Environmental Monitoring and Assessment (2006)
DOI: 10.1007/s10661-005-9163-8

PREDICTING WATER QUALITY IMPAIRED STREAM SEGMENTS USING LANDSCAPE-SCALE DATA AND A REGIONAL GEOSTATISTICAL MODEL: A CASE STUDY IN MARYLAND

ERIN E. PETERSON[1,*] and N. SCOTT URQUHART[2]
[1]*CSIRO Mathematical & Information Sciences, Queensland Bioscience Precinct, 306 Carmody Road, St. Lucia, QLD, Australia, 4067;* [2]*Department of Statistics, Colorado State University, Fort Collins, CO 80523, USA*
*(*author for correspondence, e-mail: Erin.Peterson@csiro.au)*

(Received 05 August 2005; accepted 19 December 2005)

Abstract. In the United States, probability-based water quality surveys are typically used to meet the requirements of Section 305(b) of the Clean Water Act. The survey design allows an inference to be generated concerning regional stream condition, but it cannot be used to identify water quality impaired stream segments. Therefore, a rapid and cost-efficient method is needed to locate potentially impaired stream segments throughout large areas. We fit a set of geostatistical models to 312 samples of dissolved organic carbon (DOC) collected in 1996 for the Maryland Biological Stream Survey using coarse-scale watershed characteristics. The models were developed using two distance measures, straight-line distance (SLD) and weighted asymmetric hydrologic distance (WAHD). We used the Corrected Spatial Akaike Information Criterion and the mean square prediction error to compare models. The SLD models predicted more variability in DOC than models based on WAHD for every autocovariance model except the spherical model. The SLD model based on the Mariah autocovariance model showed the best fit ($r^2 = 0.72$). DOC demonstrated a positive relationship with the watershed attributes percent water, percent wetlands, and mean minimum temperature, but was negatively correlated to percent felsic rock type. We used universal kriging to generate predictions and prediction variances for 3083 stream segments throughout Maryland. The model predicted that 90.2% of stream kilometers had DOC values less than 5 mg/l, 6.7% were between 5 and 8 mg/l, and 3.1% of streams produced values greater than 8 mg/l. The geostatistical model generated more accurate DOC predictions than previous models, but did not fit the data equally well throughout the state. Consequently, it may be necessary to develop more than one geostatistical model to predict stream DOC throughout Maryland. Our methodology is an improvement over previous methods because additional field sampling is not necessary, inferences about regional stream condition can be made, and it can be used to locate potentially impaired stream segments. Further, the model results can be displayed visually, which allows results to be presented to a wide variety of audiences easily.

Keywords: dissolved organic carbon, geostatistics, hydrologic distance, streams, water quality monitoring

1. Introduction

The Clean Water Act (CWA) of 1972 requires states and tribes located in the United States to identify water quality impaired stream segments, to create a priority ranking of those segments, and to calculate the Total Maximum Daily Load (TMDL) for

each impaired segment based upon chemical and physical water quality standards. States and tribes are also required to prepare a biennial water quality inventory that characterizes regional water quality based on the attainment of designated-use standards assigned to individual stream segments. Yet, it is impossible to physically survey every stream within a large area due to the immense number of segments, limited personnel, and the cost associated with sampling (Olsen and Ivanovich, 1993; Herlihy *et al*., 2000; USEPA, 2001). In addition, lawsuits have been filed in 38 states by environmental groups demanding that the requirements of the CWA be met in a timely fashion (Copeland, 2002). These increased pressures have led to the need to develop a rapid and cost-efficient survey method that has the ability to statistically identify potentially impaired stream segments in large areas. To address this issue, we developed a geostatistical model based on coarse-scale geographical information system (GIS) data and used it to make predictions for every stream segment in our study area. We predicted dissolved organic carbon (DOC) because it can be used as a water quality indicator (Maryland Department of Natural Resources, 1999), but these methods could also be applied to other water quality constituents. Although our results may be useful in Maryland, our primary interest lies in investigating and demonstrating a methodology which could be used by any state or tribe to predict any quantitative water quality parameter.

Dissolved organic carbon (DOC) is an important constituent of water quality because it affects the chemical and biological condition of freshwater ecosystems. DOC is a significant energy source in aquatic food webs (Wetzel, 1992), absorbs biologically harmful ultraviolet rays that penetrate the water column (Williamson *et al*., 1996; Kiffney *et al*., 1997), acts as a weak acid (Sullivan *et al*., 1989), and binds dissolved substances, such as metals, making them temporarily less bioavailable (Driscoll *et al*., 1995; Prusha and Clements, 2004).

The concentration of DOC in headwater streams is strongly influenced by the production and transport of organic matter from the terrestrial environment. The main sources are soil, groundwater, and dead terrestrial plant material (Wetzel, 1992). DOC is transported from the watershed via overland, sub-surface, or base flow and the flow path of water affects the stream concentration. Shallow sub-surface paths and overland flow through wetlands, organic soil layers, and shallow soils tend to produce water with relatively high concentrations of DOC (Mulholland, 2003). Conversely, sub-surface or base flow moving through deeper soil horizons may lose DOC, which is adsorped by the mineral soils (Qualls and Haines, 1992).

Models based on both local and coarse-scale input data have been created to explain variability in lake or stream DOC (Rasmussen *et al*., 1989; Houle *et al*., 1995; Currie and Aber, 1997; Neff and Asner, 2001; Ouyang, 2003). For our purposes, local-scale data refers to fine-scale measurements, such as depth of litter mass, which must be collected in the field. Coarse-scale or landscape-scale data represent lumped watershed attributes, such as percent wetlands or mean elevation in the watershed, which are typically calculated using GIS or remotely sensed data. Models that include locally-derived input data are not suitable for regional DOC

estimation because they require extensive and expensive field sampling (Herlihy *et al*., 2000; USEPA, 2001). Models based solely on remotely derived coarse-scale data have also been generated to explain variability in DOC concentration. There appears to be a significant tradeoff between the cost, in both time and money, of input data and the accuracy of the model predictions. For example, Creed and others (2003) delineated wetlands using LIDAR (light detection and ranging) data and were able to explain 91% of the variability in stream and lake DOC in 12 watersheds. Their results are promising, but their input data is expensive (Haneberg, 2005) and therefore unsuitable for regional monitoring at this time.

Other models have been generated using coarse-scale remotely sensed data, such as United States Geological Survey (USGS) Land Use Land Cover data (USGS, 2005) or USGS digital elevation models (DEM) (USGS, 2003), which are easily accessible and available at no cost. Yet, these models explained less variability in DOC (Eckhardt and Moore, 1990; Herlihy *et al*., 1998; Gergel *et al*., 1999; Prusha and Clements, 2004). For example, Kortelainen (1993) used latitude, catchment area/lake area ratio, and percent of watershed area covered by peatlands, fields, and upstream lakes to explain 55% of the variability in DOC collected in 978 lakes throughout Finland. Canham and others (2004) built a process-based model based on landscape data to better understand the production, transport, and loss of DOC in 428 Adirondack lakes and were also able to explain 55% of the variability in DOC. Although these models are useful, there is a need for more accurate regional models based on accessible and inexpensive input data.

We recently completed research that indicates that geostatistical models based on coarse-scale data have the ability to produce more accurate stream chemistry predictions (Peterson *et al*., in press). Geostatistical models are similar to traditional statistical models, in that they represent the broad-scale trend in the mean of the data, but relax the assumption of independence and allow spatial autocorrelation in the residuals. Local deviations from the mean are modeled using the covariance between neighboring sites. Heterogeneity in the broad-scale mean and variance are permitted, but the mean, variance, and autocorrelation structure of the error term are assumed to be stationary or similar across a study area (Bailey and Gatrell, 1995).

The covariance characterizes the strength of spatial autocorrelation between pairs of sites within a spatial neighborhood given their separation distance (Olea, 1991). A spatial neighborhood includes sites that are nearby and have a quantifiable influence upon one another. Sites outside of the spatial neighborhood are not considered to be spatially correlated. The separation distance is simply the distance traveled from one location to a second location.

The separation distance can be calculated using a variety of distance measures (Peterson *et al*., in press), but we only concern ourselves with straight-line distance (SLD) (aka Euclidean distance) and asymmetric hydrologic distance weighted by discharge volume. SLD (Figure 1a) is directionless (isotropic) and has equal correlation in all directions. In addition, all locations in a study area are considered

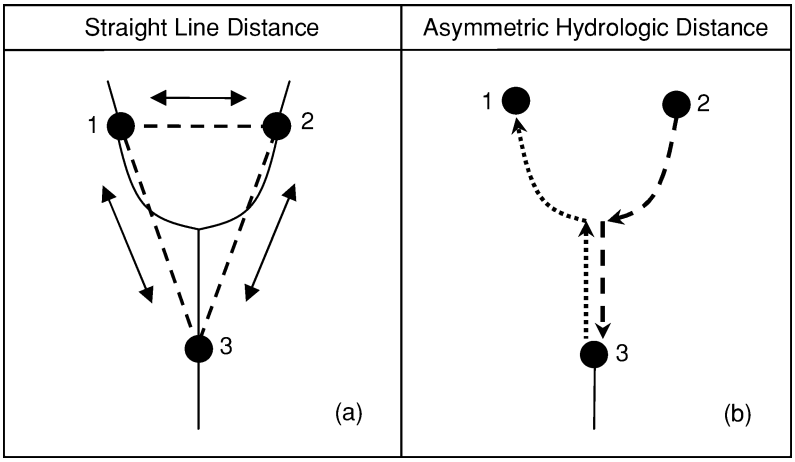

Figure 1. Straight-line distance and asymmetric hydrologic distance. The stream network is represented by a solid line while distance measurements are represented with dotted lines. Sites 1, 2, and 3 are all neighbors to one another when straight-line distance (a) is used. Sites 1 and 2 are neighbors to site 3, but not to each other when asymmetric hydrologic distance (b) is used because sites must be connected by flow to be neighbors.

potential neighbors. Hydrologic distance is the distance between two locations when movement is restricted to the stream network. Asymmetric hydrologic distance is unidirectional because movement between sites is restricted to either the upstream or downstream direction (Figure 1b). Therefore, water must flow from one location to another for two sites to be considered potential neighbors. Spatial weights are generated using metrics that represent relative network position, such as watershed area, and used to represent discharge volume (Ver Hoef *et al*., 2007; Peterson, 2005).

Geostatistical models have not typically been used to model water chemistry in stream networks (but see Gardner *et al*., 2003; Kellum, 2003; Yuan, 2004; Peterson *et al*., in press), but they have been shown to improve the accuracy of water chemistry predictions (Yuan, 2004; Peterson *et al*., in press). It is common for researchers to obtain an estimate of the model fit by removing observed sites from the dataset and making predictions at those sites (Gardner *et al*., 2003; Yuan, 2004, Peterson *et al*., in press). To our knowledge, no one has used a fitted geostatistical model to make water chemistry predictions for every *unobserved* stream segment in their study area. We created a set of geostatistical models using coarse-scale GIS data and two distance measures, SLD and weighted asymmetric hydrologic distance (WAHD). We compared the models to determine which had the most predictive ability and then used a single model to generate predictions and prediction variances for 3083 stream segments located in seven interbasins throughout Maryland.

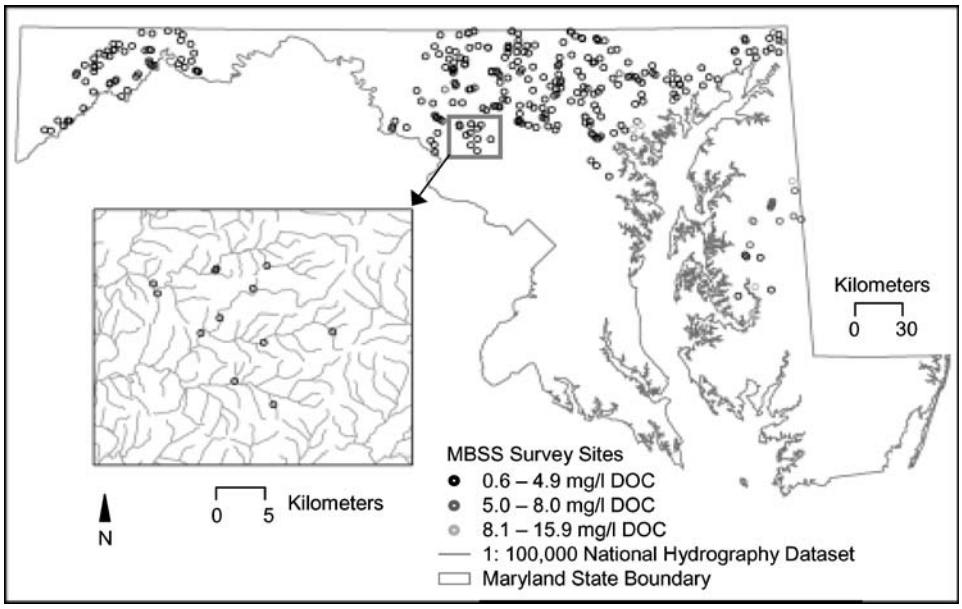

Figure 2. The Maryland Biological Stream Survey sites and their dissolved organic carbon (DOC) values in mg/l collected by the Maryland Department of Natural Resources in 1996.

2. Methods

2.1. Study area and design

The Maryland Biological Stream Survey (MBSS) data (Figure 2) were collected throughout Maryland by the Department of Natural Resources (DNR) (Mercurio *et al*., 1999). Maryland is a geographically diverse state that can be divided into five physiographic provinces: the Appalachian Plateau, the Blue Ridge, the Coastal Plain, the Piedmont, and the Valley and Ridge (Boward *et al*., 1999). Elevation increases from the eastern Coastal Plain to the Appalachian Plateau in the west.

The Maryland DNR used a probability-based survey to collect chemical, physical, and biological data from first, second, and third order non-tidal streams in 17 interbasins throughout the state (Mercurio *et al*., 1999). A stratified random sample was selected in each interbasin based on Strahler stream order (Strahler, 1957) and the number of samples collected per stream order was proportional to the number of stream order miles within the interbasin. Sampling was conducted during 1995, 1996, and 1997, but we restricted our analyses to data collected in 1996 to reduce differences in DOC resulting from interannual variation. Seven interbasins were visited and 343 DOC samples were collected at individual locations between March 1 and May 1, 1996. The samples represent the carbon that remained after filtration with a 0.45 μm filter (USEPA, 1987). They were analyzed using a

Doorman DC-80 carbon analyzer, which had a minimum detection limit of 1.0 mg per liter (Mercurio *et al.*, 1999).

2.2. GIS PRE-PROCESSING

The stream network and survey site coordinates were pre-processed in a GIS to ensure that sites were positioned on the correct stream segment. There are a variety of reasons why it is rare for GIS data collected within a stream to fall directly on a line segment representing a stream. Though points collected using global positioning systems are differentially corrected, they still have some error. Some stretches of river can move (e.g. meander) slightly from their mapped position. Streams are often represented by lines and so samples collected on the banks of a large river may not fall directly on a line segment. Digital streams datasets may contain mapping errors and generalizations, such as the absence of small tributaries and the homogenization of form, which are found when streams are represented at coarser scales. As a result of these data problems, we discarded 23 sites because the survey stream could not be identified.

Distance matrices were generated for SLD and asymmetric hydrologic distance measures (Figures 1a and 1b). We projected the data from latitude/longitude to Albers Equal Area projection (North American Datum 1983 based on the GRS1980 spheroid) before calculating the distance measurements. Projecting the data was necessary because distance between points calculated directly from latitude/longitude coordinates have a known, systematic bias associated with increasing latitude. The SLD matrix was calculated in *R* statistical software package (Ihaka and Gentleman, 1996) using northing and easting values as x, y coordinates.

The spatial weights are used to develop the WAHD measure and represent the relative influence of one site on another. If two sites are not connected by flow the spatial weight is equal to zero and a site's influence on itself is equal to 1. The spatial weights for flow-connected sites are based on watershed area, which we use as a surrogate for discharge volume. They are generated by calculating the upstream watershed area for the downstream node of each segment in the stream network using a GIS. We define a stream segment as the portion of a stream located between two confluences. When survey sites fall midway along a segment it is split into two separate stream segments. At each confluence or survey site in the network, the total upstream watershed area is calculated by summing the watershed area for the incoming stream segments. The proportional influence (PI) for each incoming segment is calculated by dividing its watershed area by the total upstream watershed area at the confluence or survey site (Figure 3). When this process is complete, every *stream segment* in the network contains an attribute that represents its PI on the segment directly downstream. The next step is to calculate the PI of one *site* on another. First, we locate the path between flow-connected sites. The PI of one site on another is equal to the product of the segment proportional influences found in the path between sites. The spatial weights matrix is simply an n by n matrix that

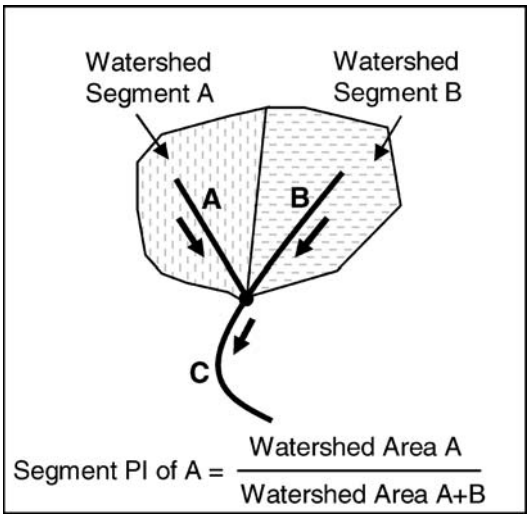

Figure 3. The segment proportional influence (PI) represents a segment's PI on the segment directly downstream. It is calculated by dividing the segment's total watershed area by the total incoming watershed area at the confluence or survey site.

contains the square root of the PI for all pairs of sites. Using the square root of the PI ensures that stationarity in the variances is maintained (Ver Hoef *et al*., 2007).

The asymmetric hydrologic distance and spatial weights matrices were calculated in a GIS using programs written in Visual Basic for Applications for ArcGIS version 8.3 (ESRI, 2002). The GIS methods used to generate these matrices are lengthy and are not the focal point of this manuscript (but see Peterson, 2005).

2.3. Statistical analysis

2.3.1. *Initial Covariate Selection*

The MBSS dataset contains coarse-scale watershed data for each survey site (Mercurio *et al*., 1999), which the Maryland DNR derived using a GIS and the 1992 National Land Cover Data (NLCD) (MRLC Consortium, 2003) (Table I). We also derived two site level attributes: Level III Omernik's ecoregion (Omernik, 1987) and geographic location, as well as, watershed level attributes: mean temperature, mean elevation, mean slope, mean precipitation, percent geology type, mean soil pH, and mean soil erodability factor (Table I). The variance inflation factor (VIF) collinearity statistic (Helsel and Hirsch, 1992) indicated that some potential covariates were significantly correlated with other covariates (VIF >10) and we removed them from further analysis. These included percent agriculture, percent forest, percent wetlands, percent high intensity urban, percent low intensity urban, percent pasture/hay/grass, percent probable row crops, percent row crops, percent transitional area, mean soil pH, mean annual minimum temperature, mean

TABLE I

Potential watershed covariates. Potential covariates include lumped watershed attributes provided in the Maryland Biological Stream Survey (MBSS) dataset, as well as, lumped watershed attributes and site level attributes that we calculated in a GIS. Potential covariates that demonstrated collinearity with other covariates are not included in this table

Covariate	Description	Spatial resolution	Source
AREA	Catchment area (ha)	30 m	USGS, 2003
URBAN	% Urban	30 m	MBSS
BARREN	% Barren	30 m	MBSS
WATER*	% Open water	30 m	MBSS
CONIFER	% Conifer or evergreen forest type	30 m	MBSS
DECIDFOR	% Deciduous forest type	30 m	MBSS
MIXEDFOR	% Mixed forest type	30 m	MBSS
EMERGWET*	% Emergent herbacious wetlands	30 m	MBSS
WOODYWET*	% Woody or shrubby wetlands	30 m	MBSS
COALMINE	% Coalmine	30 m	MBSS
EASTING	Easting–Albers Equal Area Conic	1 foot	projected from MBSS
NORTHING	Northing–Albers Equal Area Conic	1 foot	projected from MBSS
ER63-ER69*	Omernik's Level III Ecoregion	1:250,000	USEPA, 2005
MEANELEV	Mean elevation in the watershed	30 m	USGS, 2003
SLOPE	Mean slope in watershed	30 m	USGS, 2003
ARGPERC	% Argillaceous rock type in watershed	1:250,000	A. Herlihy, pers. comm.
CARPERC	% Carbonic rock type in watershed	1:250,000	A. Herlihy, pers. comm.
FELPERC*	% Felsic rock type in watershed	1:250,000	A. Herlihy, pers. comm.
MAFPERC	% Mafic rock type in watershed	1:250,000	A. Herlihy, pers. comm.
SILPERC	% Siliceous rock type in watershed	1:250,000	A. Herlihy, pers. comm.
MEANK	Mean soil erodability factor in watershed	1 km	ESSC, 1998
MAXTEMP	Mean annual maximum temperature	4 km	SCAS, 1996
MINTEMP*	Mean minimum temperature for January–April	4 km	SCAS, 1996
PRECIP	Mean precipitation for January–April	4 km	SCAS, 1996
ANPRECIP	Mean annual precipitation	4 km	SCAS, 1996

*Potential watershed covariates used in the geostatistical model selection.

maximum temperature for the months of January to April, and mean soil permeability, leaving those listed in Table I for further investigation.

We needed to further reduce the list of potential covariates (Table I) due to the processing time required for model selection. We used a Leaps and Bounds algorithm (Furnival and Wilson, 1974) to find the "best" set of covariates and used

them to develop a linear model. Ten watershed attributes were selected as potential covariates: WATER, WOODYWET, EMERGWET, FELPERC, MINTEMP, ER64, ER65, ER66, ER67, and ER69 (Table I). The WATER, WOODYWET, EMERGWET, AND FELPERC covariates represent percent open water, forested or shrubby wetland areas, perennial herbaceous wetland areas, and felsic rock type in the watershed, respectively. MINTEMP is the mean minimum temperature in the watershed for the first four months of 1996. ER64, ER65, ER66, ER67, and ER69 represent the Omernik's Level III ecoregion (Omernik, 1987) where the site is located. We checked the model residuals for signs of non-normality and transformed DOC using a $\log_{10}$ transformation. The studentized residuals were used to identify eight extreme outliers at a significance level of less than 0.01. These sites were not spatially clustered and there were no evident patterns related to DOC or watershed attributes. Therefore, the survey sites were removed from further analysis.

2.3.2. *Covariance Parameter Estimation*

We restricted the model space to all possible linear models using the 10 "best" explanatory variables determined by the initial covariate selection process described above. We evaluated nine sets of 1024 models ($2^{10} = 1024$), where each set was based on a unique distance measure and autocovariance function combination. Five sets of models used the SLD measure and one of five common autocovariance models: the exponential, spherical, Mariah (Eq. 3) (Ver Hoef *et al*., 2007), hole effect, and rational quadratic. The remaining four sets of WAHD models used moving average representations of common autocovariance functions: the exponential, spherical, linear with sill, and Mariah (Ver Hoef *et al*., 2007).

We also assumed that the model residuals were normally distributed with mean zero and variance-covariance matrix $\Sigma = \sigma^2\Omega$, where σ^2 is the variance and $\Omega = \Omega(d;\theta)$ is the covariance matrix. Note that Ω is a function of the separation distance between sites, d, given the covariance parameter vector, θ. Therefore, the model for response variable Z is written in matrix notation as $Z = X\beta + \varepsilon$, where $\varepsilon \sim N(0, \sigma^2\Omega)$. Here X is the $n \times p$ design matrix of covariates, β is a vector of coefficients of length p, and ε is a vector of n (correlated) errors.

The log-likelihood function of the parameters $(\theta, \beta, \sigma^2)$ given the observed data, Z, is

$$\ell(\theta, \beta, \sigma^2; Z) = -\frac{n}{2}\log(2\pi) - \frac{1}{2}\log|\sigma^2\Omega| - \frac{1}{2\sigma^2}(Z - X\beta)'\Omega^{-1}(Z - X\beta). \quad (1)$$

Maximizing the log-likelihood (Eq. 1) with respect to β and σ^2 yields $\hat{\beta} = (X'\Omega^{-1}X)^{-1}X'\Omega^{-1}Z$ and $\hat{\sigma}^2 = (Z - X\hat{\beta})'\Omega^{-1}(Z - X\hat{\beta})/n$. Both maximum likelihood estimators (MLE) can be written as functions of θ alone. We used the *profile* log-likelihood function, obtained by substituting the MLEs back into (Eq. 1):

$$\ell_{profile}(\theta; \hat{\beta}, \hat{\sigma}^2, Z) = -\frac{n}{2}\log(2\pi) - \frac{n}{2}\log(\hat{\sigma}^2) - \frac{1}{2}\log|\Omega| - \frac{n}{2}. \quad (2)$$

Use of the profile log-likelihood reduces the dimensionality of the maximization problem, which can substantially decrease the amount of computing time required to find a numerical solution. This is especially important when there are a large number of models to compare, as is the case here.

The covariance matrix, Ω, for SLD can be computed using any of the autocovariance functions we mentioned previously, but here we use the Mariah autocovariance function (Ver Hoef *et al.*, 2007) as an example:

$$C(d;\theta_0,\theta_1,\theta_2) = \begin{cases} \theta_0 + \theta_1 & \text{if } d = 0, \\ \theta_1 \left[\dfrac{\ln(d/\theta_2 + 1)}{d/\theta_2} \right] & \text{if } 0 < d < \theta_2, \\ 0 & \text{if } \theta_2 \leq d \text{ or two sites are not flow-connected,} \end{cases} \tag{3}$$

where θ_0 represents the nugget effect, θ_1 is the partial sill, and θ_2 is the range parameter. The nugget is estimated by $\hat{\theta}_0\hat{\sigma}^2$ where θ_0 is restricted between zero and one. The value d represents the separation distance between any two sites relative to the distance measure, e.g., SLD or WAHD.

The asymmetric hydrologic distance and PI matrices must be reformatted before they can be used to create a statistically valid covariance matrix (Ver Hoef *et al.*, 2007; Peterson, 2005). A matrix, W, is computed by taking the square root of the PI matrix. A symmetric spatial weights matrix is created by taking $A = W + W'$. Then, the asymmetric hydrologic distance matrix, d, is forced into symmetry by computing the symmetric hydrologic distance between all flow-connected sites. This may seem counter intuitive because the matrices are intended to represent asymmetric flow relationships. Nevertheless, there is a symmetric correlation between flow-connected sites. Even though a downstream site does not affect upstream sites, the conditions at the downstream site are, in part, a result of those found upstream. A model based on asymmetric hydrologic distance is dramatically different from models based on SLD or symmetric hydrologic distance (where flow direction and volume are ignored) because the spatial neighborhood for the WAHD only includes flow-connected sites. Flow connectivity is preserved in the symmetric distance matrix, while the strength of the spatial autocorrelation between flow-connected sites is represented by the spatial weights. The covariance matrix for the WAHD measure is generated by taking the Hadamard (element-wise) product of the symmetric distance and spatial weights matrices (Ver Hoef *et al.*, 2007). The product is a covariance matrix that meets the statistical assumptions necessary for geostatistical modeling (Ver Hoef *et al.*, in press).

The MLE for θ is found by maximizing the profile log-likelihood (Eq. 2) using a quasi-Newton method (Byrd *et al.*, 1995), which is in turn used to compute the MLEs for the model parameters: β and σ^2. To promote numerical stability, we standardized the response and explanatory variables to have mean zero and

unit variance. We also scaled the distances to fall between zero and one, but the estimates reported here have been converted back to the original units.

2.3.3. *Model Selection and Model Performance*

We used the spatial Akaike Information Corrected Criterion (AICC) statistic (Hoeting *et al*., in press) to select the geostatistical model with the most support in the data from each of the nine model sets. The spatial AICC is defined as

$$AICC = -2\ell_{profile}(\theta; \beta, \sigma^2, Z) + 2n\frac{p + k + 1}{n - p - k - 2}, \tag{4}$$

where n is the number of observations, $p - 1$ is the number of covariates, and k is the number of covariance parameters. It is possible to compare models with low AICC values and to identify a family of similar models, which all have a significant level of support in the data. However, we did not consider competing models here because we were primarily interested in prediction.

The nine models with the smallest AICC (one from each autocovariance function and distance measure combination) were used to generate predictions using the universal kriging algorithm (Cressie, 1993). We used a leave-one-out cross-validation method to calculate the mean square prediction error (MSPE) for each of the nine models (Eq. 5) The MSPE is defined as

$$MSPE = \frac{\sum_{i=1}^{n_p} (Z_i - \hat{Z}_i)^2}{n_p}, \tag{5}$$

where Z_i is the observed value at site i, $\hat{Z}_i$ is the predicted value at site i, and n_p is the total number of predictions. Models with small MSPE are desirable. The models constructed using different distance measures have unique variance structures and therefore cannot be compared using the spatial AICC. The MSPE provided a way to compare models constructed using different distance measures and to determine which measure, if any, was more able to account for the variability in the response variable. We generated cross-validation intervals for the covariate parameters, which contain 95% of the estimated 312 parameter values. In addition, we calculated the squared Pearson's correlation coefficient (r^2) for the predictions and observations.

2.3.4. *Geostatistical Model Predictions*

The seven interbasins surveyed in 1996 contained 3083 first, second, and third order non-tidal stream segments. We created 3083 prediction locations by calculating the location for the downstream node of each stream segment. We used the downstream node to ensure that the entire segment was located within the same watershed. This caused more than one prediction location to be positioned at stream confluences.

However, the covariates for the prediction locations represented the watershed conditions of the individual segment rather than the confluence, which would include all of the segments that flow into that location.

We generated a distance matrix that contained the SLD between both observed and unobserved sites. We used the Functional Linkage of Watersheds and Streams (FLoWs) tools (Theobald *et al.*, 2005) developed for ArcGIS version 9.0 (ESRI, 2002) to calculate the watershed covariates (WATER, EMERGWET, WOODYWET, FELPERC, and MINTEMP) for the 3083 prediction locations. We used the fitted covariances based on the Mariah autocovariance model and the universal kriging algorithm to generate predictions and their variances at the prediction locations (Cressie, 1993). The prediction values and variances were assigned back to each stream segment in a GIS to visualize the results.

3. Results

Table II contains a summary of the distribution for each variable. DOC values ranged between 0.6 and 15.9 mg/l. There were 207 sites located in ER64, 16 in ER65, 11 in ER66, 39 in ER67, and 19 in ER69. The remaining 20 sites were located in ER63, which was not included in the model. The Maryland DNR set a threshold level of 8.0 mg/l for DOC and determined that values greater than the threshold were a possible indicator of environmental stress (Maryland Department of Natural Resources, 1999). Only eight MBSS sites collected in 1996 and located west of Chesapeake Bay had DOC values greater than 5 mg/l and only two were greater than 8.0 mg/l (Figure 2). Larger DOC values were found to the north and east of Chesapeake Bay (4.8 to 15.9 mg/l). However, two of these sites were rated as naturally acidic blackwater streams and their large DOC concentrations would not be considered an indicator of stress (Boward *et al.*, 1999).

The predictive ability of the geostatistical models based on SLD and WAHD differed. The SLD models explained more variability in DOC than models based on WAHD for every autocovariance model except the spherical model (Table III).

TABLE II
Summary statistics for $\log_{10}$ dissolved organic carbon (DOC) and model covariates

Variable	Min	1st Quartile	Median	Mean	3rd Quartile	Max	σ^2
$\log_{10}$ DOC (mg/l)	−0.22	0.08	0.24	0.28	0.43	1.20	0.25
WATER (%)	0	0	0.16	0.25	0.28	4.64	0.44
EMERGWET (%)	0	0	0.13	0.26	0.35	4.85	0.44
WOODYWET (%)	0	0	0.27	1.24	1.15	22.01	3.28
FELPERC (%)	0	0	0.31	26.81	55.26	100	36.14
MINTEMP (°C)	−5.88	−3.06	−2.39	−2.49	−1.4	0.03	1.47

TABLE III
Model results. Mean square prediction error (MSPE) and the squared Pearson's correlation coefficient (r^2) for the "best" model within the straight-line distance (SLD) and weighted asymmetric hydrologic distance (WAHD) model sets

Autocovariance model	Distance measure	MSPE	r^2
Exponential	SLD	0.9394	0.7190
	WAHD	1.2337	0.6368
Spherical	SLD	1.3391	0.6029
	WAHD	1.2187	0.6428
Mariah	SLD	0.9311	0.7221
	WAHD	1.2326	0.6346
Hole Effect	SLD	1.0136	0.6983
Linear with Sill	WAHD	1.2141	0.6388
Rational Quadratic	SLD	0.9447	0.7177

However, with the exception of the SLD spherical model, the predictive ability of models within distance measure was comparable.

The SLD geostatistical models based on the exponential, Mariah, and rational quadratic autocovariance models had the lowest MSPE values, produced the most accurate predictions, and were essentially equal in their predictive ability (Table III). The rational quadratic model included six covariates: WATER, EMERGWET, WOODYWET, FELPERC, MINTEMP, and ER67. The exponential and Mariah models were similar, but excluded the ER67 covariate. Yet, the models produced dissimilar ranges of spatial autocorrelation. The range parameter for the exponential, Mariah, and rational quadradic models was 20.08 km, 7.02 km, and 11.71 km, respectively. Despite this difference, the correlation coefficients for the model predictions indicated that the models produced nearly identical predicted values ($r^2 \geq 0.990$). A comparison of the model composition, MSPE values, and r^2 values suggested that there were no distinct differences between the predictions produced by the exponential, Mariah, and rational quadratic SLD models. We limited additional model exploration to the SLD Mariah model because it had that lowest MSPE value and the largest r^2 value.

The SLD Mariah model included five covariates. DOC had a positive relationship with WATER, EMERGWET, WOODYWET, and MINTEMP (Table IV). In contrast, FELPERC was negatively correlated with DOC. The cross-validation intervals for the regression coefficients were narrow (Table IV). The model described 72% of the variability in DOC. However, there was one DOC value (observed value = 15.9 mg/l) that had an unusually large effect on the r^2 value (Figure 4) and the model only explained 66% of the variability in DOC when that observation was removed.

The square prediction error (SPE) values for the individual model predictions produced by the SLD Mariah model were between 0 and 18.706, but were generally low. Eighty-nine percent of the values were less than 1.5 and 71% of the values

TABLE IV
Cross-validation intervals for straight-line distance Mariah regression coefficients. Coefficients represent the change in $\log_{10}$ dissolved organic carbon (DOC) in mg/l per unit of X

Statistic	Water (%)	Emergwet (%)	Woodywet (%)	Felperc (%)	Mintemp (°C)
Minimum	0.0469	0.0306	0.0156	−0.0006	0.0616
Lower 5%	0.0485	0.0322	0.017	−0.0006	0.0643
Mean	0.0501	0.0344	0.0176	−0.0005	0.0655
Upper 5%	0.0522	0.0366	0.0179	−0.0005	0.0669
Maximum	0.0537	0.0425	0.0187	−0.0004	0.071
Standard Dev	0.0007	0.0009	0.0002	0.00005	0.0007

were less than 0.5. However, there appeared to be an east-west trend associated with the spatial location of the SPE values (Figure 5). The low SPE values in the western portion of Maryland indicated that the model fit the data well in this area. In contrast, larger SPE values were found in the central and eastern portions of Maryland. We examined the 35 SPE values greater than 1.5 and found that the model produced conservative estimates. It underestimated large DOC values 29 times and overestimated lower DOC values only 6 times. These errors occurred at sites where the covariate values were similar to neighboring sites, but the observed value was considerably different from nearby values. We examined other watershed characteristics that were not included in the model, such as %FOREST, %URBAN, mean slope, and watershed area, to determine whether sites with large SPE values had unique characteristics that differed from conditions at other sites collected in 1996. However, the covariate distributions taken from the sites with large SPE values were similar to the overall statistical distribution of those covariates and to the watershed covariates at nearby sites.

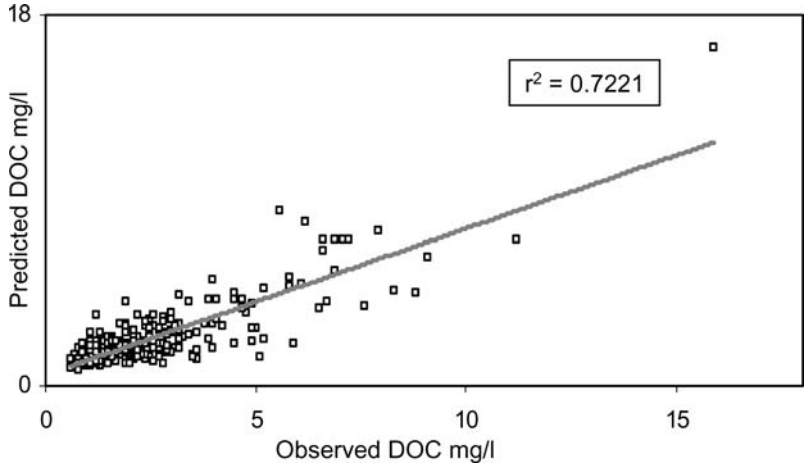

Figure 4. Observed versus predicted values of dissolved organic carbon (DOC) using the straight-line distance Mariah model.

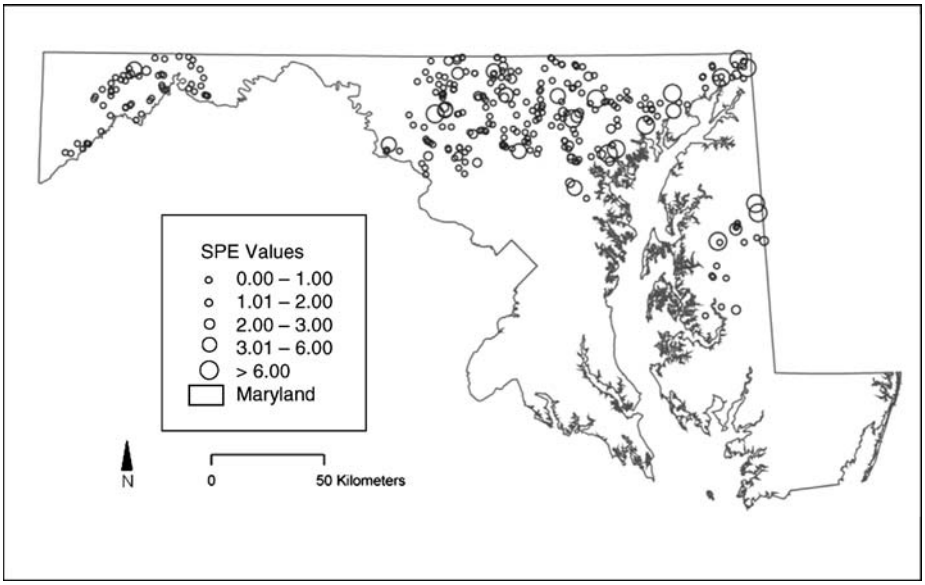

Figure 5. Square prediction error (SPE) values for the straight-line distance Mariah model. SPE values are low in western Maryland, but increase in central and eastern Maryland near Chesapeake Bay.

The parameter estimates for the SLD Mariah model used to make the predictions at unobserved segments are listed in Table V. The prediction segments represented 5973.03 km of streams in Maryland. The prediction values ranged from 0.76 to 40.44 mg/l and the prediction variances were between 0.05 and 2.6 (Table VI). In Maryland, DOC values less than 5 mg/l are considered low and values greater than 8 mg/l are high (Maryland Department of Natural Resources, 1999). The model predicted that 90.2% of streams had DOC values less than 5 mg/l, 6.7% were between 5 and 8 mg/l, and 3.1% of streams produced values greater than 8 mg/l (Figure 6). There were 18 prediction values that were greater than 15.9 mg/l and these segments also possessed the largest prediction variances (1.1 to 2.6). Although the prediction values exceeded the largest observed value in the 1996 data, they may be somewhat reasonable since the largest DOC value found in the complete MBSS dataset was 32.9 mg/l. Sixteen of the prediction values greater than 15.9 mg/l were

TABLE V

Unstandardized parameter estimates for the straight-line distance Mariah model that was used to make predictions at unobserved stream segments. The regression coefficients represent the change in $\log_{10}$ dissolved organic carbon (mg/l) per unit of X. The nugget value is the proportion nugget effect

Nugget	Sill	Range	Intercept	Water	Emergwet	Woodywet	Felperc	Mintemp
0.15	0.28	7.02	0.28	0.05	0.04	0.02	−0.0005	0.07

TABLE VI
Summary statistics for dissolved organic carbon predictions and prediction variances produced by the straight-line distance Mariah model

Variable	Min	1st Quartile	Median	Mean	3rd Quartile	Max
Predictions (mg/l)	0.8	1.5	1.9	2.7	3.0	40.4
Prediction Variance $(mg/l)^2$	0.049	0.095	0.122	0.171	0.193	2.597

located in watersheds with WATER, EMERGWET, or WOODYWET values that were substantially larger than those represented in the observed data. The other two segments with large prediction values resulted from artifacts in the streams data. The two stream segments drain directly into large reservoirs and a portion of the reservoir was erroneously included in the watershed, which caused the WATER covariate to be artificially high.

4. Discussion

Our initial model selection procedure narrowed the field of covariates to five attributes that represented watershed conditions and five that represented Omernik's ecoregions. However, the only ecoregion covariate included in the final geostatistical models was ER67, which suggested that the variability in DOC that was previously explained by Omernik's ecoregion could also be explained using the covariances between neighboring sites. The initial model selection method was non-spatial and we questioned whether other watershed covariates would have been selected if spatial autocorrelation was accounted for during the model selection process. We attempted to address this question by replacing the ecoregion covariates with three watershed covariates that were part of the MBSS dataset: percent urban, percent conifer forest type, percent mixed forest type and two watershed covariates that we calculated in a GIS: mean slope and mean annual precipitation (Table I). We generated another set of geostatistical models using the same methodology and the new set of covariates. Substituting watershed covariates for ecoregion covariates did not improve the accuracy of the model predictions. Although watershed slope and forest cover are correlated to DOC concentration in other studies (Eckhardt and Moore, 1990; Canham *et al.*, 2004; Prusha and Clements, 2004), they do not appear to be strongly related to DOC concentration in Maryland at this scale of analysis.

Five model covariates were included in the geostatistical model based on SLD and the Mariah autocovariance function: WATER, WOODYWET, EMERGWET, FELPERC, and MINTEMP. Although these watershed covariates can be used to explain variability in DOC, it is impossible to make inferences about cause and effect relationships based on a statistical correlation. In addition, some of our covariates displayed collinearity and the effects of collinear watershed covariates cannot be

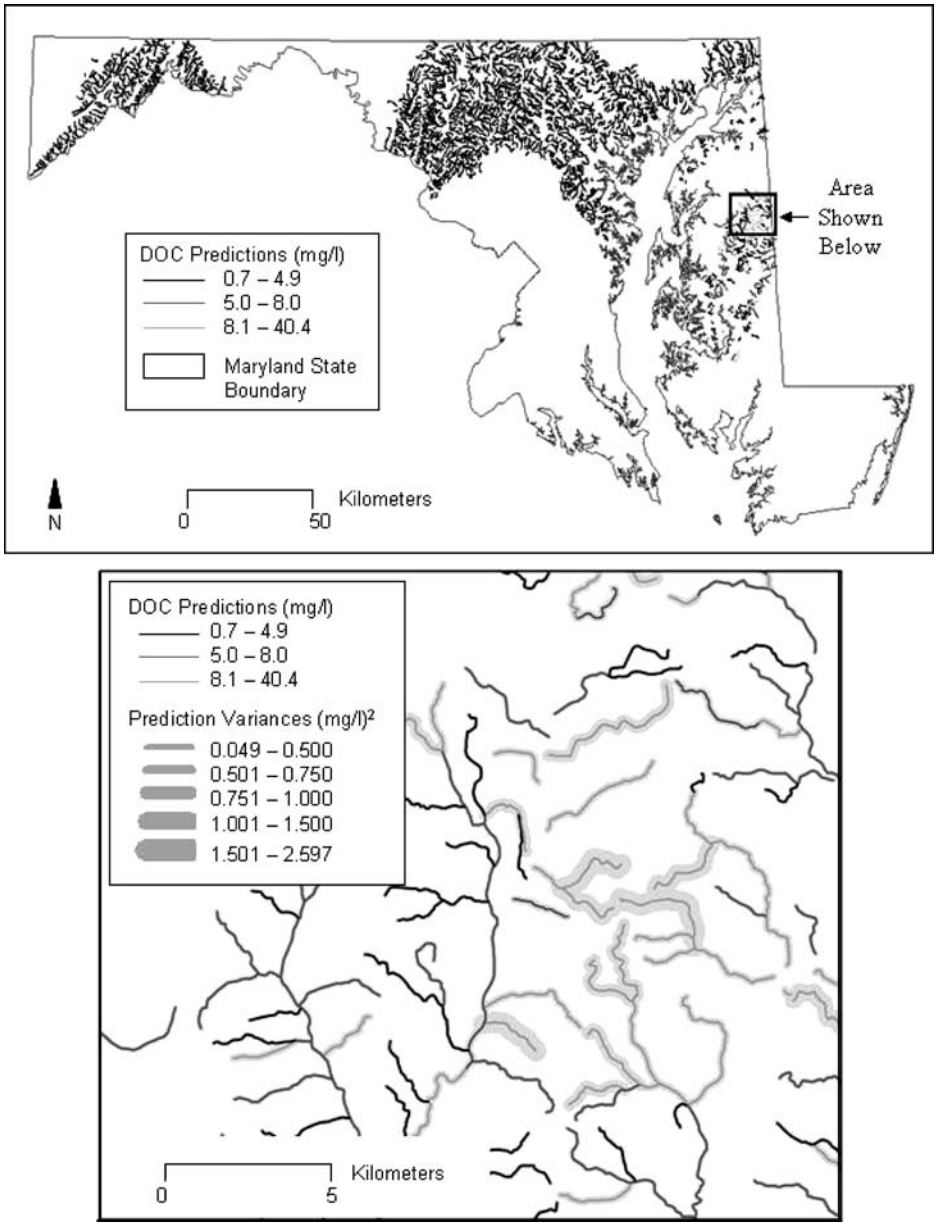

Figure 6. Map of the dissolved organic carbon (DOC) predictions and prediction variances for 3083 first, second, and third order non-tidal streams in seven interbasins throughout Maryland sampled in 1996.

separated using our methodology. Therefore, we will not speculate about cause and effect relationships in the geostatistical model.

The SLD measure consistently produced geostatistical models that described a greater amount of variability in DOC than the WAHD measure. We believe that the WAHD model performance may have been hindered by a lack of neighboring sites. We examined the spatial neighborhood for the SLD measure using a 7.02 km range of spatial autocorrelation and found that the mean number of neighbors was 6.85. Every site had at least 1 neighbor and 89 sites had more than 9 neighbors. However, the WAHD spatial neighborhood is restricted to flow-connected sites, which dramatically reduced the number of neighboring sites. We did not impose a range of spatial autocorrelation on the WAHD spatial neighborhood and instead examined all flow-connected sites. The mean number of neighbors per site using the WAHD was only 1.11. There were 170 sites that had no neighbors and only 87 sites had more than one neighbor. When a spatial neighborhood is deficient or absent for a specific site, the geostatistical model is essentially non-spatial. It has the ability to explain the broad-scale mean in the data, but does not provide additional predictive ability at that site. This is a common feature for geostatistical models. The associated standard error for prediction sites with many observed neighbors is small compared to sites that have few or no neighbors. Thus, the WAHD model had the ability to explain the broad-scale mean in the data, but did not provide additional predictive ability at sites with few or no neighbors.

The cross-validation intervals for the SLD Mariah model regression coefficients were all narrow, which indicated that the relationships between the covariates and DOC were consistent throughout Maryland (Table IV). There were few extreme regression coefficient values, but we examined the largest and smallest values and determined that the majority were not produced by common sites and that the sites were not clustered in space. This suggested that a local-scale factor, such as a point source of organic waste, affected stream DOC and was not explained by our model. The narrow cross-validation intervals for the regression coefficients and the lack of extreme outliers indicated that the spatial location of the sites was not as important as the watershed characteristics.

Spatial patterns were evident in the distribution of stream DOC concentrations throughout Maryland (Figures 5 and 7). The majority of streams west of Chesapeake Bay produced low DOC predictions with low prediction variances. However, there was a small cluster of elevated DOC predictions in stream segments located within Baltimore. The watershed conditions at these sites were not the source of elevated DOC predictions. Instead, relatively large observed values at nearby sites, which likely result from organic pollution discharged into Baltimore waterways, increased the prediction values. Stream segments to the north and east of Chesapeake Bay had larger DOC predictions and larger prediction variances. Some areas of coastal Maryland are characterized by blackwater streams, which are naturally acidic and have elevated levels of stream DOC (Boward *et al.*, 1999). We believe that the majority of the elevated stream predictions east of Chesapeake Bay are the result of

natural environmental processes. It is not surprising that the variances associated with these predictions were also large since there were only two observed sites classified as blackwater in the dataset. Consequently, the unique ecological conditions that produce blackwater streams were not well represented in the observed dataset and the model was unable to account for this natural variability.

Overall, the geostatistical model that we developed described more variability in stream DOC than previous models based solely on coarse-scale landscape data (Kortelainen, 1993; Canham, 2004). The model fit the data better in western and central Maryland compared to the eastern coastal regions (Figure 5) for a number of reasons. The regression equation was fit to the mean in the data and nearly all of the observed sites had low DOC values. In addition, there appears to be less variation in stream DOC in western and central Maryland and consequently neighboring sites tend to be similar. The separation distances for survey sites are shorter to the west of Chesapeake Bay compared to the east (Figure 2). Large separation distances result in a weaker covariance between observed and predicted sites and less confidence in the predictions. Given the statistical and spatial distribution of the observed data, it is not surprising that the model was able to predict DOC values more accurately in western and central Maryland. It may be necessary to develop a separate geostatistical model, which is fit to data collected in the coastal region to provide more accurate DOC predictions in eastern Maryland. Nonetheless, the ecological processes that influence stream DOC to the west of Chesapeake Bay appear to be similar and can be described using a single geostatistical model.

Although the geostatistical model fit the data well, it was developed to provide a general estimate of stream DOC throughout Maryland and there are clearly influential factors that were not adequately represented. For instance, the model was unable to account for abrupt differences in DOC values between neighboring sites when the sites had similar watershed conditions. These differences may result from local factors, such as point sources of organic inputs, which were not detected at our scale of analysis. It is also possible that elevated DOC values result from non-point sources of pollution and that our lumped watershed attributes were too general to capture the information. For example, a wetland area 100 meters upstream should have a larger impact on site DOC than a wetland five kilometers upstream. Lumped watershed attributes are non-spatial and any differences that result from the spatial location of the landuse within the watershed are not represented. In addition, it is challenging to represent ecological processes, such as the flow path that water takes from the terrestrial landscape to the stream, using coarse-scale lumped watershed attributes.

We acknowledge that there is a tradeoff between building a cost-efficient regional model and model accuracy. Our model was conservative, meaning that it tended to under predict DOC values. Therefore, it may not be possible to use it to identify point sources of organic pollution. However, we believe that it can be used to provide an estimate of regional stream DOC values. The conservative nature of the model gives us confidence that a large predicted value with a low

prediction variance actually represents an elevated stream DOC concentration on the ground.

The Maryland DNR analyzed the MBSS data and generated a statistically valid estimate of DOC levels in stream miles (Boward *et al*., 1999). However, their analysis did not indicate where stream segments with elevated DOC concentrations were located. We successfully generated predictions for every stream segment in the seven interbasins and evaluated the predictions using threshold values developed by the Maryland DNR (Figure 6). Although we chose to model DOC, which is not currently regulated in Maryland, the same methodology could be applied to regulated constituents, such as pH or nitrate (Peterson *et al*., in press). The Technical and Regulatory Services Administration within the Maryland Department of the Environment is currently working on a project to modify the USGS National Hydrography Dataset (NHD) (USGS, 2004) to include watershed impairments and stream-use designations by NHD segment (F. Siano, personal communication). The addition of these attributes can be used with the methodology that we presented and will provide a straightforward means of categorizing stream segment predictions into potentially impaired or unimpaired status. We believe that this methodology adds value to probability-based inferences because every stream segment in a large area is remotely surveyed in a cost-efficient manner to provide a regional estimate of stream health.

5. Conclusions

The geostatistical models that we developed generated more accurate DOC predictions than previous models, but did not appear to fit the data equally well throughout the study area. This raises the question whether it is appropriate to use a single geostatistical model to predict stream DOC throughout Maryland. Blackwater conditions were under represented in the observed data and the accuracy of model predictions might be improved if additional survey sites were located in these ecosystems. On the other hand, ecological conditions in eastern and western Maryland are dissimilar and it may be impossible to use a single model to accurately predict DOC. If the latter were true, it would be possible to develop more than one model to obtain accurate predictions of DOC throughout Maryland.

We believe that our methodology has clear advantages related to regional water quality monitoring of regulated water quality constituents, such as nitrate or pH, and that it could be used by states, territories, and tribes to comply with the Clean Water Act more easily. Existing data which has been collected using probability-based random survey designs can be used to develop geostatistical models based on SLD. Therefore, it is not necessary to collect additional field data to generate the preliminary geostatistical model. In addition, inferences about regional stream condition can be generated and this methodology can be used to locate potentially impaired stream segments in a rapid and cost-efficient manner. Each stream segment

receives a prediction value with a measure of uncertainty, which allows future field efforts to be concentrated in areas with large amounts of uncertainty or a greater potential for water quality impairment. This ensures that supplementary survey sites are located in areas where additional information about water quality conditions would be most valuable. In addition, resources can be conserved and made available for the TMDL calculation for a specific segment. The model results can also be displayed visually, which allows professionals to communicate results to a wide variety of audiences.

Acknowledgements

We would like to thank David Theobald, Melinda Laituri, Brian Bledsoe, Will Clements, and the anonymous reviewers who provided valuable comments on the manuscript. The work reported here was developed under STAR Research Assistance Agreement CR-829095 awarded by the U.S. Environmental Protection Agency to the Space Time Aquatic Resource Modeling and Analysis Program (STARMAP) at Colorado State University. This paper has not been formally reviewed by the EPA. The views expressed here are solely those of the authors. The EPA does not endorse any products or commercial services mentioned in this paper.

References

American Geological Institute: 1987, *Glossary of Geology 3rd Edition*, Thomson-Shore, Inc., Alexandria, VA, USA.

Amrhein, C. and Suarez, D. L.: 1988, 'The Use of a Surface Complexation Model to Describe the Kinetics of Ligand-Promoted Dissolution of Anorthite', *Geochimica et Cosmochimica Acta* **52**, 2785–2793.

Bailey, T. C. and Gatrell, A. C.: 1995, *Interactive spatial data analysis*, Pearson Education Limited, Essex, England.

Bennett, P. C.: 1991, 'Quartz Dissolution in Organic-Rich Aqueous Systems', *Geochimica et Cosmochimica Acta*, **55**, 1781–1797.

Boward, D., Kayzak, P., Stranko, S., Hurd, M. and Prochaska, A.: 1999, 'From the Mountains to the Sea: The State of Maryland's Freshwater Streams', EPA/903/R-99/023, Maryland Department of Natural Resources, Monitoring and Non-tidal Assessment Division, Annapolis, MD, USA.

Byrd, R. H., Lu, P., Nocedal, J. l., Zhu, C., and Siam, J.: 1995, 'A limited memory algorithm for bound constrained optimization', *Scientific Computing* **16**, 1190–1208.

Canham, C. D., Pace, M. L., Papaik, M. J., Primack, A. G. B., Roy, K. M., Maranger, R. J., Curran, R. P. and Spada, D. M.: 2004, 'A Spatially Explicit Watershed-Scale Analysis of Dissolved Organic Carbon in Adirondack Lakes', *Ecological Applications*, **14**, 839–854.

Copeland, C.: 2002, 'Water Quality: Implementing the Clean Water Act', IB89102, Congressional Research Service, Resources, Science, and Industry Division.

Creed, I. F., Sanford, S. E., Beall, F. D., Molot L. A. and Dillon P. J.: 2003, 'Cryptic Wetlands: Integrating Hidden Wetlands in Regression Models of the Export of Dissolved Organic Carbon From Forested Landscapes', *Hydrological Processes,* **17**, 3629–3648.

Cressie, N.: 1993, *Statistics for Spatial Data Revised Edition*, John Wiley and Sons, New York, NY, USA.

Currie, W. S. and Aber, J. D.: 1997, 'Model Leaching As A Decomposition Process in Humid Montane Forests', *Ecology* **78**, 1844–1860.

Driscoll, C. T., Blette, V., Yan, C., Schofield, C. L., Munson, R. and Holsapple, J.: 1995, 'The Role of Dissolved Organic Carbon in the Chemistry and Bioavailability of Mercury in Remote Adirondack Lakes', *Water, Air, and Soil Pollution*, **80**, 499–508.

Earth System Science Center (ESSC): 1998, *Soil Information for Environmental Modeling and Ecosystem Management*, ESSC, Pennsylvania State University, Web page, Accessed November 5, 2004, http://www.essc.psu.edu/soil_info/index.cgi?soil_data&index.html.

Eckhardt, B. W. and Moore, T. R.: 1990, 'Controls on Dissolved Organic Carbon Concentrations in Streams, Southern Quebec', *Canadian Journal of Fisheries and Aquatic Sciences*, **47**, 1537–1544.

Environmental Systems Research Institute (ESRI): 2002, *ArcGIS version 8.3*, Redlands, CA.

Furnival, G. and Wilson, R.: 1974, 'Regression by Leaps and Bounds', *Technometrics,* **16**, 499–511.

Gardner, B. and Sullivan, P. J.: 2003, 'Spatial and temporal stream temperature prediction: Modeling nonstationary temporal covariance structures', *Water Resources Research*, **40**, Art. No. W01102.

Gergel, S. E., Turner, M. G. and Kratz, T. K.: 1999, 'Dissolved Organic Carbon As an Indicator of the Scale of Watershed Influence on Lakes and Rivers', *Ecological Applications*, **9**, 1377–1390.

Haneberg, W. C.: 2005, 'The Ins and Outs of Airborne Lidar: An Introduction for Practicing Engineering Geologists', *Association of Engineering Geologists News* **48**, 16–19.

Hejzlar, J., Dubrovsky, M., Buchtele, J., and Ruzicka, M.: 2003, 'The Apparent and Potential Effects of Climate Change on the Inferred Concentration of Dissolved Organic Matter in a Temperate Stream (the Malse River, South Bohemia)', *The Science of the Total Environment*, **310**, 143–152.

Helsel, D. R. and Hirsch, R. M.: 1992, *Statistical Methods in Water Resources*, Elsevier Science Publishing Co., New York, NY, USA.

Herlihy, A. T., Stoddard, J. L. and Johnson, C. B.: 1998, 'The Relationship Between Stream Chemistry and Watershed Land Cover Data in the Mid-Atlantic Region, U.S.', *Water, Air, and Soil Pollution* **105**, 377–386.

Herlihy, A. T., Larsen, D. P., Paulsen, S. G., Urquhart, N. S. and Rosenbaum, B. J.: 2000, 'Designing a Spatially Balanced, Randomized Site Selection Process for Regional Stream Surveys: The EMAP Mid-Atlantic Pilot Study', *Environmental Monitoring and Assessment*, **63**, 95–113.

Hoeting, J. A., Davis, R. A., Merton, A. A. and Thompson, S. E.: 2006, 'Model Selection for Geostatistical Models', *Ecological Applications*, **16**, to appear.

Houle, D., Carignan, R., Lachance, M. and Dupont, J.: 1995, 'Dissolved Organic Carbon and Sulfur in Southwestern Quebec Lakes: Relationships With Catchment and Lake Properties', *Limnology and Oceanography*, **40**, 710–717.

Ihaka, R. and Gentleman, R.: 1996, 'R: a Language for Data Analysis and Graphics', *Journal of the Computational and Graphical Statistics*, **5**, 299–314.

Kellum, B.: 2003, 'Analysis and Modeling of Acid Neutralizing Capacity in the Mid-Atlantic Highlands Area', MS Thesis, Colorado State University, Fort Collins, CO, USA, 69 p.

Kiffney, P. M., Clements, W. H. and Cady, T. A.: 1997, 'Influence of Ultraviolet Radiation on the Colonization Dynamics of a Rocky Mountain Stream Benthic Community', *Journal of the North American Benthological Society*, **16**, 520–530.

Kortelainen, P.: 1993, 'Content of Total Organic Carbon in Finnish Lakes and Its Relationship to Catchment Characteristics', *Canadian Journal of Fisheries and Aquatic Sciences*, **50**, 1477–1483.

Maryland Department of Natural Resources: 1999, *State of the Streams: 1995–1997 Maryland Biological Stream Survey Results*, Maryland Department of Natural Resources, Annapolis, MD, USA.

Mercurio, G., Chaillou, J. C. and Roth, N. E.: 1999, *Guide to Using 1995–1997 Maryland Biological Stream Survey Data*, Maryland Department of Natural Resources, Annapolis, MD, USA.

Mulholland, P. J.: 2003, 'Large-Scale Patterns in Dissolved Organic Carbon Concentration, Flux, and Sources', in: S.E.G. Findlay, and R. L. Sinsabough (eds.), *Aquatic Ecosystems: Interactivity of Dissolved Organic Matter,* Academic Press, San Diego, CA, USA, pp. 139–157.

Multi-Resolution Land Characteristics Consortium (MRLC): 2003, 'U.S. Federal Region III land cover data set', Web page, Accessed June 17, 2005, http://www.epa.gov/mrlc/.

Neff, J. C. and Asner, G. P.: 2001, 'Dissolved Organic Carbon in Terrestrial Ecosystems: Synthesis and a Model', *Ecosystems*, **4**, 29–48.

Olea, R. A.: 1991, *Geostatistical Glossary and Multilingual Dictionary*, Oxford University Press, New York, NY, USA.

Olsen, A. R. and Ivanovich, M.: 1993, *EMAP Monitoring Strategy and Sampling Design,* Office of Research and Development, Environmental Research Laboratory Corvallis (OR): U.S. Environmental Protection Agency, Corvallis, OR, USA. Video.

Omernik, J. M.: 1987, 'Ecoregions of the Conterminous United States', *Annals of the Association of American Geographers*, **77**, 118–125.

Ouyang, Y.: 2003, 'Simulating Dynamic Load of Naturally Occurring TOC From Watershed into a River', *Water Research*, **37**, 823–832.

Peterson, E. E.: 2005, 'Predicting the likelihood of water quality impaired stream segments using landscape-scale data and a hierarchical methodology', PhD Dissertation, Colorado State University, Fort Collins, CO, USA, 293 p.

Peterson, E. E., Merton, A. A., Theobald, D. M. and Urquhart, N. S.: in press, 'Patterns of spatial autocorrelation in stream water chemistry', *Environmental Monitoring and Assessment*.

Prusha, B. A. and Clements, W. H.: 2004, 'Landscape Attributes, Dissolved Organic C, and Metal Bioaccumulation in Aquatic Macroinvertebrates (Arkansas River Basin, Colorado)', *Journal of the North American Benthological Society*, **23**, 327–339.

Qualls, R. G. and Haines, B. L.: 1992, 'Biodegradability of Dissolved Organic Matter in Forest Throughfall, Soil Solution, and Stream Water', *Soil Science Society of American Journal*, **56**, 578–586.

Rasmussen, J. B., Godbout, L. and Schallenberg, M.: 1989, 'The Humic Content of Lake Water and Its Relationship to Watershed and Lake Morphometry', *Limnology and Oceanography*, **34**, 1336–1343.

Spatial Climate Analysis Service (SCAS): 1996, *Parameter-elevation Regressions on Independent Slopes Model (PRISM)*, SCAS, Oregon State University, Web page, Accessed October 23, 2004, http://www.ocs.orst.edu/prism/

Strahler, A. N.: 1957, 'Quantitative Analysis of Watershed Geomorphology', *Transaction of the American Geophysical Union*, **21**, 913–920.

Sullivan, T. J., Driscoll, C. T., Gherini, S. A., Munson, R. K., Cooks, R. B., Charles, D. F. and Yatsko, C. P.: 1989, 'Influence of Aqueous Aluminum and Organic Acids on Measurement of Acid Neutralizing Capactiy in Surface Waters', *Nature*, **338**, 408–410.

Theobald, D. M., Norman, J., Peterson, E. and Ferraz, S.: 2005, 'Functional Linkage of Watersheds and Streams (FLoWs): Network-Based ArcGIS Tools to Analyze Freshwater Ecosystems', in: *Proceedings of the ESRI User Conference 2005*, July 25–29, 2005, San Diego, CA, USA.

U.S. Environmental Protection Agency (USEPA): 1987, 'Determination of Dissolved Organic Carbon and Dissolved Inorganic Carbon', in: *Handbook of Methods for Acid Deposition Studies: Laboratory Analysis for Surface Water Chemistry*, EPA 600/4-87/026, U.S. Environmental Protection Agency, Washington, DC, USA.

U.S. Environmental Protection Agency (USEPA): 2001, *Survey Designs for Sampling Surface Water Condition in the West*, EPA A620/R-01/004c, U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC.

U.S. Environmental Protection Agency (USEPA): 2005, *Level III Ecoregions*, Web page, Accessed August 13, 2003, http://www.epa.gov/wed/pages/ecoregions/level_iii.htm.

U.S. Geological Survey (USGS): 2003, *National Elevation Dataset*, Web page, Accessed January 4, 2005, Available at http://ned.usgs.gov/.

U.S. Geological Survey (USGS): 2004, *National Hydrography Dataset*, Web page, Accessed January 27, 2005, Available at http://nhd.usgs.gov/.

U.S. Geological Survey (USGS): 2005, *Land Use Land Cover (LULC)*, Web page, Accessed May 25, 2005, Available at http://edc.usgs.gov/products /landcover/lulc.html

Ver Hoef, J. M., Peterson, E. E. and Theobald, D. M.: 2007, 'Some New Spatial Statistical Models for Stream Networks', *Environmental and Ecological Statistics*, to appear.

Vogelmann, J. E., Howard, S. M., Yang, L., Larson, C. R., Wylie, B. K. and Van Driel, N.: 2001, 'Completion of the 1990's National Land Cover Data Set for the Conterminous United States From Landsat Thematic Mapper Data and Ancillary Data Sources', *Photogrammetric Engineering and Remote Sensing*, **67**, 650–652.

Wetzel, R. G.: 1992, 'Gradient-Dominated Ecosystems: Sources and Regulatory Functions of Dissolved Organic Matter in Freshwater Ecosystems', *Hydrobiologia*, **229**, 181–198.

Williamson, C. E., Stemberger, R. S., Morris, D. P., Frost, T. M. and Paulsen, S. G.: 1996, 'Ultraviolet Radiation in North American Lakes: Attenuation Estiamtes From DOC Measurements and Implications for Plankton Communities', *Limnology and Oceanography*, **41**, 1024–1034.

Yuan, L. L.: 2004, 'Using Spatial Interpolation to Estimate Stressor Levels in Unsampled Streams', *Environmental Monitoring and Assessment*, **94**, 23–38.