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Mercury in South Carolina Fishes, USA

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Abstract The South Carolina Department of Health and Environmental Control has collected, processed, and analyzed fish tissue total mercury (Hg) since 1976. For this study, skin-on-filet data from 1993 to 2007 were examined to determine biotic, spatial and temporal trends in tissue Hg levels for SC fishes. Because of the relatively high number of tissue Hg values below the analytical detection limits interval censored regression and censored least absolute deviations were used to construct several models to characterize trends. Large pelagic, piscivorous fish species, such as bowfin (*Amia calva* Linnaeus 1766), had higher levels of tissue Hg than smaller omnivorous species. Estuarine species had relatively low levels of tissue Hg compared to freshwater species, while two large open ocean species, king mackerel (*Scomberomorus cavalla* Cuvier 1829) and swordfish (*Xiphias gladius* Linnaeus 1758), had higher tissue Hg readings. For a given fish species, length was an important predictor of tissue Hg with larger individuals having higher levels than smaller individuals. The USEPA Level III ecoregion and water body type from where the fishes were collected were important in predicting the levels of tissue Hg. The Middle Atlantic Coastal Plain ecoregion had fishes with the highest levels of tissue Hg, while the Piedmont and Southern Coastal Plain ecoregions had the lowest. For a given ecoregion, large reservoirs and regulated rivers had fish with lower levels of tissue Hg than unregulated rivers. For reservoirs, the size of the impoundment was a significant predictor of tissue mercury with small reservoirs having higher levels of tissue mercury than large reservoirs. Landuse and water chemistry accounted for differences seen in fish of various ecoregions and waterbody types. Sampling locations associated with a high percentage of wetland area had fish with high levels of tissue Hg. Correlation analysis showed a strong positive relationship between tissue Hg levels and water column iron, total organic carbon, ammonia, and total kjedahl nitrogen, and a negative relationship with alkalinity, dissolved oxygen and pH. Results from principle component analysis revealed patterns between waterbody type and water chemistry variables that suggests hydrologic modification can have profound effects on the levels of fish tissue Hg in riverine systems. From 1993 to 2007, fish tissue Hg levels have trended lower. A spike in tissue Hg levels was observed in 2003–2005. The drying and rewetting of the landscape after the 2002 drought is hypothesized to have caused an increase in the methylation efficiencies of the system.

Keywords Mercury · Fish tissue · Advisory · Ecoregion · Censored · Wetland

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Introduction

Mercury (Hg) is a naturally occurring metal that can cause adverse health effects to exposed humans and other

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animals (Mergler et al. 2007). Mercury can be released into the environment by natural causes, such as forest fires and volcanic eruptions, or by anthropogenic activities, such as the combustion of fossil fuels (Lindberg et al. 2007). If released into the atmosphere, Hg can be deposited in terrestrial and aquatic ecosystems far from its original source (Lindberg et al. 2007). After deposition, Hg can be methylated through biochemical processes into methylmercury (MeHg), and it is this form that can be biomagnified in the food chain (Munthe et al. 2007). For this reason, various government agencies, worldwide, have issued consumption advisories for fish and other aquatic life that may pose a health risk to humans (Mergler et al. 2007).

The South Carolina Department of Health and Environmental Control (SCDHEC) began collecting, processing, and analyzing the tissue of fish and other aquatic life in 1976. Consumption advisories were first issued by SCDHEC in 1976 and continue to date (SCDHEC 2009). While tissue data were collected from 1976 to 1992, it was not until 1993 that SCDHEC began the comprehensive fish tissue monitoring efforts that exist today. Between 1993 and 2007, the agency collected and analyzed approximately 18,000 specimens from over 200 stations across South Carolina. Kamman et al. (2005b) provided analyses of a similarly large data set, but from a broader geographic range in North Eastern North America and Southern Canada. Their data were compiled from 24 different studies and provided patterns of fish tissue Hg at the subcontinental scale. Our study provides analysis of an extremely large data set of tissue Hg data collected throughout South Carolina. The data set provides an advantage over those assembled from different agencies because of the use of similar methods and analytical techniques, both temporally and spatially, making results more comparable. While the area of South Carolina is relatively small (approximately 83,000 km^2), it provides on excellent unit for ecological studies because of its diverse geographic features. We chose to rely on the ecoregion concept of Omernick (1987), and refined by Griffith et al. (2002), which stratifies the state into 5 Level III ecoregions: Blueridge (BR), Piedmont, Southeastern Plains (SEPS), the Middle Atlantic Coastal Plain (MACP), and the Southern Coastal Plain (SCP; abbreviations our own). The ecoregion concept of Bailey (1976) indicates 3 provinces in South Carolina but we chose Omernick (1987) scheme, which in our opinion better reflects patterns and processes seen in aquatic systems of South Carolina. Features such as elevation and geology in these ecoregions contribute to the diversity in the biological, chemical and physical features of South Carolina's waterbodies, which in turn has a profound effect on fish tissue Hg levels. Our study provides a comprehensive analysis of species, spatial, and temporal trends of Hg in the tissue of South Carolina fishes along with conceptual models to account for observed patterns.

Materials and methods

Datasets

The SCDHEC began collecting fish tissue total mercury data in 1976. From 1976 to 1992, both freshwater and saltwater specimens were collected statewide using a variety of techniques including hook and line, seining, and electroshocking. Whole fish and headless- eviscerated fish were processed during this period. This historic data set contains a relatively small number of specimens and was not used in the current analysis. In 1993, the SCDHEC began a more comprehensive fish tissue monitoring and advisory program. Skin-on-filets were used exclusively and lengths and weights of each specimen were recorded. Figure 1 shows sample locations of specimens collected between 1993 and 2007. Approximately half of the freshwater stations were sampled annually while the others were sampled once every 5 years (SCDHEC 2008). All freshwater species were collected using Smith-Root or Duracraft Electrofishing Boats according to the *SCDHEC Environmental Investigations Standard Operating Procedures and Quality Assurance Manual* (SCDHEC 2001). Fish tissue were processed and analyzed as outlined in SCDHEC (2001). Fishes off the South Carolina coast were collected by the South Carolina Department of Natural Resources (SCDNR) Marine Resources Research Institute (MRRI) as part of their Marine Resource Monitoring Assessment and Prediction (MARMAP) Program and the Southeast Area Monitoring and Assessment Program: South Atlantic Program (SEAMAP; SCDNR 2009). Estuarine fishes were collected during routine trammel netting conducted by the Inshore Fisheries Section of MRRI. Tissue from these saltwater species were obtained by SCDHEC staff and processed in a SCDHEC laboratory according to the above-cited procedures. King mackerel (*Scomberomorus cavalla*, Cuvier 1829) tissue samples were obtained by SCDHEC staff in cooperation with the SCDNR at the conclusion of select South Carolina king mackerel fishing tournaments. For large pelagic and estuarine fishes, a portion of the skin-on-filet measuring approximately 10 cm × 8 cm was cut from behind the right pectoral fin. For smaller saltwater species and all freshwater species, the entire skin-on-filet cut from the right side of each specimen was processed. All tissue Hg values were reported in milligrams/kilogram wet weight and are denoted in parts per million (ppm). The SCDHEC manages tissue data in a Microsoft Access database. Data are publicly available through USEPA (2009a).

Total fish tissue mercury was determined by the SCDHEC Analytical Radiological Environmental Sevices Division (ARESD) using cold vapor absorption spectrophotometry. Homogenized samples were digested as

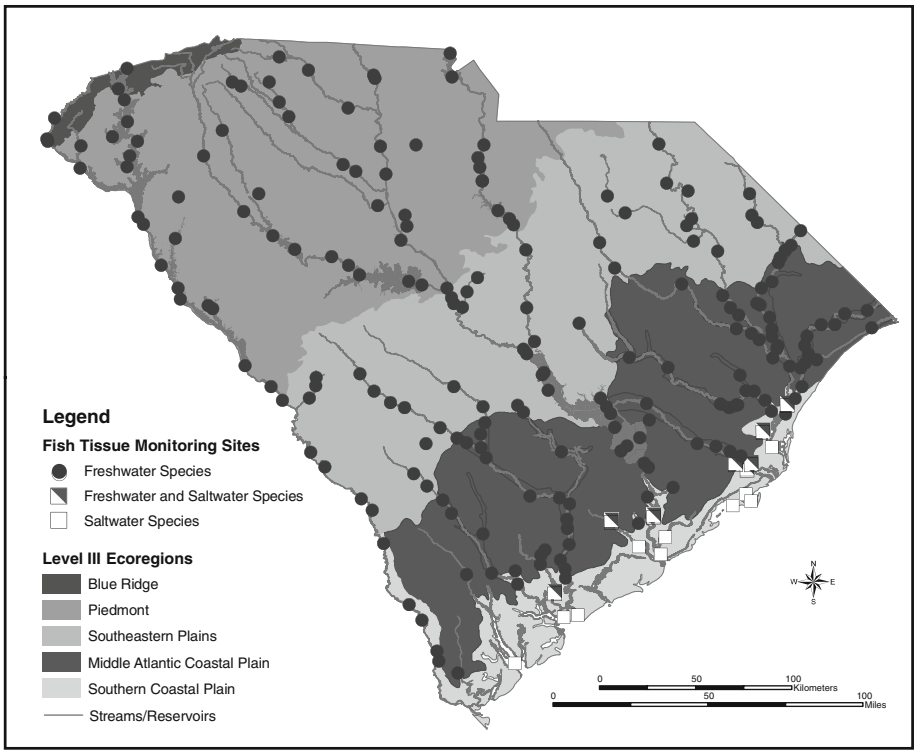

Fig. 1 Fish tissue sampling sites in South Carolina

described in EPA method 245.6 (EPA 1991). Samples were prepared in sets of 10 with an associated reagent blank and quality control (QC) samples. Instrumentation was calibrated using 5 levels of standards. Each set of 10 samples was analyzed with their associated QC samples. Method Detection Limits (MDL) and an Initial Demonstration of Performance (IDP) were performed by each analyst using a specific instrument prior to analysis of any samples. The QC data associated with each set of samples included: Quality Control Samples (QCS), Laboratory Reagent Blank (LRB), Laboratory Fortified Blank (LFB), and a Laboratory Fortified Matrix (LFM). The IDP was used to characterize instrument performance prior to analysis of samples. This included the linear calibration range, MDL, and analysis of QCS. An IDP was performed annually by each analyst and the calculated MDL values were determined with a minimum of 7 replicates. The LFB and LFM were blanks run with each batch of samples to determine accuracy. The LFB was a spiked distilled water sample while the LFM was a blindly selected sample from a set of 10 samples. The spiking level for both the LFB and LFM were alternated with each 10 samples between a low and a high level of spiking concentrations with acceptable ranges being 85–115% and 70–130%, respectively. Method detection limits were calculated to be 0.021 ppm but because of programmatic needs were reported as 0.25 ppm from 1993 to 2003 and 0.10 ppm from 2004 to 2007. During this time span values below the reporting limits were given the value 0.05 ppm for the issuance of consumption advisories. The SCDHEC ARESD laboratory obtains its certification through the USEPA.

Advisory criteria in South Carolina for a given species and waterbody combination are shown in Table 1. The SCDHEC uses multiple sampling stations to develop consumption advisories for an entire waterbody or a portion of a waterbody for a given species in a given year (SCDHEC 2009).

Fish tissue data were spatially analyzed through a geographic information system (GIS; ESRI 2008). Land use classifications were obtained from the National Land Cover Data (NLCD; USEPA 2009b). The NLCD was developed from 30-meter Landsat Thematic Mapper (TM) data acquired by the Multi-resolution Land Characterization (MRLC) Consortium. The NLCD data has a consistent land cover data layer for the entire U.S., with 21 possible land cover classes represented. We aggregated NLCD land cover classes into 5 categories, which we defined as: water (included water), developed (included developed open space, developed low intensity, developed medium

Table 1 SCDHEC Fish tissue Hg criteria

Tissue Hg levels	Advisory
0–0.24 ppm	No restrictions
0.25–0.66 ppm	1 Meal per week
0.67–0.99 ppm	1 Meal per month
≥1.0 ppm	Do not eat any

Table 2 Summary of fish tissue mercury (Hg) data and water column data processed by the South Carolina Department of Health and Environmental Control (SCDHEC)

Sample	Units	Year	*N*	Source	Analysis	Data location
Tissue Hg (Whole Fish)	mg kg^{-1}	1976–1987	382	SCDHEC	APHA 3112B	www.epa.gov/storet/
Tissue Hg (Headless-Eviscerated)	mg kg^{-1}	1976–1988	566	SCDHEC	APHA 3112B	www.epa.gov/storet/
Tissue Hg (Freshwater Skin-on-Fillet)	mg kg^{-1}	1993–2007	17,903	SCDHEC	APHA 3112B	http://map1.epa.gov/
Fish Tissue (Saltwater Skin-on-Fillet)	mg kg^{-1}	1998–2007	851	SCDNR/SCDHEC	APHA 3112B	Contact SCDHEC—Bureau of Water
Alkalinity	mg l^{-1}	2000–2006	3,233	SCDHEC	APHA 2320B	www.epa.gov/storet/
Total Organic Carbon (TOC)	mg l^{-1}	2000–2006	1,406	SCDHEC	APHA 5310B	www.epa.gov/storet/
Dissolved Oxygen (DO)	mg l^{-1}	2000–2006	4,184	SCDHEC	APHA 4500 HB	www.epa.gov/storet/
Iron (Fe)	ug l^{-1}	2000–2006	1,423	SCDHEC	APHA 3120B	www.epa.gov/storet/
Ammonia	mg l^{-1}	2000–2006	3,400	SCDHEC	APHA 4500; APHA 350.2-1	www.epa.gov/storet/
Nitrogen Kjeldahl (TKN)	mg l^{-1}	2000–2006	3,373	SCDHEC	EPA 351.2	www.epa.gov/storet/
Nitrogen, Nitrate + Nitrite (NN)	mg l^{-1}	2000–2006	4,288	SCDHEC	EPA 353.2; APHA 4500	www.epa.gov/storet/
pH	–	2000–2006	4,187	SCDHEC	APHA 4500 OG	www.epa.gov/storet/
Turbidity	NTU	2000–2006	4,179	SCDHEC	APHA 2120 (B)	www.epa.gov/storet/
Phosphorous (P)	mg l^{-1}	2000–2006	3,057	SCDHEC	EPA 365.3	www.epa.gov/storet/

Only fish tissue data collected between 1993 and 2007 were used in this study. Water chemistry data represents only the 77 stations used in this study

intensity, developed high intensity, and barren land), agriculture (included scrub/shrub, grasslands/herbaceous, pasture/hay, cultivated crop), forest (included deciduous forest, evergreen forest, mixed forest) and wetlands (included emergent herbaceous wetlands and woody wetlands). Water column chemistry data were collected by SCDHEC as part of the statewide ambient water quality monitoring program (SCDHEC 2008). Data analyses were performed in a SCDHEC laboratory using procedures outlined in USEPA (2007). These data were uploaded to the USEPA (2009c) STORET system and are publicly available. Water flow data were obtained from the US Geological Surveys National Water Information System (USGS 2009). Table 2 summarizes data and Fig. 1 indicates sampling locations.

Statistical analysis

To obtain statewide predicted tissue Hg values for each species, censored interval regression models, described below, were used to account for the relatively large number of values below the reporting limits (0.25 ppm before 2004 and 0.10 ppm starting in 2004). Tissue Hg values were calculated after adjusting for the quadratic effect of the mean length for each species. The maximum likelihood estimation was used to test for the effect of length on Hg levels for each species of fish. Only species with at least 20 individuals were included to increase the reliability of the estimates. Statistical analyses were performed with SAS Institute's SAS/STAT software (v.9.1.3 SAS Institute 2002) and StataCorp's STATA software (v10 StataCorp 2009).

To determine spatial and temporal trends for fish tissue Hg, the largemouth bass (*Micropterus salmoides*, Lacepede 1802) was chosen as a species deemed an effective surrogate for statewide overall trends. Largemouth bass are ubiquitous in freshwaters of South Carolina, top piscivores, and well represented in the dataset.

The presence of censored data, or readings that fall below a reporting or detection limit for a subset of observations, poses challenges to researchers. A number of options are available in the face of censored data. Truncated models, or models that include only readings above detection limits, are not an appropriate option since they discard information from the censored observations and lead to biased results. Rounding values below detection limits to a single, arbitrary value may also lead to biased results (Helsel 2005). Rather, specific statistical models have been developed to simultaneously incorporate information from both censored and non-censored observations. The tobit model, developed in Economics by Tobin (1958) is an early and widely used model across a number of disciplines in the analysis of censored data; we refer to the generalization of this model as Interval Censored Regression (ICR). While it is available in most statistical packages and straight-forward to implement and interpret, ICR is sensitive to the assumption of a normally-distributed error term, and may lead to inconsistent estimates when this assumption is violated. Logging the dependent variable may potentially transform a non-normal error into one that

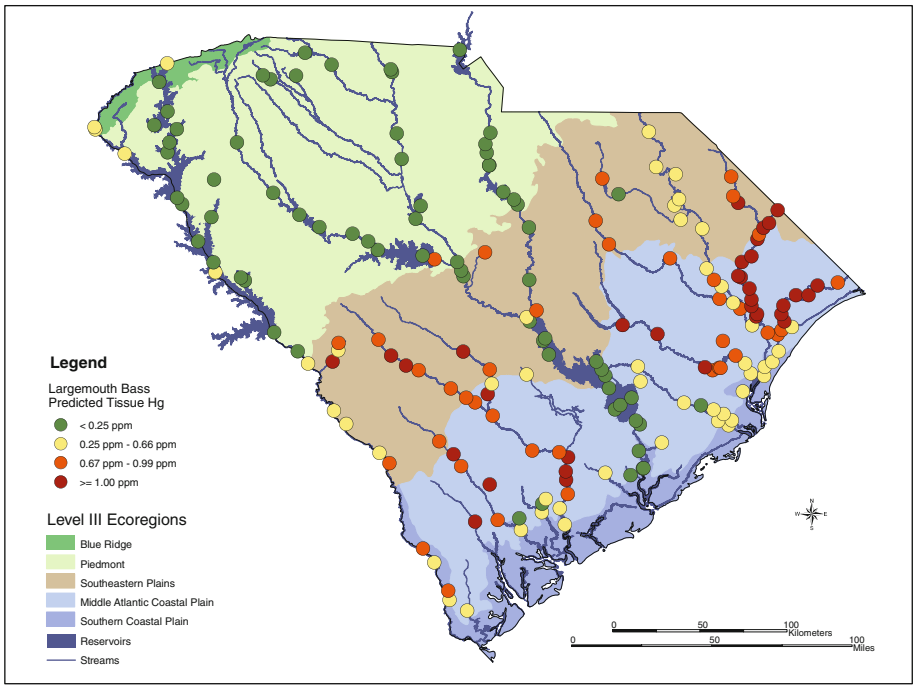

Fig. 2 Predicted tissue mercury levels for largemouth bass in South Carolina adjusted to the mean length of 371 mm and the year 2007

is normally distributed, but does not work for all distributions. Non-parametric alternatives, such as the censored least absolute deviations (CLAD) model (Powell 1984), can be used in the face of violations of the normality assumption. A form of quantile regression, CLAD does not assume normality and predicts median, rather than mean, values. CLAD models use a reduced sample size due to the additional censoring required by the models. The CLAD has not been used to our knowledge in the analysis of fish tissue data, but can serve as a potentially important tool in this regard.

We used both ICR and CLAD to model the effects of various independent variables on the levels of tissue Hg in largemouth bass. Of the 4,860 largemouth bass observations, 27.1% had Hg readings below the reporting limits. In order to assess normality of the error in our models, we examined the third and fourth moments of the generalized residuals (Cheshire and Irish 1987) of the uncensored Hg readings for the ICR model. Normality was rejected in all of the statistical models using both an untransformed and a log-transformed Hg value, indicating that the interval censored regression model may be inconsistent (Greene 2003). All models were also run using Powell's (1984) CLAD estimator. Because of the violations of normality, predicted values are reported for both ICR and CLAD. In a limited number of cases, small cell sizes for variable interactions, described below, led to negative predicted medians from the CLAD model. These medians occurred at low mean values from the ICR models and indicated low levels of tissue Hg.

All models controlled for year dummy variables, which allow for non-linear time effects, and fish length. Several functional forms were examined to model the effects of length, including linear effects, quadratic effects, and a restricted cubic spline function of length with four knots chosen according to Harrell's (2001) recommended percentiles. Both the quadratic form and the restricted cubic spline model maximized the likelihood function for the ICR models and produced similar predicted values. The quadratic form was chosen for both the ICR and CLAD models.

The first model evaluated Hg levels as a function of length, dummy variable for station, and dummy variable for year for largemouth bass. The ICR model was used to generate predicted values for each station. The 2007 values were calculated and stratified into 4 groups that correspond to the advisory thresholds of the SCDHEC (see Table 1). Each station was symbolized on a state coverage of South Carolina in GIS to correspond to one of these 4 groups (Fig. 2).

The second model evaluated Hg as a function of length, dummy variables for ecoregion, dummy variables for year, dummy variables for the type of waterbody (unregulated river, regulated river, small reservoir, medium reservoir, or large reservoir) and waterbody-ecoregion interactions. The limit of each reservoir was determined by standards set force by the National Hydrography Dataset (USEPA 2009b). We classified reservoirs as small (mean = 1.06 km^2, range 0.12–3.44 km^2), medium (mean = 18.38 km^2, range 4.84–38.42 km^2) and large (mean = 211.79 km^2, range

46.52–361.13 km^2). Unregulated rivers were defined as those that lacked any major physical alterations. Regulated rivers were classified as those with major physical alternations, such as large dams within their watersheds but not within the bounds of the reservoir. For ICR the maximum likelihood test for differences in parameter estimates was used as the test statistic. To determine which groups differed, a series of individual comparisons were performed as described in Helsel (2005) with each variable serving as the reference condition in a series of tests. Both ICR and CLAD were used for this model.

To assess temporal trends, predicted tissue Hg values in largemouth bass were calculated for the years 1993–2007 for unregulated rivers, in the MACP ecoregion after adjusting for the mean length of 371 mm. Values obtained from ICR were plotted against year. Annual median runoff data (in mm/day) were obtained for the state of South Carolina from USGS (2009). The 3-year moving average was calculated for median runoff for the years 1993–2007 using data from 1991 to 2007. These values were plotted with predicted Hg values against year for 1993–2007.

Some rivers flow through multiple ecoregions in South Carolina. A third model tested the hypothesis that no differences occurred in tissue Hg levels in length adjusted largemouth bass collected from a single river that crossed over different ecoregions. Eight different rivers were included in this model. ICR and CLAD models were run using dummy variables for waterbody name, dummy variable for ecoregion, dummy variables for waterbody name-ecoregion interactions, length, and dummy variable for year. A series of individual comparisons were performed, using the maximum likelihood test, to test differences in tissue Hg in largemouth bass from segments of rivers in different ecoregions.

To examine the relationship of surface water chemistry and surrounding landuse on tissue Hg of largemouth bass, sites that contained both tissue Hg and water chemistry data were identified. Of the 199 sampling sites that contained tissue Hg data, 77 were regularly monitored for surface water chemistry. For these 77 sampling sites the following chemistry data were available: Alkalinity (Alk), Total Organic Carbon (TOC), Dissolved Oxygen (DO), Iron (Fe), Ammonia (Amm), Kjeldahl Nitrogen (TKN), Nitrate + Nitrite (NN), Total Phosphorous (P), pH (pH), and Turbidity (Tur). For most stations, monthly readings were available for each sampling site. To compute summary statistics, the arithmetic means for Alk, TOC, DO, Fe, pH and Tur for samples collected between 2002 and 2006 were calculated. Because there were a large number of readings below the detection limit for P (DL = 0.02 mg l^{-1}), NN (DL = 0.02 mg l^{-1}), TKN (DL = 0.1 mg l^{-1}), and Amm (DL = 0.05 mg l^{-1}), predicted values were calculated for these variables using interval censored regression. To meet assumptions of normality these values were first log-transformed and, after estimates were generated, retransformed to obtain predicted values.

Land cover percentages were calculated for 12 digit hydrologic units (HU) associated with the 77 stations. While none of the hydrologic units were true watersheds, we considered these small units appropriate to access the effects of local land cover on tissue Hg. Land cover percentages were also calculated for each Level III ecoregion in South Carolina.

Correlations between predicted tissue Hg for largemouth bass and water chemistry and land cover variables were evaluated for all sites using Spearman correlations. A principle component analysis was run on the ten water quality variables and the first three components captured 77% of the total dataset variation. The component scores for each station were plotted against the stations corresponding predicted tissue Hg reading.

Results and discussion

Species trends

The six species in the SCDHEC dataset with the highest predicted tissue Hg values were piscivores (Table 3). Studies have shown a strong correlation with tissue Hg and some variable associated with fish size such as age, length, and weight (Gilmour and Riedel 2000). Some studies have suggested that age is a slightly better predictor than length (Peles et al. 2006), however, age data are not always readily available. For this study, length was a highly significant predictor for tissue Hg for most fish species. The freshwater species having the highest normalized predicted tissue Hg concentration was bowfin (*Amia calva* Linnaeus 1766), with a value of 0.89 ppm. Bowfin are large piscivores that have been collected primarily in the coastal plain ecoregions. Of the 73 specimens with tissue Hg values of >=3.0 ppm, 53 were bowfin. One bowfin specimen had an extremely high value of 7.0 ppm. Of the 3,102 bowfin specimens only 404 (13%) had levels below 0.25 ppm. While the statewide predicted tissue Hg concentrations for largemouth bass is lower than for bowfin, these species have comparably high levels in certain rivers in the MACP where the two species are sympatric. Two large piscivores showing relatively lower levels of tissue Hg were striped bass (*Morone saxatilis*, Walbaum 1772; 0.23 ppm) and smallmouth bass (*Micropterus dolomieu*, Lacepede 1802; 0.22 ppm). This is likely related more to these species geographic range than some unknown ecological reason. Indeed smallmouth bass tissue Hg levels in lakes of Northeast U.S.A. and Southeast Canada (mean = 0.59 ppm; Kamman et al. 2005b) were comparable to South

Table 3 Length-adjusted Hg estimates for fishes of South Carolina. (Calculated using interval censored regression. Skin-on-Filets only. Species with $n < 20$ not included)

Scientific name	Common name	N/% Below detect	Mean length (mm)	Predicted Hg (ppm)	Hg (ppm) max	Trophic group[d]	Life history
Scomberomorus cavalla	King Mackerel	126/0%	1105[ab]	0.98	3.8	P	Saltwater-Offshore
Amia calva	Bowfin	3035/11%	540[ab]	0.89	7.0	P	Freshwater
Pylodictis olivaris	Flathead Catfish	179/22%	547[ab]	0.89	3.7	P	Freshwater
Xiphias gladius	Swordfish	32/11%	1153[ab]	0.62	2.4	P	Saltwater-Offshore
Esox niger	Chain Pickerel	859/29%	380[ab]	0.55	5.2	P	Freshwater
Micropterus salmoides	Largemouth Bass	4860/27%	371[ab]	0.53	4.0	P	Freshwater
Chaenobryttus gulosus	Warmouth	499/39%	193[ab]	0.38	1.5	P(V)	Freshwater
Perca flavescens	Yellow Perch	113/50%	235[ac]	0.36	1.3	I(P,G)	Freshwater
Micropterus punctulatus	Spotted Bass	41/39%	332[ab]	0.35	1.0	P	Freshwater
Ictalurus furcatus	Blue Catfish	696/54%	550[ab]	0.28	4.0	P(I,G)	Freshwater
Pomoxis nigromaculatus	Black Crappie	688/65%	255[ac]	0.28	2.6	P(I,V)	Freshwater
Lepomis auritus	Redbreast Sunfish	656/55%	190[ab]	0.27	2.4	I(G)	Freshwater
Lepomis microlophus	Redear Sunfish	2547/64%	228[ab]	0.26	2.9	I	Freshwater
Ictalurus punctatus	Channel Catfish	723/63%	458[ab]	0.25	2.7	P(I)	Freshwater
Morone saxatilis	Striped Bass	81/42%	583[ac]	0.23	1.1	P	Diadromous
Micropterus dolomieu	Smallmouth Bass	24/38%	327	0.22	0.51	P	Freshwater
Lepomis macrochirus	Bluegill	1625/69%	197[ab]	0.22	2.4	I(G)	Freshwater
Scomberomorus maculates	Spanish Mackerel	85/76%	394[ab]	0.20	0.59	P	Saltwater-Nearshore
Coryphaena hippurus	Mahi Mahi	32/69%	1137[ac]	0.18	0.66	P	Saltwater-Offshore
Ameiurus catus	White Catfish	35/86%	376	0.16	1.7	I(P)	Freshwater
Cynoscion regalis	Spotted Weakfish	68/74%	382[ab]	0.12	0.54	V(P)	Saltwater-Nearshore
Cynoscion nebulosus	Spotted Seatrout	91/74%	381	0.11	0.47	V(P)	Saltwater-Nearshore
Mugil cephalus	Striped Mullet	25/80%	271[ac]	0.11	0.23	G	Diadromous
Leiostomus xanthurus	Spot	33/53%	204[ac]	0.10	0.13	V	Saltwater-Nearshore
Sciaenops ocellatus	Red Drum	160/74%	485[ac]	0.09	0.36	V(P)	Saltwater-Nearshore
Paralichthys lethostigma	Southern Flounder	126/81%	389	0.07	0.38	P	Saltwater-Nearshore

P Piscivore, *I* Insectivore, *V* Invertivore, *G* generalist

[a] Likelihood ratio test indicated length as a quadratic effect on tissue Hg significant at [b] $p < 0.0001$ and [c] $p < 0.05$. [d] Trophic status obtained in part from Barbour et al. (1999)

Carolina statewide, predicted Hg levels for largemouth bass (0.53 ppm). Several species of catfish are found in South Carolina and all in the dataset except the flathead catfish (*Pylodictus olivaris*, Rafinesque 1818) ranked low on the list of species in terms of predicted tissue Hg levels. The blue catfish (*Ictalurus furcatus*, Lesueur 1840), the channel catfish (*Ictalurus punctatus*, Rafinesque 1818) and the white catfish (*Amerius catus*, Linnaeus 1758) are omnivorous and will consume fish but also invertebrates and some plants (Jenkins and Burkhead 1993) which could account for their lower rank. The flathead catfish is a top piscivore that can grow in excess of 1,000 mm and weigh over 34 kg (Carroll and Hall 1964). While not endemic in SC, routine electrofishing conducted by SCDHEC over the last decade indicates it has successfully invaded many waterbodies in the state.

Estuarine and nearshore ocean fishes such as southern flounder (*Paralichthys lethostigma*, Jordan and Gilbert 1884) and red drum (*Sciaenops ocellata*, Linnaeus 1766) had relatively low levels of tissue mercury (Table 3). Gilmour and Riedel (2000) found a similar pattern in Maryland with fishes in estuarine waters having lower levels of mercury than freshwater species. Gilmour and Henry (1991) hypothesized that MeHg production in estuarine sediments is limited by sulfide. In more recent studies Hammerschmidt et al. (2004) and Hammerschmidt and Fitzgerald (2006) found that methylation does occur in estuaries but more research remains to fully understand the bioaccumulation process in these systems. Mercury can and does accumulate in the tissue of saltwater species, but our data and other studies (Cai et al. 2007) indicate that species most affected are large, offshore predators

(Table 3). Predicted tissue Hg levels for king mackerel (mean length = 1105 mm, predicted Hg = 0.98 ppm) was the highest for any species. This is in close agreement for values reported by Adams and McMichael (2007) for Atlantic king mackerel collected off the coast of Florida (mean = 0.94 ppm) and by Cai et al. (2007) in the Gulf of Mexico off the Texas and Louisiana coasts (mean = 0.96). However, when modeled for the mean length of king mackerel in the Florida dataset (904 mm) the South Carolina king mackerel predicted Hg values were much lower (0.45 ppm). When modeled for the mean length (840 mm) of the Gulf of Mexico specimens reported by Cai et al. (2007) the South Carolina predicted Hg values were even lower (0.36 mm). This suggests a decreasing trend from the Gulf of Mexico, to the Atlantic Ocean off the Florida coast, to the Atlantic Ocean off the Carolina coasts. The cause of this pattern deserves further investigation. A similar pattern was found in South Carolina Spanish mackerel (*Scomberomorus maculates*, Couch 1832) values reported here (predicted Hg = 0.18 ppm) and the Florida Spanish mackerel values (mean Hg = 0.32 ppm) reported by Adams and McMichael (2007). Swordfish (*Xiphias gladius* Linnaeus 1758) off the coast of South Carolina were also found to have elevated tissue mercury (mean = 0.64 ppm), however, mahi mahi (*Coryphaena hippurus* Linneaeus 1758) was an open ocean species with relatively low levels of tissue Hg (0.15 ppm; Table 3). Mahi mahi can grow to over 1000 mm and reach weights of 18 kg in less than 12 months (Hammond 1998). However, the species is relatively short lived compared to other large pelagic predators, which could account for the relatively lower levels of tissue Hg (Cai et al. 2007) but other life history traits could be involved.

Spatial trends

Table 4 shows the spatial analyses of landuse by Level III ecoregion. As this table shows, the SEPS, the MACP, and the SCP ecoregions all have a high percentage and surface area covered by wetlands. The MACP has the highest total area and percentage of woody wetlands while the SCP near the Atlantic Ocean has the highest area and percentage of emergent herbaceous wetlands. Several studies have shown the importance of water chemistry and landscape characteristics on the methylation efficiency within a watershed (Kamman et al. 2003, 2005a; Shanley et al. 2005). Wetlands are understood to be important regions for Hg methylation (Munthe et al. 2007). Paller et al. (2004) found that water column Hg and tissue mercury in the asiatic clam (*Corbicula fluminea*, Muller 1778) in the Savannah River were elevated below tributaries. They speculated that wetlands adjacent to these tributaries were important locations for methylation and the tributaries were conduits to the mainstem of the Savannah River. Recently, Guentzel

Table 4 Land cover area and percent of total for Level III ecoregions in South Carolina

Ecoregion	Blue Ridge (66)		Piedmont (45)		SEPS (65)		MACP (63)		SCP (75)	
Landuse	Area (km^2)	% Of total	Area (km^2)	% Of total	Area (km^2)	% Of total	Area (km^2)	% Of total	Area (km^2)	% Of total
Open water	39.3	3.3	921.5	3.3	472.2	2.0	331.1	1.5	598.3	10.8
Developed, open space	34.9	2.9	1939.1	6.9	1206.5	5.1	871.4	4.0	228.4	4.1
Developed, low intensity	1.3	0.1	695.7	2.5	546.4	2.3	293.7	1.4	147.4	2.7
Developed, medium intensity	0.2	0.0	190.2	0.7	160.5	0.7	73.6	0.3	48.8	0.9
Developed, high intensity	0.1	0.0	90.1	0.3	54.2	0.2	18.1	0.1	17.9	0.3
Barren Land	2.8	0.2	261.3	0.9	44.5	0.2	23.1	0.1	35.0	0.6
Deciduous forest	830.8	69.0	8232.7	29.5	1958.6	8.2	869.7	4.0	128.4	2.3
Evergreen forest	139.5	11.6	7476.9	26.8	5152.8	21.6	5656.9	26.3	1063.0	19.2
Mixed forest	86.0	7.1	370.1	1.3	647.9	2.7	345.5	1.6	89.4	1.6
Scrub/Shrub	6.5	0.5	261.7	0.9	354.2	1.5	930.1	4.3	124.9	2.3
Grassland/Herbaceous	18.4	1.5	2248.5	8.0	3055.5	12.8	1971.8	9.2	288.7	5.2
Pasture/Hay	40.7	3.4	4651.3	16.6	1577.1	6.6	1026.1	4.8	109.2	2.0
Cultivated crops	1.7	0.1	43.2	0.2	3967.4	16.6	2104.3	9.8	84.8	1.5
Woody Wetlands	1.3	0.1	557.4	2.0	4552.1	19.1	6899.4	32.0	930.8	16.9
Emergent Herbaceous Wetland	0.0	0.0	1.8	0.0	91.6	0.4	122.4	0.6	1627.7	29.5
Total	1203.7	100.00	27941.6	100.00	23841.6	100.00	21537.2	100.00	5522.9	100.00

(2009) demonstrated the importance of wetlands on water column Hg in South Carolina and found a strong correlation between water column total Hg and total organic carbon. In Louisiana, Hall et al. (2008), found that wetlands had a very high MeHg production potential.

Our data adds further support to the role of wetlands to the methylation process. Figure 2 shows the predicted tissue Hg concentrations for largemouth bass for year 2007. These were stratified based on the SCDHEC advisory criteria. There are two main regions that have high levels of tissue Hg; the northern portion of the MACP and the southern portion of the MACP. Also noteworthy is a distinct region in the central portion of the MACP and SEPS with lower levels of tissue Hg. Most of the Piedmont appears to have low levels of tissue Hg, while the small portion of the BR appears relatively higher than the Piedmont. Results from Model 2 are shown in Table 5. Predicted means, from the ICR model, and predicted medians, from the CLAD model, were comparable in most ecoregion-waterbody type combinations. The highest levels of tissue Hg were found in the MACP followed by the SEPS ecoregions (Table 5). The lowest levels were seen in the Piedmont and the SCP. Unregulated rivers had the highest levels of tissue Hg while large reservoirs had fish with some of the lowest values. Rypel et al. (2008) found a similar pattern in fish tissue Hg in two Alabama rivers with tissue Hg readings being much higher in an unregulated river versus a reservoir. Reservoir size was an important predictor of tissue Hg in the coastal ecoregions with larger reservoirs having fish with lower levels of tissue Hg than smaller reservoirs. Predicted tissue Hg values in unregulated rivers in the SEPS and MACP were not significantly different from one another (Chi-Square = 0.22, $p = 0.64$), while they were in regulated rivers (Chi-Square = 71.59, $p < 0.0001$) with fish from the MACP showing elevated values for this waterbody type relative to the SEPS.

Table 6 shows the predicted tissue Hg values for length normalized largemouth bass for rivers that drain across different ecoregions. While a statistically significant difference between ecoregions was not detected for all rivers there is a distinct pattern in these eight rivers that is consistent with the patterns observed overall for the Level III ecregions. For a given river, the levels of tissue Hg for largemouth bass collected in the Piedmont increase if the river flows into the SEPS, increases still more once in the MACP and decreases in the SCP at the freshwater–saltwater interface. The increase from the SEPS to the MACP is more pronounced in regulated rivers such as the Great Pee Dee, and the Savannah, than in unregulated rivers such as the Combahee, Little Pee Dee, and Lynches (Table 6).

Table 5 Tissue Hg estimates for largemouth bass in South Carolina modeled for length as a quadratic, ecoregion, waterbody type, and year effects using censored interval regression

Waterbody type[a] Ecoregion[b]	River-unregulated	River-regulated	Reservoir-large	Reservoir-medium	Reservoir-small
Blue Ridge (66)	–	–	–	0.40 (ICR) A,a 0.41 (CLAD) (in ppm)	0.58 (ICR) A,a 0.62 (CLAD) (in ppm)
Piedmont (45)	0.44 (ICR) A,a 0.42 (CLAD) (in ppm)	0.22 (ICR) AB,a 0.07 (CLAD) (in ppm)	0.24 (ICR) AB,a 0.13 (CLAD) (in ppm)	0.17 (ICR) BC,b NV[c] (CLAD) (in ppm)	0.11(ICR) C,b NVc (CLAD) (in ppm)
Southeastern Plains (65)	1.03 (ICR) A,b 1.05 (CLAD) (in ppm)	0.36 (ICR) B,b 0.28 (CLAD) (in ppm)	0.18 (ICR) C,b NV[c] (CLAD) (in ppm)	0.78 (ICR) D,c 0.76 (CLAD) (in ppm)	0.91 (ICR) E,c 0.92 (CLAD) (in ppm)
Middle Atlantic Coastal Plain (63)	1.04 (ICR) A,b 1.05 (CLAD) (in ppm)	0.56 (ICR) B,c 0.52 (CLAD) (in ppm)	0.18 (ICR) C,ab 0.01 (CLAD) (in ppm)	–	0.53 (ICR) A,a 0.51 (CLAD) (in ppm)
Southern Coastal Plain (75)	0.47 (ICR) A,a 0.30 (CLAD) (in ppm)	0.36 (ICR) B,c 0.27 (CLAD) (in ppm)	–	–	0.14 (ICR) C,b NV[c] (CLAD) (in ppm)

Predicted mean calculated using interval censored regression models (ICR). Median calculated using least absolute deviations (CLAD). Values shown for year 2006 and length = 371 mm

[a] ICR model indicated that, for a given ecoregion, predicted tissue mercury from waterbody types with the same capitol letter are not statistically different at $p < 0.05$ [b] For a given waterbody, tissue mercury from ecoregions with the same lower case letter are not statistically different at $p < 0.05$. Maximum likelihood test used to test for differences between cells. [c] NV = CLAD models predicted negative mercury levels

Table 6 Predicted mean and median Hg values for largemouth bass in rivers contained within multiple ecoregions modeled for year, length as a quadratic, ecoregion, and river

Ecoregion[a] River	*N* % Censored	Piedmont	Southeastern Plains	Middle Atlantic Coastal Plain	Southern Coastal Plain
Great Pee Dee	$N = 306$ $C = 23\%$	–	0.60 (ICR) A 0.58 (CLAD) (ppm)	0.93 (ICR) B 0.90 (CLAD) (ppm)	0.70 (ICR) A 0.59 (CLAD) (ppm)
Savannah	$N = 260$ $C = 23\%$	0.33 (ICR) A 0.23 (CLAD) (ppm)	0.57 (ICR) B 0.54 (CLAD) (ppm)	0.98 (ICR) C 1.02 (CLAD) (ppm)	–
Combahee	$N = 121$ $C = 8\%$	–	1.00 (ICR) A 1.08 (CLAD) (ppm)	1.01 (ICR) A 1.08 (CLAD) (ppm)	0.58 (ICR) B 0.25 (CLAD) (ppm)
Black	$N = 163$ $C = 5\%$	–	–	1.28 (ICR) A 1.29 (CLAD) (ppm)	0.71 (ICR) B 0.81 (CLAD) (ppm)
Edisto	$N = 214$ $C = 5\%$	–	–	1.11 (ICR) A 1.11 (CLAD) (ppm)	0.77 (ICR) A 0.73 (CLAD) (ppm)
Waccamaw	$N = 311$ $C = 5\%$	–	–	1.28 (ICR) A 1.31 (CLAD) (ppm)	0.74 (ICR) B 0.76 (CLAD) (ppm)
Little Pee Dee	$N = 247$ $C = 0\%$	–	1.32 (ICR) A 1.28 (CLAD) (ppm)	1.56 (ICR) B 1.52 (CLAD) (ppm)	–
Lynches	$N = 129$ $C = 3\%$	–	1.05 (ICR) A 0.97 (CLAD) (ppm)	1.07 (ICR) A 1.14 (CLAD) (ppm)	–

Predicted mean calculated using interval censored regression (ICR); Median calculated using censored absolute deviations (CLAD); Values shown for year 2006 and length = 371 mm

[a] ICR model indicated for a given waterbody, predicted tissue Hg from ecoregions with the same letter were not statistically different at $p < 0.05$. Maximum likelihood test used to test for differences between cells

Land cover and water chemistry appear to account for patterns in tissue Hg for Level III ecoregions. Table 7 shows a correlation matrix for tissue Hg for length normalized largemouth bass, water chemistry, and landuse classification. Tissue Hg was negatively correlated with pH ($r = -0.74$, $p < 0.0001$), DO ($r = -0.48$, $p < 0.0001$), and Alk ($r = -0.28$, $p < 0.05$) and positively correlated with TOC ($r = 0.55$, $p < 0.0001$), Amm ($r = 0.42$, $p < 0.05$), Fe ($r = 0.43$, $p < 0.0001$), and TKN ($r = 0.29$, $p < 0.05$). Table 7 also shows correlations between land cover percentages associated with 12 digit HUs, water chemistry and tissue Hg values for stations within these HUs. Tissue Hg was negatively correlated with percent water ($r = -0.67$, $p < 0.0001$) and percent forest ($r = -0.44$, $p < 0.0001$) and positively correlated with percent wetlands ($r = 0.61$, $p < 0.0001$) and percent agriculture ($r = 0.35$, $p < 0.05$). While the positive correlation with percent wetland landuse was not surprising, the negative correlation with percent forest landuse was unexpected. Studies have noted higher fish tissue Hg in more remote forested regions than in developed watersheds (Gilmour and Riedel 2000; Kamman et al. 2005b). However, inspection of the data showed that most areas with high percent forest landuse were regulated rivers in the Piedmont, which have fish with low levels of tissue Hg. Water chemistry variables that were very highly correlated ($p < 0.0001$) with land cover variables included pH (positive for % Water and negative for % Wetlands and % Agriculture), TOC (negative for % Water, positive for % Wetlands and % Forest), DO (positive for % Water, negative for % Wetlands) and Iron (negative for % Water, positive for % Wetlands). Twelve digit HUs with the highest percent water represent large reservoirs while those with low values represent rivers.

Results of the principle component analysis are shown in Table 8. The first three components explained 77% of

Table 7 Results of Spearman correlation analyses relating predicted tissue Hg values in largemouth bass with chemical and landscape variables

	Alk	TOC	DO	Iron	Amm	TKN	NN	pH	Phos	Turb	Hg
Hg	–0.28**	0.55*	–0.48*	0.43*	0.42**	0.29**	–0.06	–0.74*	0.20	–0.14	–
% Water	0.13	–0.54*	0.49*	–0.49*	–0.42**	–0.34**	–0.11	0.69*	–0.29**	–0.02	–0.67*
% Developed	–0.26**	–0.24**	0.12	–0.16	0.11	–0.21	0.02	0.00	–0.25**	–0.20	–0.10
% Forest	–0.05	–0.50*	0.23**	–0.29**	–0.23**	–0.35**	–0.02	0.24**	–0.21	–0.01	–0.44*
% Agriculture	–0.32**	0.07	–0.08	0.25**	0.35**	0.07	0.31**	–0.48*	0.11	–0.01	0.35**
% Wetlands	0.24**	0.73*	–0.65*	0.58*	0.45**	0.60*	–0.06	–0.42*	0.46*	0.30**	0.61*

* Spearman r significant at $p < 0.0001$

** Spearman r significant at $p < 0.05$

the variance in the water chemistry variables. As indicated by the component loadings, Component 1 increases with increasing levels of TKN, Fe, Phos, and TOC. Water bodies scoring high on Component 1 thus have higher levels of organic nitrogen, total phosphorous, iron and organic carbon than waterbodies lower on this component. Component 2 assumes increasing values with increasing Turb and NN and decreasing TOC. Component 3 describes an acidity gradient with this component score increasing with increasing Alk and pH. Figures 3, 4 and 5 show scatter plots with predicted fish tissue Hg values plotted against each component score for the 77 sites. For these plots, different symbols were assigned to reservoirs, regulated rivers, and unregulated rivers. For clarity, stations were not subdivided further into ecoregions and reservoir size class. Predicted tissue Hg was highly correlated with Component 1 ($r = 0.455$, $p < 0.0001$; Fig. 3). Reservoirs had low Component 1 scores, and similarly low tissue Hg levels, while unregulated rivers tended to have high scores. Regulated rivers showed no clear pattern on Component 1. Component 2 was negatively correlated with tissue Hg ($r = -0.451$, $p < 0.0001$; Fig. 4). Regulated rivers had high Component 2 scores indicting high turbidity and inorganic nitrogen, and low levels of TOC while unregulated rivers scored low on Component 2. Predicted tissue Hg was negatively correlated with Component 3 ($r = -0.386$, $p = 0.0005$). Many studies have demonstrated the relationship between fish tissue Hg and an acidity gradient (Driscoll et al. 1994; Kamman et al. 2005b) and Component 3 also captures this phenomenon (Fig. 5). However, of greater interest is the demonstration that tissue Hg from

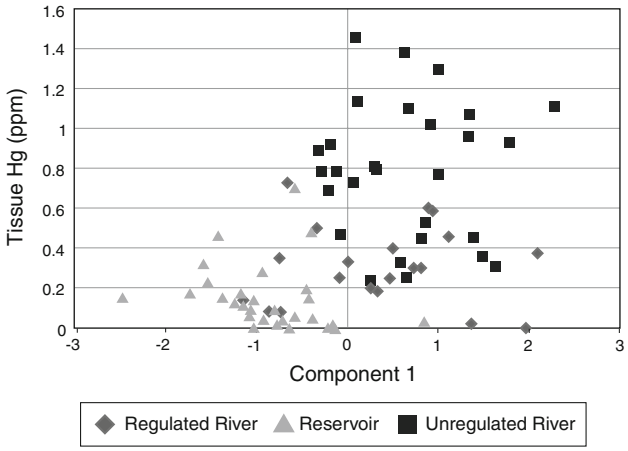

Fig. 3 Scatter plot of length adjusted predicted tissue Hg for largemouth bass in relation to component 1 score from a principal component analysis of 10 surface water quality variables. Component 1 assumes increasing values with increased iron, total phosphorous, total kjeldahl nitrogen, and total organic carbon

unregulated rivers had lower component scores than regulated rivers and reservoirs. The principle component analysis indicated that unregulated rivers tended to have higher levels of water column iron, organic nitrogen, and phosphorous than reservoirs. They were less turbid, had lower levels of inorganic nitrogen, high amounts of organic carbon and were more acidic than reservoirs or regulated rivers. Regulated rivers were more turbid and had higher levels of inorganic nitrogen than other waterbody classes. While all component scores were correlated with fish tissue Hg levels, the mechanistic causation of various water chemistry variables is in need of further study.

Table 8 Results of a principle component analysis of water column chemistry variables; component loadings that are shown in bold print contributed the most to each component and were used for interpretation

Component name	Variance explained by component	Alk	Amm	DO	Iron	NN	pH	Phos	TKN	TOC	Tur
Component 1	38.4%	0.39	0.65	–0.53	**0.78**	0.43	–0.48	**0.78**	**0.78**	**0.68**	0.55
Component 2	22.4%	0.37	0.13	0.36	0.17	**0.75**	0.43	0.15	–0.47	**–0.64**	**0.73**
Component 3	16.2%	**0.77**	–0.33	–0.00	–0.34	–0.34	**0.67**	0.32	0.30	0.22	0.01

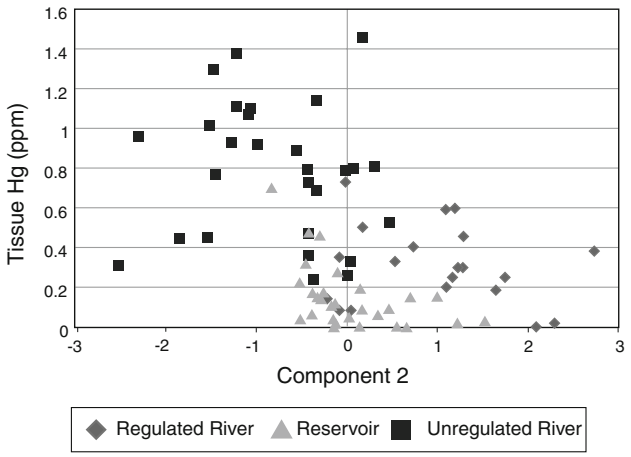

Fig. 4 Scatter plot of length adjusted predicted tissue Hg for largemouth bass in relation to component 2 score from a principal component analysis of 10 surface water quality variables. Component 2 assumes increasing values with decreasing total organic carbon, increasing turbidity, and increasing nitrate + nitrite

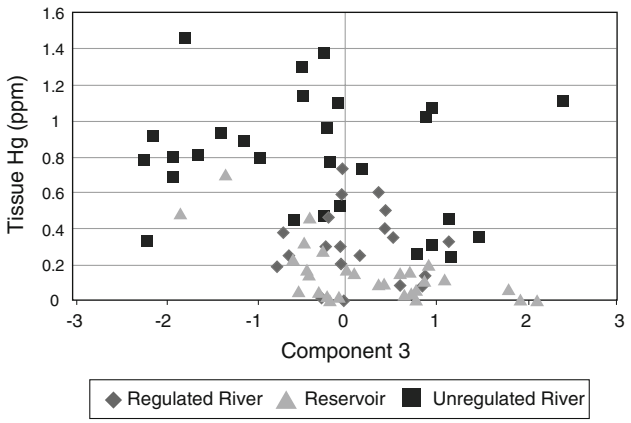

Fig. 5 Scatter plot of length adjusted predicted tissue Hg for largemouth bass in relation to component 3 score from a principal component analysis of 10 surface water quality variables. Component 3 assumes increasing values with increasing pH and alkalinity

Taken together, along with the current body of literature, the above results support the following conceptual model. Much of the landscape in the MACP and SEPS is composed of wetlands (Table 4). These wetlands, with their characteristic biogeochemistry, are important in microbial growth and metabolism and the regulation of the methylation process of Hg and subsequent bioaccumulation. Tributaries entering the mainstem rivers of the SEPS and MACP ecoregions serve as important conduits for MeHg transport. The adjacent wetland floodplains of the mainstem rivers are also important in MeHg production. Flooding has been shown to increase the production of MeHg by increasing the rate of organic matter decomposition leading to anoxic conditions, which stimulate the growth of bacteria involved in the methylation process (St. Louis et al. 2005). Seasonal inundation provides an avenue for MeHg transport to the rivers channel either directly in the water column or through trophic transfer of prey fish that rely on these regions to spawn and feed. As a river meanders through the SEPs and the MACP, the potential for MeHg bioaccumulation in fish tissue increases as more tributaries draining landscapes associated with wetlands enter the river. The magnitude of bioaccumulation in regulated rivers is more apparent than in unregulated rivers because of the relative lower levels of tissue Hg in rivers downstream of dams. The biogeochemistry of a river can be altered by hydrologic modification, particularly the construction of large reservoirs. Large dams can affect a riverine system both upstream and downstream of the dam. The upstream effect is obvious, with large parts of the landscape inundated. Downstream of a dam, flooding is often reduced and the connectivity with the floodplain can be lost (Poff et al. 1997; Richter et al. 2003), which can lead to the reduction of the methylation efficiency of the riverine system and the transfer of MeHg to the main river channel. Smaller reservoirs retain more connectivity with their surrounding wetlands than larger reservoirs and this is reflected in the relatively higher levels of tissue Hg in fishes. As the river enters the SCP ecoregion and begins to become brackish, bioaccumulation is reduced. Forested wetlands are replaced with emergent wetlands (Table 4) and there is a reduction in allochthonous input to the system. Changes in the landscape, water chemistry, and hydrology at the freshwater–saltwater interface are all likely to play a role in Hg methylation and bioaccumulation.

Temporal trends

Figure 6 shows the normalized predicted Hg values for unregulated rivers in the MACP, depicting an overall decreasing trend in tissue mercury since 1993. After remaining relatively stable in the late 1990's and early 2000's there was an increase in predicted tissue Hg in 2004 and 2005. In 2006 and 2007 the levels returned to what might be considered a baseline level. Paller and Littrell (2007) reported a similar increase in fish tissue Hg in 2004 from the previous 2 years in the Savannah River. Figure 7 shows a plot of median runoff for South Carolina and the 3-year moving average of median runoff from 1993 to 2007. Some studies have found that the drying and rewetting of soils strongly effect Hg methylation (Gilmour et al. 2004; Rumbold and Fink 2006). Gilmour et al. (2004) demonstrated in field and laboratory studies that there is a pulse of MeHg production in soils after drying. They hypothesized that MeHg production is stimulated in dried soils that have been rewet by the oxidation of reduce sulfur and organic matter. While laboratory studies have demonstrated a rapid pulse of MeHg production after dried soils have been rewet, there is likely a time lag for Hg to bioaccumulate in large

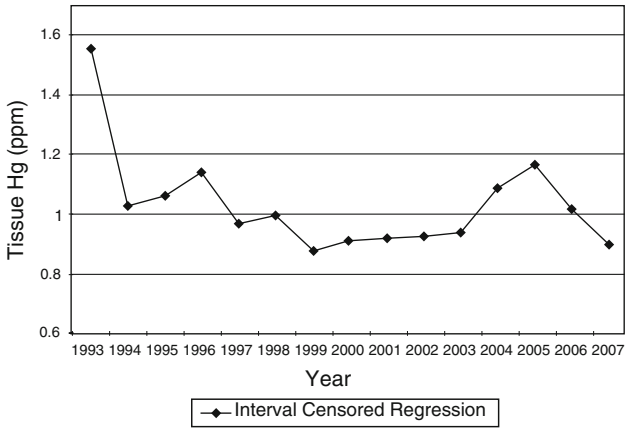

Fig. 6 Length adjusted predicted tissue mercury values for largemouth bass using interval censored regression for unregulated rivers of the Middle Atlantic Coastal Plain ecoregion

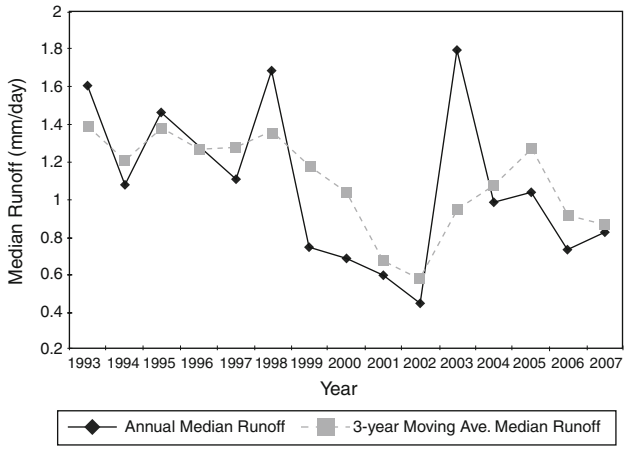

Fig. 7 Annual median runoff (mm/day) and the 3-year moving average of annual median runoff for South Carolina

predatory fish such as largemouth bass. Other factors could be involved such as the effects of flooding and its creation of anoxic conditions that was discussed above. However, there was a fairly large increase in runoff in 1998 from the previous 2 years without the corresponding increase in tissue Hg levels. The primary difference was 2001 and 2002 were years of major droughts followed by extremely high flows in 2003 in coastal rivers (Fig. 7). As shown in Fig. 8 this lag in the bioaccumulation response is captured better by the 3-year moving average of median runoff than annual values. These findings add support to the hypothesis of Gilmour et al. (2004). An important variable missing from our analysis was water column sulfate data, which has been shown to be important in the methylation process in a variety of studies (Munthe et al. 2007). Water column total Hg and MeHg data were also unavailable.

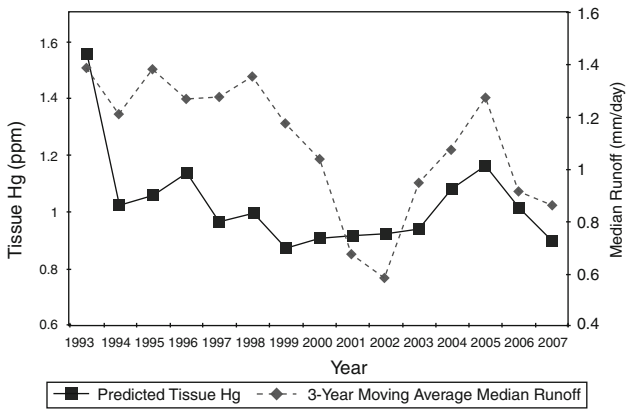

Fig. 8 Length adjusted predicted tissue Hg for largemouth bass calculated from interval censored regression and the 3-year moving average of annual median runoff in relation to the years 1993–2007

Conclusions

In South Carolina, unregulated rivers were found to have higher levels of tissue Hg than regulated rivers. Poff et al. (1997) reviewed the importance of the natural flow regime to flora and fauna in a river and its floodplain. However, determining the natural flow of a regulated river can be difficult. While using elevated levels of a potentially toxic substance in fish tissue as an indicator of natural hydrology may be unappealing, our data suggests that high levels of fish tissue Hg, at least in parts of the southeastern U.S., is indicative of a riverine system that has retained its historic flow regime. This is not to suggest abandoning the goal of flow restoration in order to prevent Hg bioaccumulation. It is merely to highlight the notion that a variety of data can add insight into complex environmental issues.

Fishes collected from estuaries and near shore saltwater species had some of the lowest levels of tissue Hg in the SCDHEC dataset. There have been other studies that reported similar findings (Gilmour and Riedel 2000), however, the reasons for this phenomenon are poorly understood. Heyes et al. (2006), Mason et al. (1999), and Hammerschmidt et al. (2004) provided insight into the methylation process of Hg in estuaries but the bioaccumulation process in fish tissue needs further study. The methylation and bioaccumulation process in the open ocean is even less understood. Kraepiel et al. (2003) suggested that the source of MeHg to apex predators such as tuna was the deep sea. Chen et al. (2008), however, proposed that most methylation and accumulation occurred in shallow sediments and MeHg was transferred to open ocean predators during their nearshore seasonal visits. Because many open ocean fishes are commercial species, the understanding of the Hg methylation and bioaccumulation processes here is arguably more important to human health on a global scale than for freshwater wild-caught fishes.

Lastly, our findings demonstrate the importance of proper stratification of landscape variables in ecological studies. The importance of ecoregions in large-scale environmental studies cannot be overstated. In most instances this requires large datasets to capture the variability that is typically found in the natural world. In a national analysis Hammerschmidt and Fitzgerald (2006), suggested a link between atmospheric mercury deposition and mercury in freshwater fish using political boundaries, in the form of states of the U.S., as units of study. Because of differences in regulations between different political jurisdictions, political boundaries are sometimes useful units for display, but they rarely have any true ecological meaning. Over the last two decades the watershed, both real topographic watersheds but more often in the form of hydrologic units, has tended to be the unit of choice to show geographic patterns in ecological data (Omernick 2003). In a national study Brumbaugh et al. (2001), characterized water and fish tissue Hg levels utilizing large basins as study units. In a recent report, the USEPA (2009d) characterized fish tissue Hg for the United States by 8 digit hydrologic units. In a review of the use of watersheds and hydrologic units Omernick (2003) indicated that only roughly 45% of hydrologic units on a national map were true watersheds and many crossed multiple ecoregions. He noted that for ecological studies watersheds and ecoregions should be complementary and proposed that ecoregions be used for extrapolating and reporting information. Our study adds support to this paradigm. But, while Resh and Kobzina (2003) reported that Omernick (1987) paper was the 4th most cited journal article in aquatic ecology, a paradigm shift has been slow to occur for many researchers in academia and government institutions.

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