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Influence of Physiochemical and Watershed Characteristics on Mercury Concentration in Walleye, *Sander vitreus*, M.

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Abstract Elevated mercury concentration has been documented in a variety of fish and is a growing concern for human consumption. Here, we explore the influence of physiochemical and watershed attributes on mercury concentration in walleye (*Sander vitreus,* M.) from natural, glacial lakes in South Dakota. Regression analysis showed that water quality attributes were poor predictors of walleye mercury concentration ($R^2 = 0.57$, $p = 0.13$). In contrast, models based on watershed features (e.g., lake level changes, watershed slope, agricultural land, wetlands) and local habitat features (i.e., substrate composition, maximum lake depth) explained 81% ($p = 0.001$) and 80% ($p = 0.002$) of the variation in walleye mercury concentration. Using an information theoretic approach we evaluated hypotheses related to water quality, physical habitat and watershed features. The best model explaining variation in walleye mercury concentration included local habitat features ($W_i = 0.991$). These results show that physical habitat and watershed features were better predictors of walleye mercury concentration than water chemistry in glacial lakes of the Northern Great Plains.

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Atmospheric deposition of mercury is a major factor contributing to mercury (Hg) contamination in aquatic food webs (Watras et al. 1995). Methylmercury (MeHg) is the organic, bioavailable form of Hg that accumulates to toxic levels in top-level predators in aquatic systems (Lathrop et al. 1991; Suedel et al. 1994). Mercury concentration in fish often varies considerably among water bodies and has been linked to a variety of chemical, environmental and biological attributes that affect methylmercury formation and transport (Watras et al. 1995; Sackett et al. 2009).

Physiochemical attributes such as lake productivity, pH, nutrient concentration, and habitat conditions are known to influence methylation efficiency and ultimately fish mercury concentrations (Allen-Gil et al. 1995), which implies that local effects play an important role in mercury accumulation (Lange et al. 1993). Watershed characteristics can also influence methylmercury production because factors such as soil type, vegetation density, and surrounding land use affect limnological conditions in receiving waters (Kalff 2002) and have been shown to influence mercury accumulation in aquatic food webs (Allen-Gil et al. 1995; Sackett et al. 2009).

Predicting mercury concentration in fish has important implications for freshwater monitoring and assessment programs. Predictive models of fish mercury are usually developed from physiochemical factors that can be limited in their application to regional or even lake-specific use. The relative importance of local- versus watershed-level effects on mercury accumulation in walleye has not been documented, but attempts could prove useful for monitoring and assessment programs (Sackett et al. 2009). Unlike water quality measures that can vary considerably within and among years, watershed attributes are likely to be less variable from year-to-year. The purpose of this study was to evaluate the relative influence of physiochemical (water quality and habitat conditions) and watershed-level characteristics on mercury concentration in walleye (*Sander vitreus,* M.).

Materials and Methods

We used data from 17 natural, glacial lakes in eastern South Dakota to develop and evaluate predictive models of fish mercury concentration (Fig. 1). Candidate lakes were selected to reflect the growing conditions experienced by fish prior to Hg sampling. Thus, we only included lakes where water quality data were available 1–3 years prior to fish sampling. The lakes used in our study are typical of many shallow (<10 m), polymictic lakes in the Prairie Pothole Region of the US and Canada, and range in productivity from eutrophic to hypereutrophic (Stukel 2003; Table 1). We collected tissue samples from a total of 686 walleye during summer months from 2002 to 2007 using a combination of electrofishing, trap-nets, and experimental gill nets (see Selch et al. 2007). Composite samples (2–7 per lake), based on homogenized tissue (2 g) from five fish, were analyzed for total mercury using cold vapor atomic fluorescence spectrometry (Selch et al. 2007). We used maximum walleye mercury concentration reported for each lake as our response variable.

Watershed-level variables were quantified using a variety of data sources (Table 1). Lake surface area was calculated from digitized 1:25,000 maps or from USGS topographic quadrangles. Slope within the basin was determined using land cover data based on Landsat 5 Thematic Mapper imagery from 1992. South Dakota Geographic Analysis Program (GAP) data were used to determine watershed size, and percent of agricultural land within the watershed (Smith et al. 2002). Wetlands within 1 km of the lake were delineated from US Fish and Wildlife Service (2000) National Wetland Inventory maps (1:24,000). Details on changes in surface area between these two time periods are provided in Selch et al. (2007).

Correlation analysis was used to evaluate relationships among all predictor variables to (1) preclude the use of correlated variables in our models and (2) reduce the number of predictor variables. Forward stepwise multiple regression analysis was used to develop predictive models of walleye mercury concentration based on water quality attributes, local habitat conditions or watershed variables. Variables were included in the model only if they significantly ($p < 0.05$) reduced the unexplained sum of squares. Each predictor category was analyzed separately. Using

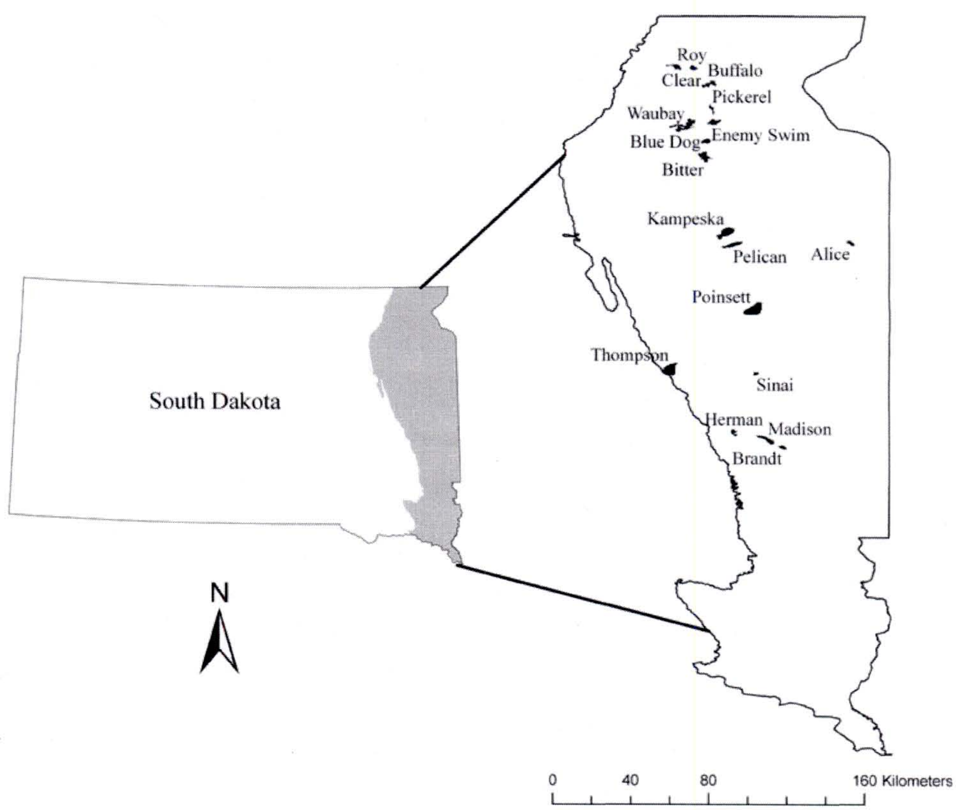

Fig. 1 Location of 17 glacial lakes in eastern South Dakota

Table 1 Predictor variables from forward stepwise regression analysis to predict walleye mercury concentration

Predictor category	Variable	Code	Min	Max
Water quality[a]	Alkalinity (mg/L)	ALK	136.00	368.00
	Total dissolved solids (mg/L)	TDS	235.50	1936.50
	Conductivity (μS/cm)	COND	482.00	3122.60
	Total phosphorus (mg/L)	TP	0.02	0.35
	Ph	PH	7.69	9.30
	Total kjeidal nitrogen (mg/L)	TKN	0.60	2.55
	Ammonium (mg/L)	AMM	0.02	0.80
	Nitrogen to phosphorus ratio	NP	1.63	50.50
	Trophic state index based on phosphorus	TSI	46.61	89.38
Local habitat[b]	Vegetation coverage (%)	VEG	0	31
	Sediment composition - silt (%)	SILT	49	86
	Sediment composition - detritus (%)	DET	0	18
	Fetch (m)	FETCH	2.7	14.5
	Maximum lake depth (m)	DMAX	2.7	12.5
	Mean lake depth (m)	DMEAN	1.4	5
Watershed[c]	Surface area change (%)	SACH	−4.8	236.3
	Wetlands within 1 km (ha)	WET	58.67	2669.81
	Slope of basin (m)	SLOPE	0.6	5.2
	Agricultural land (%)	AG	15.9	66.7
	Watershed size (ha)	WS	1604	8899
	Watershed size to lake surface area ratio	WSSA	1.26	20.84
	Surface area (ha)	SA	261	2894

[a] South Dakota Department of Environment and Natural Resources (http://denr.sd.gov/des/sw/wqmonitoring.aspx)

[b] Stukel (2003)

[c] Smith et al. (2002), Selch et al. (2007), U.S. Fish and Wildlife Service (2000)

predictor variables identified in each of the previous analyses, we then developed a combined model for predicting walleye mercury concentration. Thus, we developed four candidate models that could be evaluated using an information theoretic approach (Burnham and Anderson 2002; Table 2). Akaike's information criterion (AIC) was then used to rank the candidate models and determine the best predictive model, and thus provide insight into which category was more important in influencing the variation in walleye mercury concentration. When comparing models using AIC, the model with the lowest value corrected for small sample size (AICc) was considered best.

Results and Discussion

Mercury concentration in walleye ranged from 0.10 ppm (Lakes Herman, Pickerel, and Poinsett) to 1.75 ppm (Bitter Lake). At present, only one of our study lakes (Bitter Lake) is posted with a fish health advisory (>1 ppm). The Environmental Protection Agency (EPA) recommends that lakes with fish contaminant levels >0.3 ppm be listed with a fish consumption advisory. Using this criterion, five of the lakes in our study would be considered candidates for fish consumption advisories.

Six variables were included in the best model for water quality and explained 57% of the variation in walleye mercury tissue concentration ($df = 6.16$; $R^2 = 0.57$, $p = 0.13$; Table 2). The most important variable was alkalinity that explained 22% of the variation and was positively related to walleye mercury concentration. High alkalinity (>20 mg/L) is known to increase phosphorus availability in lakes (Wurts and Durborow 1992); thus, the positive correlation between alkalinity and walleye Hg concentration may be related to lake productivity. Related studies have shown that productivity of glacial lakes is positively correlated with Hg concentration in walleye (Selch et al. 2007). Selch et al. (2007) found that walleye growth was positively correlated to mean Hg concentration, and concluded that 'growth dilution' normally associated with reduced mercury concentration may not manifest in glacial lake walleye populations because of the link between productivity and Hg accumulation.

Habitat features associated with walleye mercury concentration included percent detritus, percent silt, and maximum water depth that explained 80% of the variation in fish tissue concentration ($df = 3.16$; $R^2 = 0.80$, $p = 0.002$; Table 2). Walleye mercury concentration was positively related to detritus and maximum depth, consistent with other studies (Jackson 1991). Methylation efficiency is generally higher in fine sediments with high organic content (Ullrich et al. 2001). Organic matter plays an important role in methylation by providing an energy-yielding substrate for bacteria in methylmercury cycling

Table 2 Multiple linear regression models for predicting walleye mercury concentration

Predictor category	Parameter[a]	Parameter estimate	Partial R[b]
Water quality	Intercept	−2.46	–
	ALK	0.003	0.22
	TDS	0.0006	0.09
	TSI	−0.022	0.1
	AMM	−0.720	0.04
	pH	0.406	0.08
	NP	−0.014	0.03
Local habitat	Intercept	−0.925	–
	DET	0.022	0.45
	SILT	0.012	0.08
	DMAX	0.040	0.26
Watershed	Intercept	0.982	–
	SACH	0.005	0.59
	SLOPE	−0.142	0.11
	AG	−0.010	0.08
	WETSA	−0.278	0.04
Combined[b]	Intercept	0.594	–
	SACH	0.003	0.21
	TSI	−0.007	0.16
	SLOPE	−0.129	0.16
	DMAX	0.48	0.22

[a] Definitions for parameter codes are given in Table 1

[b] The combined model was generated using all parameters identified

(Compeau and Bartha 1985). Moreover, anoxic conditions associated with organic matter decomposition is known to enhance methylation efficiency (Ullrich et al. 2001), and may contribute to increased Hg concentration in walleye. In addition, deeper lakes are more likely to experience periods of summer stratification that contribute to anoxic conditions and increased methylation efficiency (Snodgrass et al. 2000).

Watershed characteristics included percent surface area change, watershed slope, percent agriculture in the watershed, and the watershed-to-lake surface area ratio ($df = 4.16$; $R^2 = 0.81, p = 0.001$; Table 2). These four variables explained 81% of the variation in walleye mercury concentration. High mercury levels may be the result of mercury deposition in adjacent terrestrial soils that became flooded (Selch et al. 2007). Lower slope in adjacent shorelines and near-shore sediments, where there are higher methylation rates (Snodgrass et al. 2000), allows for more area to become flooded. Similarly, the total area of wetlands (ha) within one km of the lake was a moderately important variable in the model, consistent with findings by Simonin et al. (2008). In addition, percent agricultural land exhibited a positive relationship with walleye mercury concentrations. Previous studies have reported that basins with dominant agricultural land have significant nutrient runoff (e.g., nitrogen, phosphorus) which stimulates mercury-methylating bacteria (Sackett et al. 2009), however, the insignificant relationship between nitrogen and phosphorus and fish mercury levels suggest that land use practices are important to mercury loading in ways other than their influence on nutrient levels (Sackett et al. 2009).

A combined model that used variables from the three predictor categories, included four predictor variables and in general provided little improvement over other models, explaining 76% of the variation in mercury tissue concentration ($df = 4.16$; $R^2 = 0.76, p = 0.013$; Table 2). Percent change in surface area (i.e. dry vs. wet years), watershed slope and maximum depth were positively associated with walleye mercury concentration, whereas trophic state index was inversely related to mercury concentration.

The AIC model selection approach showed that local habitat conditions were the best supported model in explaining mercury concentration in walleye (Table 3). Water quality measurements were poor predictors which may be a result of the inherent variability of these measurements (e.g., not measured on fine-enough time scales) or the complex interactions between water chemistry variables and methylation rates and bioaccumulation (Lange et al. 1993). Similarly, watershed factors may be measured on too broad a scale and may not account for other important factors affecting methylation rates (Rich and McMahon 2003).

Large-scale watershed features such as topography, soils, vegetation, and land use can influence local lake

Table 3 AIC results for four candidate models used to predict mercury concentration in walleyes

Predictor category	Model	K	N	RSS	AIC_c	Δ_i	W_i
Local habitat	DET SILT DMAX	4	13	0.057	−17.687	0.000	0.991
All variables	SACH TSI SLOPE DMAX	5	13	0.127	−7.542	10.144	0.006
Watershed	SACH SLOPE AG WETSA	5	15	0.482	−5.724	11.963	0.003
Water quality	ALK TDS TSI AMM Ph NP	7	17	1.157	6.603	24.289	0.000

The number of model parameters (K), sample size (N), residual sum of squares (RSS), Akaike's information criterion for small sample size (AIC_c), distances between the best model and the *i*th model (Δ_i), and renormalized AIC model weights (W_i) are given habitat features such as lake size, depth, nutrient inputs, and sediment composition. During the mid-1990's, eastern South Dakota experienced several consecutive years of high precipitation which caused an increase in surface runoff and dramatic increases in lake water levels that inundated many adjacent wetlands and previously unexposed vegetation and soils (Kahara et al. 2009). Surface runoff and increased water levels can increase dissolved organic matter (DOM), resuspend sediment mercury and thus increase methylation and uptake, and lower dissolved oxygen allowing for higher rates of mercury methylation (Selch et al. 2007; Sackett et al. 2009). Previous work has shown that increased water levels were positively related to fish mercury concentration, but other lake-specific factors likely contributed to variation in walleye mercury levels (Selch et al. 2007). Our findings show that local habitat features such as sediment composition (detritus, silt) and water depth, are linked to variation in walleye mercury concentration. These data can prove useful for developing future monitoring and assessment programs by identifying lake types with specific local habitat features that are susceptible to mercury accumulation in fish.

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