considering a single variable alone.<sup>21</sup>

What these kriging approaches have in common is that they are linear estimators, and a more general approach to estimating at unsampled locations is the Bayesian Maximum Entropy (BME) method of modern space/time geostatistics.<sup>22</sup> The BME approach can be a non-Gaussian, nonlinear estimator, which can incorporate non-Gaussian soft data and any nonlinear relationship between primary and secondary variables and results in a combined spatiotemporal correlation model. Some comparisons of the BME approach with traditional kriging can be found in Christakos et al. and Pang et al.<sup>23,24</sup> The BME method provides a rigorous mathematical framework to process a wide variety of knowledge bases. Site-specific knowledge includes both hard data (e.g., monitoring data measured without error) and soft data (e.g., data with some associated uncertainty). Soft data can also be generated for a primary variable by expressing the relationship between it and one or more secondary variables in terms of a probability distribution.<sup>28</sup> In this respect, BME becomes a more generalized type of universal kriging.

With respect to river networks, river-BME has been developed as an extension of the BME framework by incorporating river distances into the geostatistical estimation of water quality parameters on a basin-wide scale.<sup>25,26</sup> The traditional approach used in kriging and BME relies on the Euclidean distance for the calculation of the correlation models. Money et al. showed that, for some water quality parameters, river-BME provided more accurate estimation maps than the Euclidean-based approach (Euclidean-BME). These studies, however, only examined ambient environmental parameters that were not inherently restricted by the configuration of the river network. Though estimation accuracy improved in these studies, we hypothesized that the estimation accuracy for variables affected by the configuration of the river network (i.e., mercury in fish whose movements are restricted to the river) could be further improved using river distance because the distance between estimation points may be better represented by a river distance rather than a straight-line, or Euclidean, distance.

**Secondary Variables Influencing the Bioaccumulation of Mercury.** Even though the primary focus of this work was the investigation of estimation accuracy using river distances, it is also beneficial to show how river-BME can be used to incorporate any secondary variables of interest into the space/time estimation process. The methylation and subsequent bioaccumulation of mercury is a complex biogeochemical process that can involve numerous secondary variables. A recent series of studies has examined several potential correlates to fish tissue mercury, including pH, sulfate, and dissolved organic carbon (DOC).<sup>5,11</sup> We chose two secondary variables: one that is a relatively reliable predictor of *FishHg* (pH) and a second whose correlation is highly uncertain (water column Hg; *WCHg*). Low pH has been shown to increase the amount of methylmercury

released from sediments, increasing its bioavailability.<sup>27,28</sup> *WCHg*, on the other hand, is typically present in very low amounts (i.e., ppt levels) and must undergo transformation to become bioavailable; however, according to Southworth et al.,<sup>29</sup> minute concentrations of aqueous mercury are capable of generating methylmercury at rates significant enough to warrant consumption advisories. We recognize that the relationship between these variables and *FishHg* is complex and involves a multitude of factors; however, we generate single relationships in this study to determine if knowledge of a single secondary variable (one that is abundant vs one that is scarce) can influence the river-based mapping accuracy of *FishHg*.

Therefore, the objectives of this study are as follows: (1) determine if the use of river distance in the covariance calculation can improve the mapping accuracy of *FishHg* at unsampled locations, using existing data; (2) determine if soft data generated from a relatively abundant secondary variable and a scarce secondary variable can provide additional mapping accuracy; and (3) apply the resulting geostatistical model to illustrate the spatiotemporal trends in *FishHg* for two river basins in eastern North Carolina.

## ■ MATERIALS AND METHODS

**Data and Study Area.** The case study involves the Cape Fear and Lumber River Basins in eastern North Carolina (Figure S1, Supporting Information). Both basins have active fish consumption advisories, and the entire Lumber Basin was listed as impaired in the state's 303(d) list of impaired waters as required by the Clean Water Act.<sup>30</sup> The Lumber Basin is approximately 3300 square miles and is primarily forested (60%) or agricultural (30%). The Cape Fear Basin, at 9300 square miles, is the largest basin in the state and contains close to 20% of the total population, or around 2 million people.<sup>31,32</sup>

Our database was compiled from several sources (Table S1, Supporting Information). *FishHg* data were obtained from the North Carolina Department of Environment and Natural Resources (NCDENR) and through the North Carolina Division of Water Quality (NCDWQ) Fish Tissue Assessment Program. The database of *FishHg* and secondary variables was assembled by researchers at North Carolina State University, and a complete description of this database can be found in Sackett et al.<sup>33</sup> Only those data within the Cape Fear and Lumber Basins were used for the period 1990–2004. Collocated pH data and *FishHg* were obtained from this database, and additional pH measurements were downloaded from the National Water Information System through the United States Geological Survey (NWIS-USGS). Surface water total mercury data were collected by NCDWQ as part of the Eastern Regional Mercury Study and combined with data downloaded from the NWIS.<sup>34,35</sup> The few duplicate measurements (i.e., data collected at the same location on the same day) were averaged to a single value.

**Generation of Fish Tissue Mercury Soft Data from Multiple Secondary Variables.** The *FishHg* data in this study were considered hard data (that is data from observations with little to no explicit uncertainty). However, the availability of secondary variables provides an opportunity to generate additional soft data about *FishHg*. Soft data are derived from uncertain observations and can take both Gaussian and non-Gaussian forms (i.e., intervals, fuzzy logic). Additionally, Money et al. described a linear regression framework for generating soft data from secondary water quality variables in the context of creating *E. coli*

soft data from turbidity measurements.<sup>26</sup> In this study, we use a similar approach to generate soft data for *FishHg* based on either pH or WCHg, for reasons described previously.

To fully illustrate the potential effects of river distance on *FishHg* estimates, we found the common downstream outlet for the Cape Fear and Lumber basins, essentially treating them as one continuous network. There were a total of 143 points in the combined system where both *FishHg* and pH were measured. Using these collocated points, a simple regression analysis was performed using log-transformed data to create a relationship of predicted *FishHg* given pH (eq 1;  $R$ -squared = 0.17):

$$\log -\text{FishHg} = -0.6\text{pH} + 3.3 \quad (1)$$

where log-*FishHg* is expressed in log-mg/kg (or ppm) and pH is in standard units. Using this relationship, the log-*FishHg* prediction variance was calculated using the *predint* function in Matlab (see Figure S2, Supporting Information, for the prediction bounds). Finally, for every space/time point where pH (but not log-*FishHg*) was measured, a Gaussian probability distribution function (PDF) was constructed for log-*FishHg* with a mean given by eq 1 and a variance corresponding to the prediction variance at the measured pH. This resulted in soft log-*FishHg* data of Gaussian probabilistic type at 356 space/time points. We should note that it was not our goal to fully model the pH-*FishHg* relationship but rather to devise a simplistic relationship based on the available data and extract what information we could from that relationship to generate soft data. The soft data, in turn, takes into account this inherent uncertainty by way of the variance of the Gaussian PDF.

There were a total of 35 points where both *FishHg* and WCHg were measured during the study period. Again, using these collocated points, we constructed a simple relationship to predict *FishHg* using log-transformed data (eq 2;  $R$ -squared = 0.03):

$$\log -\text{FishHg} = 0.25\log -\text{WCHg} - 3.40 \quad (2)$$

where log-*FishHg* is expressed in log-mg/kg (or log-ppm) and log-WCHg is expressed in log-ng/L. For every space/time location where WCHg was measured, a Gaussian probability distribution function was constructed for log-*FishHg*, with a mean given by eq 2 and variance corresponding to the prediction variance at the measured log-WCHg. This resulted in soft log-*FishHg* data of Gaussian type at an additional 80 space/time locations.

The models shown in eqs 1 and 2 are simplified expressions of a complex system that has many potential secondary variables. The pH alone accounted for approximately 17% of the variability in *FishHg*, while surface water mercury accounted for only 3% of the variability, which is consistent with the idea that methylmercury formation and bioaccumulation are influenced by a combination of several factors. Scatter plots for the regressions and summary statistics for the *FishHg*, pH, and SWHg are described in Supporting Information.

**Integrating Hard and Soft Data.** The BME method of modern space/time geostatistics was used to integrate these hard and soft data and obtain statistical estimates of log-*FishHg* at unmonitored locations. Both Euclidean-BME and river-BME procedures consist of defining the prior general knowledge (e.g., covariance) and site-specific knowledge (e.g., monitoring data, soft data). BME consists of epistemic knowledge base blending, which operates like Bayesian updating, to obtain a posterior PDF characterizing log-*FishHg* at any point on the river.

The BME method (Euclidean-BME) is described fully in Christakos<sup>24</sup> and Serre et al.,<sup>36</sup> and a summary of the typical BME equations appears in De Nazelle et al.<sup>37</sup> The BMElib numerical implementation is described in Serre et al.,<sup>36</sup> Serre and Christakos,<sup>38</sup> and Christakos et al.<sup>39</sup> The river-BME framework and *riverlib* extensions to BMElib are fully described in Money, along with several water quality applications.<sup>40</sup>

#### Space/Time Covariance Models That Use River Distances.

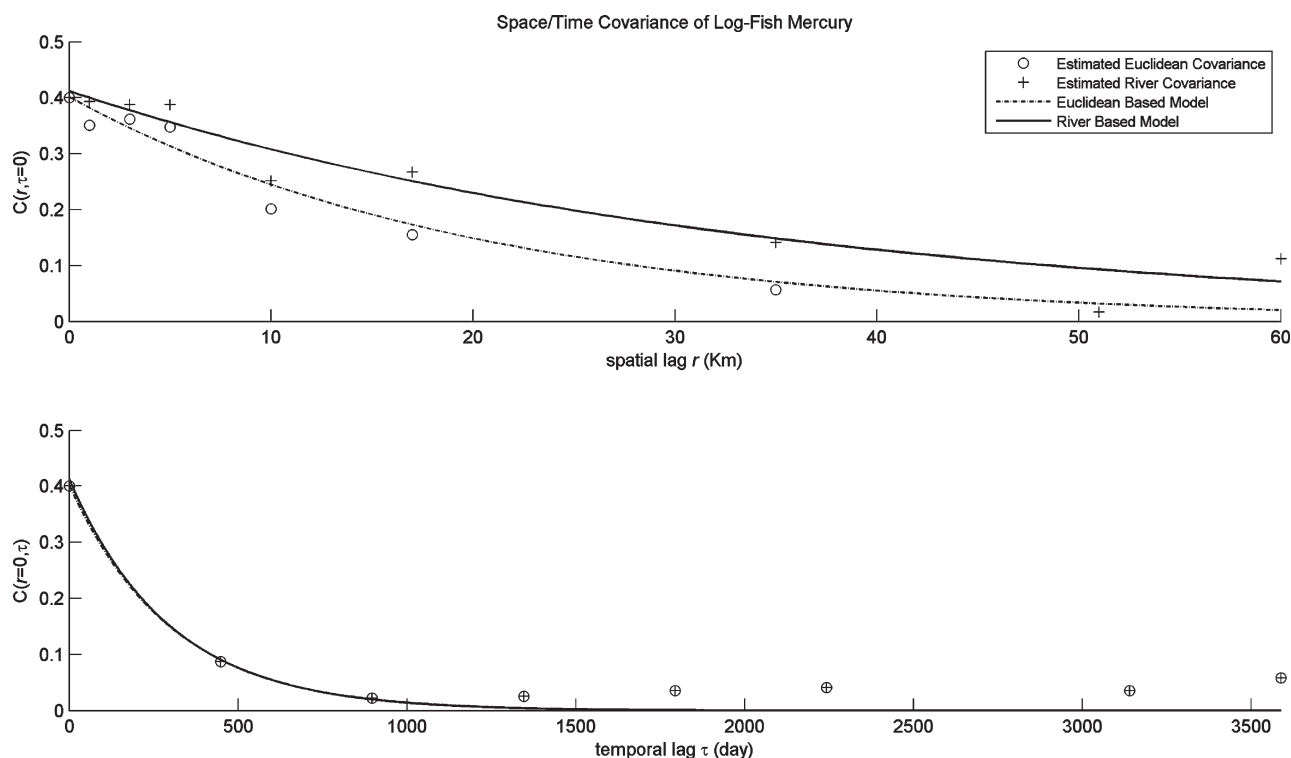
As with previous water quality studies using river-BME, a covariance model is selected that uses either a Euclidean or river distance. We restrict our model choice to the isotropic exponential covariance model since it has been shown to be permissible when river distances are used.<sup>41,42</sup> Both flow and overland transport can affect the correlation between points; however, using a purely flow-weighted covariance could bias the correlation by not taking into account overland transport and vice versa. In addition, using only flow in the correlation model in this study could eliminate too many data points along parallel reaches, resulting in too few spatial neighbors to perform an accurate estimation at unknown locations. Finally, fish can move upstream and downstream, and this would not be taken into account if only flow distance in the correlation was used. Therefore, we used the isotropic river distance to penalize the correlation between points on parallel reaches but not fully disregard them when calculating the covariance and estimation. Using this model, the space/time separable covariance of log-*FishHg* between space/time points  $\mathbf{p} = (s, t)$  and  $\mathbf{p}' = (s', t')$  is expressed as

$$\text{cov}(\mathbf{p}, \mathbf{p}') = c_0 \exp\left(\frac{-3h}{a_r}\right) \exp\left(\frac{-3\tau}{a_t}\right) \quad (3)$$

where  $t$  and  $t'$  are times,  $h = d_\alpha(s, s')$  and  $\tau = |t - t'|$  are the spatial and temporal lags, respectively, and  $d_\alpha(s, s') = \alpha d_R(s, s') + (1 - \alpha)d_E(s, s')$  is an  $\alpha$ -weighted average of the Euclidean distance  $d_E(s, s')$  and the river distance  $d_R(s, s')$ . In this study, we used either  $\alpha = 0$  (Euclidean distance) or  $\alpha = 1$  (river distance). For each value of  $\alpha$ , the parameters ( $c_0$ ,  $a_r$ ,  $a_t$ ) of the covariance model (3) were obtained using a least-squares fitting between the covariance function and experimental covariance values calculated from the hard log-*FishHg* data. Therefore, the general BME assumptions for this study include a Gaussian space/time random field, zero mean trend, the covariance function (eq 3), and Gaussian soft data.

**Comparing Euclidean and River Estimations.** A comparison was made between estimations using the river distance described above and estimation using the typical Euclidean distance, where soft data from measured pH and measured WCHg were included in both cases. A cross-validation analysis was performed to calculate the mean square error (MSE) of four different scenarios to determine the best model for estimating basin-wide log-*FishHg* (Table S2, Supporting Information). Each hard data point was removed, one at a time, and re-estimated using the remaining hard and soft data. The estimated value was then compared to the measured value to obtain the MSE. Scenario 1 used the measured log-*FishHg* data with Euclidean-BME. Scenario 2 contained the same data as Scenario 1, except river-BME was used. Scenario 3 built upon Scenario 2 by adding in the pH data (incorporated as the soft Gaussian data constructed using eq 1). Scenario 4 built upon Scenario 2 by adding in Gaussian soft data from WCHg using eq 2. The method with the lowest MSE was then used in the assessment and estimation of *FishHg* for the Cape Fear and Lumber Basins.





**Figure 1.** Spatial (top) and temporal (bottom) covariance of log-*FishHg* in the Cape Fear and Lumber Basins, North Carolina. Experimental covariance values estimated from data are shown with markers, while the covariance models obtained by fitting eq 3 to the markers are shown with lines. The covariance was calculated and modeled using both a Euclidean distance (dashed line) and river distance (plain line);  $R$ -squared values were 0.9219 for the river model ( $SSE = 0.01$ ) and 0.9294 for the Euclidean model ( $SSE = 0.008$ ).

**Estimation of Fish Tissue Hg.** Using the selected scenario within the BME framework, we estimated log-*FishHg* at equidistant estimation points (i.e., distributed at a fixed interval of 0.1 km) along the combined Cape Fear and Lumber network. For each estimation point, we selected the hard and soft log-*FishHg* data situated in its local space/time neighborhood and calculated the corresponding BME posterior PDF describing log-*FishHg* at that estimation point. The variance of the BME posterior PDF provided an assessment of the estimation uncertainty, while the back-log transform of the mean of the BME posterior PDF was used as an approximation of the median estimator for *FishHg* concentrations. This estimate was then used to produce choropleth maps of estimated *FishHg* concentration and calculate the fraction of river miles that exceeded the specified action levels.

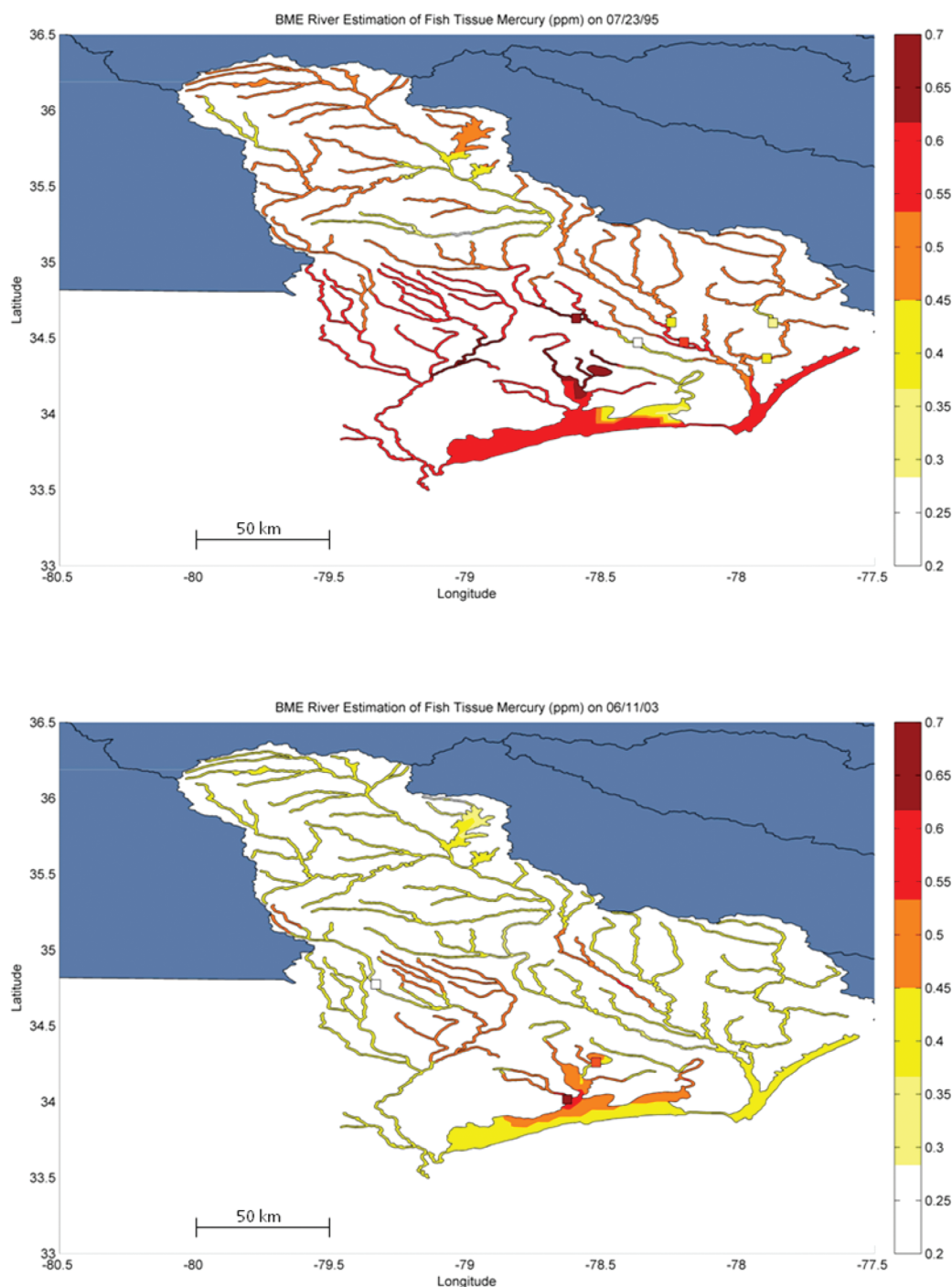
**Assessment of Impaired River Miles.** The fraction of river miles impaired at any given time was calculated by determining the fraction of equidistant estimation points that exceeded a given action level for *FishHg*. There are currently three different action levels for *FishHg*. The Food and Drug Administration (FDA) has determined a consumer action level of 1.0 ppm (or mg/kg).<sup>43</sup> The state of North Carolina has declared a more stringent action level of 0.4 ppm.<sup>44</sup> In addition, the USEPA has set the most stringent mercury action level at 0.3 ppm.<sup>45</sup> For the Cape Fear and Lumber Basins, the fraction of total river miles exceeding each of these threshold concentration values was calculated independently.

## RESULTS AND DISCUSSION

**Covariance Analysis.** The structure of the covariance model (with parameters  $c_0$ ,  $a_r$ , and  $a_t$ ; eq 3) provided insight into the

variability and correlation between *FishHg* data points (Figure 1). The variance and temporal range were  $c_0 = 0.41 \log\text{-ppm}^2$  and  $a_t = 890$  days, respectively, for both models. The spatial range  $a_r$  was 58 km for the Euclidean model and increased almost 2-fold to 102 km for the river model. Hence, the spatial covariance range ( $a_r$ ) indicated that 95% of the correlation in *FishHg* was lost after about 58 km across land, compared to 102 km along the river, with a quicker loss of correlation at distances less than 500 m when the Euclidean distance was used. This suggested that, by accounting for river distance, *FishHg* was spatially correlated over longer distances than if the constraints of the river network were not taken into account. This makes sense physically, given that fish are inherently restricted to movement pathways that follow the river network configuration. Conversely, if a Euclidean distance was used, the correlation between measurements of *FishHg* can be lost over a short distance because fish do not travel across land. The typical range of fish movement may also be a factor in the loss of more than 50% of the correlation after only 10 km. The heterogeneous fish samples in this study have a home range of 30 m to more than 1 km, depending on the species. Temporally, *FishHg* may remain highly correlated for a period of about 2–3 years. This is understandable given that bioaccumulated mercury may change gradually over time, depending upon the characteristics of the water body and fish community. The majority of fish samples in this study were obtained from young adult Largemouth Bass (22%), Sunfish (25%), and Bowfin (12%), with typical lifespans ranging from 7 years (Bowfin) to more than 20 years (Bass and Sunfish).

**Cross-Validation Analysis.** The cross-validation analysis resulted in mean square errors of:  $MSE_1 = 0.3040$  ( $\log\text{-ppm}^2$ ) for

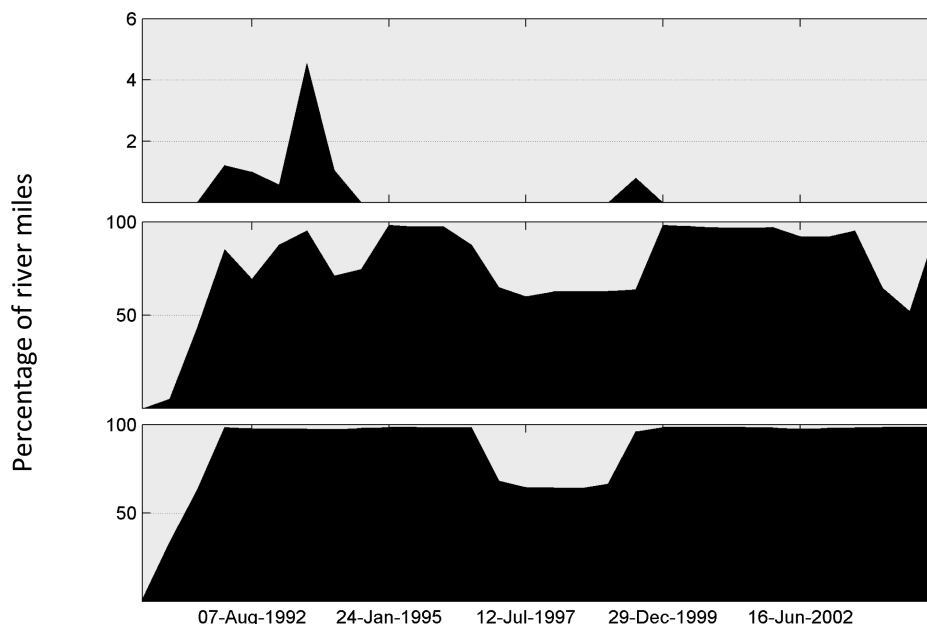


**Figure 2.** River-BME fish tissue mercury estimations (ppm) in the Cape Fear and Lumber Basins on July 23, 1995 (Top) and June 11, 2003 (Bottom). Squares indicate locations of actual fish tissue measurements; a map of the variance across stream segments can be found in Figure S5 in Supporting Information.

Scenario 1,  $MSE_2 = 0.2637$  ( $\log\text{-ppm}^2$ ) for Scenario 2,  $MSE_3 = 0.2556$  ( $\log\text{-ppm}^2$ ) for Scenario 3, and  $MSE_4 = 0.2555$  ( $\log\text{-ppm}^2$ ) for Scenario 4. Using river-BME over Euclidean-BME, with only hard data, reduced estimation error by  $(MSE_1 - MSE_2)/MSE_1 = 13\%$ . This was a larger reduction than that obtained in previous studies that examined river-BME for DO and for *E. coli*.<sup>25,26</sup> Those studies resulted in a 10–11% decrease in error. This suggests that river-BME is particularly useful for parameters, such as fish data, that are known to be restricted by

the river network configuration and affected by the ability of fish to move both upstream and downstream.

The incorporation of soft *FishHg* data via pH as a secondary variable in river-BME further reduced the MSE by  $(MSE_2 - MSE_3)/MSE_2 = 3\%$ . Even though this is a smaller reduction than that seen from soft data in the *E. coli* study by Money et al.,<sup>26</sup> it is significant because fewer soft data points were available in this study. In the *E. coli*/turbidity study, there were over 700 additional soft data points added to the analysis and covering a



**Figure 3.** Percentage of river miles with fish tissue mercury median estimate exceeding mercury action levels set by the FDA (top; 1.0 ppm), North Carolina (middle; 0.4 ppm), and the EPA (bottom; 0.3 ppm).

much smaller land area. In this study, there were only  $\sim 300$  additional soft data derived from pH. Hence, the estimation error may be even further reduced if more data points can be included as secondary variables.

The incorporation of WCHg in river-BME also reduced the MSE by  $(\text{MSE}_2 - \text{MSE}_4)/\text{MSE}_2 = 3\%$ . This result is significant because the MSE reduction from WCHg is as strong as that obtained from pH, even though there were only  $\sim 30$  additional soft data points derived from WCHg, while there were  $\sim 300$  soft data points derived from pH.

Overall, when river-BME with pH as a secondary variable was used, there was a  $(\text{MSE}_1 - \text{MSE}_3)/\text{MSE}_1 = 16\%$  reduction in estimation error as compared to Euclidean-BME without soft data. This suggests that accounting for the hydrogeography of the system as well as variables that affect the bioaccumulation of mercury will result in more accurate estimations of fish tissue mercury along unsampled streams.

**Assessment of Fish Tissue Mercury.** Using river-BME with pH as the secondary variable (Scenario 3), we obtained median estimates of *FishHg* concentrations calculated every 180 days over the study period between 1990 and 2004 (Figure 2). A movie showing the *FishHg* levels estimated across the study area for each of these times can be viewed in Supporting Information. In the combined basin, the median estimate of *FishHg* exceeded the most stringent action level of 0.3 ppm in more than 90% of river miles for a majority of the study period. There were more fluctuations in the percent of impaired river miles when the action level was increased to the current North Carolina level of 0.4 ppm; however, over 50% of river miles still had median estimates of *FishHg* exceeding 0.4 ppm for almost the entire study period. In addition, during the years 1990–1994, between 1 and 4% of river miles had a median estimate of *FishHg* above even the most lenient action level of 1.0 ppm set by the FDA. Another small peak was seen in 1998; however, at least with respect to the FDA, the majority of waters remained below this action level. No river miles had a median estimate of *FishHg*

exceeding the FDA action level since 1999, according to these results (Figure 3). Generally, the Lumber Basin exhibited higher potential, both spatially and temporally, for contaminated fish. Our modeling results were consistent with current trends; the entire Lumber Basin has been listed as impaired for fish tissue mercury since at least 2002.<sup>30</sup> As expected, due to the spatial and temporal scarcity of the measurements during the study period, the uncertainty in our estimations (via the estimation variance; Figure S6, Supporting Information) increased when the estimation was performed on days when no measurements were taken and in areas far away from measured values. This result further illustrates the need for additional sources of soft data.

One interesting result is an apparent decline in overall fish tissue mercury concentrations in the southeastern portion of the study area between 1991 and 2004. As Figure 2 and the supplementary movie (link in Supporting Information) show, concentrations remained well above 0.5 ppm until the past few years of the study period, when levels decreased to less than 0.4 ppm in many instances. An examination of mercury deposition trends in this region during this time period suggests that decreased deposition may have played a role in the estimated decrease in fish tissue mercury. Results from the mercury deposition network (MDN), which is part of the National Atmospheric Deposition Program,<sup>46</sup> show total deposition above  $18 \text{ ug/m}^2$  in 1995 and then fluctuation between 9 and  $14 \text{ ug/m}^2$  over the last three years of the study period.

In sum, our study adds to the recent literature emphasizing the importance of the use of river distances to estimate environmental quality parameters along river networks, and to our knowledge, it is the first study to do so in a space/time river-BME framework applied to a fish environmental parameter. First, we find that using a river geostatistical framework is particularly relevant for a fish environmental parameter because fish have the ability to swim both down and up stream, which is consistent with the way the river distance  $d_R(s, s')$  is calculated between any points  $s$  and  $s'$ . We recognize that a flow-and-distance model, as

described by Ver Hoef et al.,<sup>41,42</sup> may also provide relevant correlation functions, and the incorporation of flow-weighted distances would be an important next step. Second, we demonstrated the ability of river-BME to efficiently integrate a secondary variable such as pH, which resulted in estimation maps that were overall 16% more accurate than maps obtained with the classical estimation approach ignoring river distances and secondary variables. Third, we illustrate that our river-based geostatistical framework can also improve estimation accuracy of fish tissue mercury using a highly uncertain and weak correlate, such as WCHg, which means that more accurate maps of fish tissue mercury can be produced in areas where stronger correlates (such as pH, DOC, or sulfates) may not be measured.

River-BME provides a good framework for further decreases in estimation error as more data on these secondary variables become available. This case study represents an idealized river network, where the only restriction on distance is the configuration of the network; however, other barriers, such as the presence of dams, could influence the correlation structure for fish tissue mercury. Future model refinement should examine the distribution of dams along with other variables to determine if further restrictions are needed. Future work will also consider the joint integration of additional secondary data from multiple sources, which should lead to further reductions in estimation error. FishHg can vary significantly due to a suite of biotic and abiotic factors. Therefore, distinguishing between the natural spatiotemporal trends and species specific trends can be difficult if the monitoring data is heterogeneous, as in this study. Wentz<sup>47</sup> described an interesting approach to this problem by developing a statistical model for distinguishing trends in FishHg concentration using a combination of covariance and multiple linear regression. Consequently, incorporating additional information about species type and habitat patterns, as well as DOC, sediment data, and other variables, could result in even more accurate maps. Overall, the framework developed in this study is a good starting point and can aid environmental managers in the identification of areas where sampling resources and advisories can be more efficiently targeted.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Figures showing the study area and data locations, along with tables describing the estimation scenarios; additional regression statistics, along with maps of the estimation variance; and a movie link depicting spatiotemporal trends in fish tissue for every 180 days of the study period. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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