

1 RUNNING HEAD: Measuring downstream influence of headwater disturbance

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5 **Use of spatially explicit physicochemical data to measure downstream impacts of**  
6 **headwater stream disturbance**

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24 **Abstract**

25 Regulatory agencies need methods to quantify the influence of headwater streams  
26 on downstream water quality as a result of litigation surrounding jurisdictional criteria  
27 and the influence of mountaintop removal coal mining activities. We collected  
28 comprehensive, spatially-referenced physicochemical data (pH, dissolved oxygen,  
29 temperature, and specific conductance) from the partially mined Buckhorn Creek, KY  
30 watershed in summer 2005 (n = 239 sites) and spring 2006 (n = 494 sites). We found  
31 conductivity was >10X higher in mined streams than in forested streams.  
32 Semivariograms, which quantify the degree of spatial dependence in chemistry values,  
33 indicated summer temperatures in both mined and unmined portions of the watershed had  
34 similar lag distances (ca. 5 km). Data for other parameters and seasons however, violated  
35 model assumptions because of strong confluence effects in headwaters. We therefore  
36 developed a post-hoc predictive model for water physicochemistry downstream of  
37 confluences using watershed areas as weighting factors. This weighted-average model  
38 accurately predicted downstream conductivity (mean absolute error [MAE] = 55.34  $\mu\text{S}$   
39  $\text{cm}^{-1}$ ), pH (MAE = 0.16 units), and temperature (MAE = 0.41°C) for confluences in  
40 Buckhorn Creek and two additional watersheds with headwater disturbance in WV and  
41 OH. Use of semivariograms or predictive confluence models can help regulatory agents  
42 identify downstream influence of headwater streams and presence of a “significant  
43 nexus” with downstream waters.

44 **Keywords:** conductivity, geostatistics, mining, ph, temperature, valley fill

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47 **1. Introduction**

48 Headwater streams, both individually and cumulatively, are important  
49 components of stream networks that can ultimately influence health of downstream  
50 aquatic ecosystems [*Gomi et al.*, 2002; *Meyer and Wallace*, 2001; *Naiman et al.*, 1987;  
51 *Vannote et al.*, 1980; *Wipfli and Gregovich*, 2002; and see featured collection in *Journal*  
52 *of American Water Resources Association*, 2007, Vol. 43(1)]. State and Federal  
53 regulations however, have traditionally afforded less protection to headwater streams  
54 than to larger downstream waters because of their abundance on the landscape and more  
55 variable hydrologic periods. Small headwaters are also not usual direct sources of  
56 drinking water, commerce, or recreation. Permits for filling (Clean Water Act [CWA]  
57 §401 & §404) or discharging to (CWA § 402) intermittent, and particularly ephemeral,  
58 headwater streams are sometimes not required or, if so, critical reviews by regulatory  
59 agencies and any mitigation requirements have typically been less than for downstream  
60 waters [e.g., *Department of Defense*, 2007]. Such inadequate protection of headwater  
61 streams and the failure to properly mitigate their loss has been criticized in a recent  
62 federal court decision [*Ohio Valley Environmental Coalition v. United States Army Corps*  
63 *of Engineers, et al.*, No. 03, 05-0784, 2007].

64 Language of the CWA, which often references “navigable waters” or “waters of  
65 the United States”, also does not clearly indicate the extent of CWA jurisdiction and has  
66 created confusion among regulatory agencies and the public. This has resulted in a  
67 number of Federal court cases that have specifically challenged whether the CWA applies  
68 to headwater streams and isolated wetlands [see special issues of *Wetlands* 2003, Vol.  
69 23(3); *Wetlands* 2007, Vol. 43(1); and *Natural Resources and Environment* 2007, Vol.

70 22(1)]. A 2001 Supreme Court decision first questioned whether some headwater  
71 streams and isolated wetlands could be considered jurisdictional under the Clean Water  
72 Act [*Solid Waste Agency of Northern Cook County (SWANCC) v. U.S. Army Corps of*  
73 *Engineers*, 531 U.S. 159, 2001]. A subsequent joint decision then required that non-  
74 navigable waters must be “relatively permanent” or “possess a significant nexus” to  
75 navigable waters to be considered jurisdictional [*John A. Rapanos et al. v. United States*,  
76 U.S., No. 04-1034, 2005; and *June Carabell et al. v. United States Army Corps of*  
77 *Engineers and the United States Environmental Protection Agency*, U.S., No. 04-1384,  
78 2005].

79 As a result of these decisions, regulatory agencies are faced with the challenge of  
80 accurately measuring hydrologic permanence of headwater streams and their degree of  
81 influence on the quality of downstream, navigable waters [*Leibowitz et al.*, 2008]. Some  
82 state and federal agencies have developed tools for both measuring permanence and for  
83 ecological assessment in headwater streams [*Fritz et al.*, 2006; *NCDWQ*, 2005; *OEPA*,  
84 2002]. However, directly quantifying the influence of headwater streams on downstream  
85 resources is difficult given the large spatial scale and the mosaic of disturbance that often  
86 exists among headwater tributaries within branched stream networks. Determining the  
87 presence of a “significant nexus” may therefore require stream ecologists to move beyond  
88 the habitat or reach spatial scales that are typically the focus of stream studies. Spatially  
89 explicit studies that incorporate measures from throughout stream networks may be a  
90 useful strategy for quantifying the downstream influence of headwater streams and to  
91 help identify presence of a “significant nexus”.

92 In the central Appalachians, headwater streams are often buried under fill material  
93 as a result of coal mining activities. The largest fills result from mountaintop removal  
94 mining (MTM) where overburden is placed in adjacent stream valleys, creating valley  
95 fills (VF). During a single ten year span (1992-2002), it was estimated that more than  
96 1,200 miles of headwater streams were impacted by MTM/VF activities [USEPA, 2003].  
97 Though sediment ponds constructed downstream of fills facilitate deposition of fine  
98 particles, the total dissolved solids (TDS) can remain high downstream because there are  
99 currently no feasible methods for their removal. Elevated ion concentrations are  
100 produced from groundwater leaching the valley fill materials. Stream conductivity at  
101 filled sites can be 100X greater than for unmined streams in the region [Bryant *et al.*,  
102 2003] (i.e., from ca. 50  $\mu\text{S cm}^{-1}$  to 5,000  $\mu\text{S cm}^{-1}$ ) and evidence suggests that conductivity  
103 can remain high for decades after fill construction [Merricks *et al.*, 2007].

104 Ionic constituents resulting from valley fills are conserved and therefore  
105 potentially impact water quality far downstream. Potential cumulative effects of multiple  
106 valley fills within a watershed must also be taken into consideration as required by the  
107 National Environmental Policy Act (NEPA) and other federal permitting programs (e.g.,  
108 CWA Section 404[b][1] 40 CFR §230, Nationwide Permit Program 33 CFR §330).  
109 However, as with measuring the downstream influence of impaired headwater streams,  
110 methods for measuring cumulative downstream effects are also lacking. Measurements  
111 of cumulative effects are complicated by the large temporal and spatial scales involved  
112 and the potential interaction of multiple stressors [Reid, 1998].

113 The study objective was to develop or refine methods that better quantify the  
114 influence of headwater streams and cumulative effects of headwater disturbance on

115 downstream water quality. Our efforts focused on, but were not limited to, MTM/VF and  
116 associated specific conductance (surrogate for TDS) in streams of the central  
117 Appalachians. We took multiple approaches that included geostatistical analysis of  
118 extensive field-collected physiochemical data and development of predictive models for  
119 water chemistry downstream of confluences.

## 120 **2. Methods**

### 121 **2.1 Study Areas**

122 The Buckhorn Creek (BC) watershed (drainage area 118 km<sup>2</sup>) is in the Dissected  
123 Central Appalachian Plateau ecoregion [Level IV (69d); *Woods et al.*, 2002] of eastern  
124 Kentucky, U.S.A., and lies at the juncture of Breathitt, Knott, and Perry Counties (Figure  
125 1). The ecoregion is unglaciated, consisting of steep ridges and narrow valleys and is  
126 underlain with Pennsylvanian sandstone, shale, siltstone, and coal (*Woods et al.*, 2002).  
127 Robinson Forest (RF) (drainage area 60 km<sup>2</sup>) lies within the BC watershed and is a  
128 research forest operated by the University of Kentucky. The two major subwatersheds  
129 included in RF are drained by Clemons Fork and Coles Fork, both of which are  
130 tributaries to the BC mainstem. Much of the remainder of the Buckhorn watershed has  
131 been heavily mined for coal, and includes some gas drilling, low density housing, and  
132 pasture (Figure 1). Coal mining in the watershed includes presence of multiple MTM/VF  
133 operations [*Wunsch et al.*, 1999].

134 The BC watershed was sampled during summer 2005 (Sept. 12-14) and spring  
135 2006 (May 1-4) to cover base and average stream flow conditions, respectively. Multi-  
136 probe (Hydrolab®) measurements (pH, dissolved oxygen [mg/l], temperature [°C], and  
137 conductivity [ $\mu\text{S cm}^{-1}$ ]) and latitude/longitude were recorded at stream sites every 100-

138 500 m in both seasons (summer: n = 239; spring: n = 494). Data were collected from  
139 origin of surface flow in multiple mined and reference headwater streams downstream to  
140 the confluences with the mainstem Buckhorn Creek and along the Buckhorn mainstem to  
141 the confluence with the receiving stream, Troublesome Creek. Special attention was  
142 given to stream confluences during data collection to measure any tributary effects on  
143 receiving streams. Multi-probe measures were collected ca. 100 m above the confluence  
144 on each tributary and ca. 100 m above and below the tributary confluence on the  
145 receiving stream. Multi-probes were calibrated daily and duplicate measures were  
146 collected within 10 m for every 25 sampling locations.

## 147 **2.2 Geospatial Analysis**

148 Unlike conventional statistical tests that typically require observations to be  
149 independent and normally distributed (e.g., ANOVA, *t*-test,  $\chi^2$ ), geostatistics refers to a  
150 set of statistical tools that are specifically used to model the degree of spatial dependence  
151 among values. Geostatistics are therefore particularly valuable for describing spatial  
152 patterns within complex stream networks where site values are often spatially correlated.  
153 Modeling spatial dependence can provide ecologically meaningful information about  
154 many aspects of stream network dynamics and have been successfully used to describe  
155 spatial patterns in stream physiochemistry parameters [*Dent and Grimm, 1999; Gardner*  
156 *et al., 2003*] as well as cutthroat trout distribution [*Ganio et al., 2005*].

157 Geospatial methods use some measure of statistical distance to model the degree  
158 of spatial dependence between sites within the spatial domain. Following recent  
159 development of GIS tools, stream researchers have made increasing use of hydrologic, or  
160 in-stream, distance measures when exploring spatial patterns in stream networks [e.g.,

161 Gardner et al., 2003; Peterson et al., 2007; Ver Hoef et al., 2006]. Hydrologic distance is  
162 the shortest distance between points within the stream channel network and it may be  
163 further divided into either symmetric or asymmetric by incorporating a directional  
164 component. Symmetric stream distance is simply the distance between any two points  
165 along the stream network, regardless of flow direction, so that all sites within the network  
166 can be connected. For asymmetric stream distance, two sites within the stream network  
167 can only form a distance pair if one site is either contributing to or receiving flow from  
168 the other. Asymmetric distance is thus limited to either the upstream or downstream  
169 direction [Peterson et al., 2007]. Since our primary objective was aimed at longitudinal  
170 changes in water chemistry, we used unweighted, asymmetric (downstream) stream  
171 distance when calculating spatial dependence.

172 A semivariogram is a geostatistical tool that quantifies the change of spatial  
173 dependence with increasing distance among observations, or how site pairs covary with  
174 separation distance. Data points that are closer together are expected to be more similar  
175 than those that are farther apart. All observations from the stream network are binned by  
176 distance and semivariance is calculated as half the average, squared difference between  
177 pairs of points located a given distance apart:

178 
$$\hat{\gamma}(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [z(x_i) - z(x_i + h)]^2$$

179 where  $\hat{\gamma}(h)$  is the estimated variogram value for distance  $h$ ;  $z(x)$  is the value of a variable  
180 at location  $x$ ;  $z(x+h)$  is the value of the same variable some distance away; and  $N(h)$  is  
181 the number of pairs of observations separated by  $h$ . Semivariograms plot  $\hat{\gamma}(h)$  as a  
182 function of distance  $h$  [Liebhold et al., 1993; Rossi et al., 1992] and are typically

183 interpreted by fitting theoretical models [e.g., *Dent and Grimm, 1999; Peterson et al.,*  
184 *2007; Schlesinger et al., 1996*]. The nugget refers to the semivariance value at lag  
185 distance zero and is usually  $>0$  because of fine scale sampling variability (or variability at  
186 distances smaller than the minimum sampling distance) or measurement error. Error  
187 increases with increasing lag distance on the x-axis because the number of observations  
188 used for semivariance calculation declines. For the spherical semivariogram model, the  
189 point where semivariance levels off is referred to as the *sill* and the lag distance where the  
190 sill occurs is the *range*. The range indicates the average distance over which values are  
191 spatially correlated, or average “patch size” [*Dent and Grimm, 1999*]. At least 30 pairs of  
192 points should be included for each separation distance when plotting semivariograms  
193 [*Cressie, 1993*]. Also implicit in semivariogram models is the assumption of stationarity,  
194 which states that spatial dependence must be the product only of distance between two  
195 points in the spatial domain and not their specific locations within the domain [*Cressie,*  
196 *1993*].

197       The National Hydrologic Database (NHD) underestimated total stream coverage  
198 for BC, resulting in many observations that were not associated with mapped stream  
199 channels. A new stream network was therefore generated for the watershed using the  
200 ArcHydro 9 toolset for ArcGIS 9.1. The stream network was constructed using a 30 m  
201 Digital Elevation Model (DEM) available from the Seamless Data Distribution System of  
202 the USGS. Flow direction and flow accumulation grids were then created from the DEM.  
203 The new stream network was then generated using a minimum threshold of 35 cells  
204 flowing into the destination cell for initiation of a stream channel. Observations were  
205 snapped to the new ArcHydro stream network and distances between observations were

206 calculated with the Fast Network Shortest Path extension for ArcView 3.2. Distance  
207 pairs that were not flow connected were manually removed. Multi-probe values were  
208 then merged with the distance dataset. Empirical semivariograms were estimated with a  
209 function developed for R statistical software [*R Development Core Team, 2009*] using the  
210 Cressie-Hawkins robust estimator. Spherical semivariogram models were then fitted  
211 with the variofit function in geoR [*Ribeiro and Diggle, 2001*] using weighted least  
212 squares and Cressie's weights.

### 213 **2.3 Predictive Model Development**

214 Initial analysis of empirical semivariograms revealed the stationarity assumption  
215 was often violated for measured parameters because of strong tributary influences,  
216 primarily in the headwaters. As a result of these model violations in the semivariogram  
217 approach, a post hoc deterministic model was developed using only a weighting factor  
218 and chemistry data from three locations at each stream confluence. Watershed area was  
219 used as the weighting factor for tributary influence, both because of the known  
220 correlation between watershed area and stream discharge [e.g., *Knighton, 1998*] and the  
221 relative ease of drainage area measurement. Such a deterministic model may be used to  
222 predict water chemistry values below confluences within the watershed, regardless of  
223 location or degree of spatial dependency. The weighted average model simply  
224 incorporates watershed area and parameter values from two confluent tributaries:

$$225 \quad y_{ij} = d_i * x_i / (d_i + d_j) + d_j * x_j / (d_i + d_j)$$

226 where:  $y$  = downstream water chemistry value,  $i$  and  $j$  = contributing tributaries,  $x_i$  =  
227 water chemistry measurement on tributary  $i$ ,  $d_i$  = drainage area of tributary  $i$ ,  $x_j$  = water  
228 chemistry measurement on tributary  $j$ ,  $d_j$  = drainage area of tributary  $j$ .

229 Model performance was first evaluated by the average difference between  
230 observed (*O*) and predicted (*P*) values using the root mean square error (RMSE):

$$231 \quad \text{RMSE} = \left[ N^{-1} \sum_{i=1}^N (P_i - O_i)^2 \right]^{0.5}$$

232 Additionally, mean absolute error (MAE) was calculated because it is less sensitive to  
233 extreme values than RMSE [Willmott, 1982] and provides a more intuitive measure of  
234 model error:

$$235 \quad \text{MAE} = N^{-1} \sum_{i=1}^N |P_i - O_i|$$

236 Both of these difference measures are preferred over use of the correlation coefficient (*r*)  
237 or coefficient of determination (*R*<sup>2</sup>) because such measures of significance are not  
238 consistently related to accuracy of model prediction [Willmott, 1982]. Furthermore,  
239 confluence site locations were not random and thus violate assumptions of conventional  
240 tests for significance.

241 The deterministic model was first developed with data collected at confluences  
242 within the BC watershed in both spring (*n* = 78 confluences) and summer (*n* = 22  
243 confluences). The model was then tested with additional confluence data collected from  
244 watersheds in two other states using the same sampling methods, but only at confluence  
245 locations. Confluences from an urbanizing watershed (Little Miami River) in Clermont  
246 Co., OH were sampled in Sept. 2006 (*n* = 37 confluences) (Fig. 2). Clermont County lies  
247 in the Pre-Wisconsinan Drift Plains of the Eastern Corn Belt Plains ecoregion [Level IV  
248 (55d), Woods *et al.*, 1998] and is underlain by pre-Wisconsinan glacial till and thin loess.  
249 An additional watershed with multiple valley fills was also sampled in southern WV  
250 (Twentymile Creek watershed, Nicholas Co., WV [*n* = 14 confluences]) in May 2007

251 (Figure 2). The Twentymile Creek watershed lies within the same Central Appalachian  
252 Plateau ecoregion as the BC watershed, but differs by having a trellised drainage basin  
253 rather than the dendritic pattern found in BC.

### 254 **3. Results**

#### 255 **3.1 Water Chemistry**

256 There were strong hydrologic differences between the two sampling seasons in  
257 the BC watershed. Summer discharge of the BC mainstem, measured near its confluence  
258 with Troublesome Creek, dropped to < 20% of spring discharge, from  $0.95 \text{ m}^3 \text{ s}^{-1}$  in  
259 spring to only  $0.18 \text{ m}^3 \text{ s}^{-1}$  in summer. Less than half (48%) the number of locations were  
260 sampled during the summer dry period ( $n = 239$  locations) than in spring ( $n = 494$   
261 locations) due to this contraction of the stream network.

262 Water chemistry results often revealed distinct patterns, both seasonally and  
263 longitudinally, and indicated differences between RF and the remainder of the BC  
264 watershed (Table 1, Figures 3-5). Since our sampling design was aimed at testing for  
265 spatial dependency and the sites do not constitute a random sample, comparisons of water  
266 chemistry values between seasons and between mined and unmined portions of the  
267 watershed are for descriptive purposes only. The most obvious differences were apparent  
268 for stream conductivity in both spring and summer (Table 1, Figure 3). In both seasons,  
269 conductivity values within the RF averaged ca.  $100 \mu\text{S cm}^{-1}$ , whereas outside of RF,  
270 values averaged  $>1000 \mu\text{S cm}^{-1}$  and  $>2500 \mu\text{S cm}^{-1}$  in spring and summer, respectively.  
271 Within RF, three small tributaries draining to Clemons Fork (CF) from the north  
272 (Millseat Branch, Rich Hollow, and Maple Hollow) had springtime conductivities  
273 ranging from  $200\text{-}800 \mu\text{S cm}^{-1}$ , whereas other CF tributaries typically ranged from  $40\text{-}70$

274  $\mu\text{S cm}^{-1}$ . In the upper and lower portions of the BC watershed, as in RF, small headwater  
275 tributaries that were forested generally had conductivity values  $<100 \mu\text{S cm}^{-1}$  and were  
276 typically dry in summer. Spring conductivities in the entire BC watershed (excluding  
277 RF) ranged from 32-3190  $\mu\text{S cm}^{-1}$ , whereas during the summer dry period, values ranged  
278 from 93-11810  $\mu\text{S cm}^{-1}$  (Table 1). In summer, three measurements in one upper BC  
279 tributary, Eli Fork, were  $>11,000 \mu\text{S cm}^{-1}$ , but the majority of measures (82%) were  
280 between 2000-3000  $\mu\text{S cm}^{-1}$ .

281 Differences between RF and the rest of the BC watershed (upper and lower BC)  
282 were less apparent for other parameters. Stream temperatures generally displayed the  
283 expected longitudinal and seasonal trends, with warmer temperatures in summer and  
284 cooler temperatures in headwaters (Table 1, Figure 4). Average stream temperatures  
285 were slightly cooler in RF than in the surrounding watershed for both seasons. Outside of  
286 RF, headwater temperatures were also often higher than both the RF headwaters and  
287 locations much farther downstream. Dissolved oxygen and pH measures generally  
288 followed a spatial pattern similar to temperature. Values for pH were circumneutral (6.5-  
289 7.5) and were consistent between seasons. Average pH values were ca. 0.5 units lower in  
290 RF than in the surrounding portion of the BC watershed in both seasons (Table 1, Figure  
291 5). Dissolved oxygen (D.O.) was the most variable parameter, as expected, and was  
292 influenced by stream temperature, canopy cover, and hour of collection. Dissolved  
293 oxygen concentrations were therefore not mapped or modeled as other parameters.  
294 Median D.O. values were nearly identical for RF and the other BC tributaries in spring  
295 (ca. 9.5 mg/l), but RF values were slightly lower than BC in summer (5.5 mg/l and 8.0  
296 mg/l, respectively) (Table 1).

## 297 3.2 Geospatial Analysis

298 Summer temperatures in the upper BC watershed fit the spherical semivariogram  
299 model (Figure 6). Sites within RF were placed in 100 m bins, whereas sites from the rest  
300 of the BC watershed were placed in 200 m bins to ensure a minimum of 30 distance pairs  
301 in each bin. The nugget, sill, and range for RF were 0.59, 1.40, and 5152.78, respectively  
302 (Figure 6a). Corresponding nugget, sill, and range values for upper BC were 0, 3.74, and  
303 5250.00 (Figure 6b). The sill of the Buckhorn semivariogram was thus 2.7X greater the  
304 sill for CF, indicating greater temperature variation in the mined portion of the watershed.  
305 No nugget was fit to the mined model, suggesting that all spatial dependency was  
306 captured by the model. Despite these differences in variation and nugget effect, the range  
307 for both CF and BC was ca. 5200 m, indicating that temperature is spatially dependent  
308 over this stream length.

309 Violations of the stationarity assumption prevented fitting conductivity, pH, and  
310 spring temperature data to semivariogram models because of strong confluence effects  
311 that often occurred between adjacent sampling locations. For example, covariance  
312 between two points 300 meters apart with an intervening tributary was not the same as  
313 covariance for two points 300 meters apart without an intervening tributary.  
314 Conductivity in the headwaters of BC showed higher semivariance at shorter lag  
315 distances resulting from high variability in headwater tributary values (e.g.,  $< 100 \mu\text{S cm}^{-1}$   
316  $^1$  to  $>3,000 \mu\text{S cm}^{-1}$ ). Thus, spatial dependence between points was conditional on their  
317 locations within the stream network. Non-stationarity even occurred in RF because of the  
318 tributary influences associated with the few streams that had locally elevated  
319 conductivity. The confluence effect was most evident in the abrupt changes in

320 conductivity along the BC mainstem, where major forested tributaries lowered  
321 conductivity and mined tributaries increased it in both spring (Figure 7a) and summer  
322 (Figure 7b). The magnitude of change in BC conductivity was directly related to the  
323 discharge and conductivity of the contributing stream.

### 324 **3.3 Predictive Modeling**

325 Despite the large difference in stream discharge between seasons, the confluence  
326 model showed a strong ability to predict downstream conductivity, pH, and temperature  
327 in the BC watershed in both spring and summer (Table 2). Model error for conductivity  
328 was greater than for pH and temperature in both seasons, largely because of the much  
329 greater range of observed values within the watershed (Table 2). Model error for  
330 conductivity showed a general increase with increasing conductivity. RMSE and MAE  
331 were therefore greater during the summer low flow period and in the mined portion of the  
332 watershed than during higher flows and for unmined areas. Model average error in  
333 summer was  $158.18 \mu\text{S cm}^{-1}$ , whereas error dropped to  $34.56 \mu\text{S cm}^{-1}$  in spring. Error  
334 associated with the predicted pH values was stable between seasons, averaging 0.18 units  
335 in both spring and summer. Predicted temperature values however, had higher error in  
336 summer (MAE = 0.68) than in spring (MAE = 0.43) (Table 2), but average model error  
337 for the year was only ca.  $0.5^\circ \text{C}$ .

338 Confluence data from the additional watersheds in WV and OH followed similar  
339 trends, indicating the model predictions for conductivity, temperature, and pH were  
340 robust across different landuse types and geologic regions (Table 3). Conductivity values  
341 were generally lower in the urbanizing Little Miami River, OH (LMR) watershed than in  
342 the Twentymile Creek, WV (TMC) watershed where extensive coal mining has taken

343 place (Table 3). Model error for conductivity was again higher in each of these  
344 watersheds than for other chemistry variables. Furthermore, model error for TMC  
345 confluences was more than 4 times higher than that of the LMR. Average model error  
346 (MAE) was  $98.20 \mu\text{S cm}^{-1}$  and  $21.79 \mu\text{S cm}^{-1}$  for the TMC and LMR confluences,  
347 respectively (Table 3). Temperature regimes were similar between the two watersheds  
348 and MAE was ca.  $0.25^\circ \text{C}$  for each. There was a greater range of pH values in TMC than  
349 LMR, and MAE was correspondingly higher for TMC (0.19 pH units) than for LMR  
350 (0.11 pH units) confluences (Table 3).

351         Given the strong predictive performance across seasons and geographic locations,  
352 data from all confluences in the BC, LMR, and TMC watersheds were thus combined and  
353 model errors were recalculated. The resulting full model MAE was  $55.34 \mu\text{S cm}^{-1}$  for  
354 conductivity (RMSE = 103.03)(Figure 7a), 0.16 pH units (RMSE = 0.29) (Figure 7b),  
355 and  $0.41^\circ\text{C}$  for temperature (RMSE = 0.66) (Figure 7c). The conductivity model  
356 predictions had greater error when observed values were  $>1,500 \mu\text{S cm}^{-1}$  so error terms  
357 were also calculated for confluences above and below this threshold value. When  
358 including only confluences where observed values were  $<1,500 \mu\text{S cm}^{-1}$  ( $n = 114$   
359 confluences), MAE and RMSE decreased to only  $19.58 \mu\text{S cm}^{-1}$  and 39.57, respectively.  
360 However, when observed confluence values were  $>1,500 \mu\text{S cm}^{-1}$  ( $n = 37$  confluences),  
361 MAE and RMSE increased to  $165.54 \mu\text{S cm}^{-1}$  and 253.32, respectively.

## 362 **4. Discussion**

### 363 **4.1 Water Chemistry**

364         Conductivity measures downstream of fills in both BC and TMC were typically  
365  $>1,000 \mu\text{S cm}^{-1}$ , which is consistent with other coal mining studies from the eastern

366 United States [*Fulk et al.*, 2003; *Hartman et al.*, 2005; *Howard et al.*, 2001; *Kennedy et*  
367 *al.*, 2003; *Kennedy et al.*, 2004; *Merricks et al.*, 2007; *Pond*, 2004; *Pond et al.*, 2008].  
368 Furthermore, these values were from 10-25X greater than forested streams in RF and  
369 >2X levels associated with the loss of sensitive Ephemeroptera taxa [*Howard et al.*,  
370 2000; *Pond*, 2004; *Pond et al.*, 2008]. Elevated conductivity in BC is primarily attributed  
371 to conservative ions such as sulfate, calcium, manganese, magnesium, and iron. As these  
372 ions are transported downstream there is little biological uptake or physical adsorption, so  
373 they tend to accumulate in the downstream direction where multiple fills are located in  
374 the same watersheds. At the headwaters of the BC watershed, Eli Fork conductivity was  
375 nearly ¼ that of seawater during summer sampling ( $>11,000 \mu\text{S cm}^{-1}$ ). The unusually  
376 high conductivity we measured on Eli Fork in summer had however, returned to ca. 100  
377  $\mu\text{S cm}^{-1}$  the following spring. The frequency of such transient events and the associated  
378 potential acute toxicity effects in small streams of the Appalachian region remain poorly  
379 understood.

380 As in previous mining studies [*Howard et al.*, 2001], filled headwater streams in  
381 BC also had slightly higher pH and temperature when compared to nearby forested  
382 streams. Increased temperatures were likely caused by the numerous ponds located  
383 downstream of fills and by a general reduction in canopy cover compared to RF.  
384 Elevated pH possibly resulted from increased buffering capacity of fill materials. Mining  
385 companies also frequently add chemicals to the sediment ponds downstream of fills to  
386 regulate pH and facilitate deposition of potentially harmful metals [*Skousen et al.*, 1998].

## 387 **4.2 Geospatial Analysis**

388           Semivariograms provide a relatively simple tool for quantifying the degree of  
389 spatial dependence for water physicochemical values within stream networks [e.g., *Dent*  
390 *and Grimm*, 1999; *Ganio et al.*, 2005], from small headwaters to large downstream rivers.  
391 Our semivariograms for summer temperature in RF and upper BC watersheds both had a  
392 similar range of ca. 5 km, indicating temperature measures are significantly related to  
393 each other over this stream length. This 5 km distance thus represents a quantifiable  
394 linkage in temperature from headwaters to downstream (or between any two points <5  
395 km apart within these watersheds). Temperatures were slightly higher in the upper BC  
396 watershed, likely due to effects multiple ponds below valley fills and less canopy cover  
397 than in RF. The absence of strong confluence effects for summer temperature may have  
398 been due to the low flows and greater influence of ambient air temperature along the  
399 continuum.

400           The semivariogram approach, however, failed for the spring season and other  
401 water quality parameters because of high semivariance at shorter lag distances that  
402 resulted from the strong differences in water chemistry, especially conductivity, between  
403 some small mined and forested tributaries. *Likens and Buso* [2006] found similar  
404 tributary effects downstream of human disturbances on the lower Hubbard Brook  
405 mainstem. Other researchers have also noted potential non-stationarity when applying  
406 geostatistics to data from stream networks [e.g., *Ganio et al.*, 2005] and have discussed  
407 alternative distance measures and weighting factors that may better address the issue  
408 [e.g., *Gardner et al.*, 2003; *Peterson et al.*, 2006; *Peterson et al.*, 2007; *Ver Hoef et al.*,  
409 2006].

#### 410 **4.3 Predictive Modeling**

411 As a result of non-stationarity and confluence effects, we developed a post-hoc  
412 deterministic model that used only a single weighting factor, watershed area, along with  
413 water chemistry values from only stream confluences. Errors associated with model  
414 predictions were small relative to observed range of values in the BC watershed.  
415 Furthermore, the model showed strong predictive ability for watersheds in two adjacent  
416 states. The TMC and BC watersheds are located within the same ecoregion and have  
417 been subject to similar disturbances from mountaintop removal mining and valley filling  
418 and gas well drilling. The glaciated LMR watershed in southern OH, however, has very  
419 different geologic and topographic features compared to the Central Appalachian BC and  
420 TMC watersheds and has been subject to heavy suburban development. Yet the model  
421 again showed strong predictive ability for conductivity, pH, and temperature in this  
422 watershed, indicating model predictions are robust across varying geographic areas and  
423 disturbance types. Though the confluence measurements used in the model were  
424 collected in the near vicinity (~ 100 m) of tributary junctions, the downstream predictive  
425 ability is not diminished because mainstem conductivity changed little between tributary  
426 junctions in the BC watershed (see Figures 3 and 7). Some watersheds however, may  
427 have greater groundwater influx that would contribute to model error.

428 Conductivity had the largest error of the three parameters modeled, due largely to  
429 the extensive range of observed values at tributary junctions. There was no apparent  
430 trend in direction of conductivity error, either high or low, among predicted values. Error  
431 tended to be greater for mined confluences where conductivity measures were  $>1,000 \mu\text{S}$   
432  $\text{cm}^{-1}$ , or  $>10\text{X}$  higher than that of adjacent forested tributaries. For the mined tributaries,  
433 error in the discharge to watershed area relationship may also have contributed to error in

434 predicted conductivity values. Stream discharge is highly correlated with watershed area  
435 [e.g., *Gordon et al.*, 1995], however during mountaintop removal mining the landscape  
436 and topography are so drastically altered that contributing areas often change and are  
437 difficult to delineate. Watershed areas used in our model were based on pre-mine  
438 topographic coverages because the disturbance was relatively recent (<10 years old) and  
439 updated maps were unavailable. The hydrologic effects of the fills themselves and  
440 associated sediment ponds may also have contributed to model errors. Hydrologic  
441 studies by the U.S. Geological Survey have shown that valley-filled streams have higher  
442 flows when compared to unmined streams in West Virginia [*Messinger and Paybins*,  
443 2003; *Wiley et al.*, 2001]. The greater discharge from filled streams has been attributed to  
444 reduced evapotranspiration due to loss of vegetation and soils during mining [*Messinger*  
445 *and Paybins*, 2003]. These findings were supported by our observations during the  
446 summer dry period in BC, when many forested tributaries were dry, or nearly so, yet  
447 valley filled streams of similar size often continued to flow. Given the difficulty in  
448 delineating source areas and potential fill effects on hydrology, use of an alternative  
449 weighting factor, such as mean annual discharge, would likely reduce model error. These  
450 small streams are rarely gauged however, so reliable discharge data are typically  
451 unavailable.

#### 452 **4.4 Applications**

453 The value of our deterministic model is in its simplicity and potential ease of use  
454 for regulatory agents. The model requires no special software or programming skills, yet  
455 can be easily used to estimate potential downstream impacts of disturbance from a  
456 proposed permit action. For example, regulators of CWA §401 & 404 (i.e., “dredge and

457 fill” activities) could use the model to evaluate valley fill permit applications based on the  
458 potential increase in conductivity and potential degradation of aquatic life downstream of  
459 proposed permit locations. This would only require a conservative estimate of the  
460 conductivity increase associated with a proposed valley fill, information that could be  
461 easily gathered from similar existing fills in the watershed or ecoregion or use of existing  
462 data sources. In this manner, the effects of elevated TDS (i.e., conductivity) from a  
463 single valley fill at the head of a watershed, or cumulative effects of multiple fills within  
464 a watershed, could be conservatively estimated several kilometers downstream without  
465 need for extensive data collection or modeling efforts. Conductivity measures are easily  
466 collected *in situ* with affordable sondes or multi-probes and data from the streams where  
467 impacts are proposed and the surrounding watersheds could potentially be required along  
468 with CWA §401/404 permit applications.

469         As an example of how the predictive model could be used by regulators, we  
470 modeled downstream effects on stream conductivity if valley fills were proposed for the  
471 undisturbed Clemons Fork watershed within RF (Figure 9). For simplicity, we assumed  
472 placement of a valley fill would increase conductivity to  $2,000 \mu\text{S cm}^{-1}$  (the approximate  
473 annual mean of actual filled streams in the greater BC watershed) immediately  
474 downstream of hypothetical fills. Observed springtime baseflow conductivity values  
475 were used elsewhere for “non-filled” tributary streams. We modeled placement of 1-4  
476 fills separately to evaluate potential cumulative effects. Results indicated that, with  
477 placement of a single fill, conductivity of the immediate receiving streams were elevated  
478 to  $>500 \mu\text{S cm}^{-1}$ , but the majority of the CF watershed remained safely below this  
479 threshold (Figure 9a). Placement of a second fill, however, elevated conductivity such

480 that the majority of the CF mainstem was near or above  $500 \mu\text{S cm}^{-1}$ . With addition of a  
481 3<sup>rd</sup> and 4<sup>th</sup> fill, conductivity of the entire CF mainstem increased to  $>700 \mu\text{S cm}^{-1}$  and  
482 actually increased conductivity of the larger receiving stream, BC, as well (Figure 9c and  
483 9d).

484           Given the documented accumulation of ions downstream and resulting adverse  
485 biological effects, valley filled headwater streams may have a detrimental cumulative  
486 downstream effect that outweighs their individual size and relative discharge regime.  
487 The conservative nature of the dissolved ions downstream of fills and absence of  
488 appropriate and viable treatment technologies suggests that the only way to mitigate for  
489 elevated conductivity may be dilution from undisturbed forested tributaries. The  
490 importance of dilution was evident in our hypothetical CF example, where placement of a  
491 single fill had relatively small effects compared to those of multiple fills. The effect of  
492 dilution, and the absence thereof, is also evidenced by the difference in conductivity of  
493 the Buckhorn mainstem between seasons. During the spring wet period, forested  
494 tributaries effectively reduced mainstem conductivity such that BC conductivity near the  
495 mouth was  $838 \mu\text{S cm}^{-1}$ , whereas in summer when most forested headwater streams were  
496 dry, conductivity at the BC mouth was ca.  $2510 \mu\text{S cm}^{-1}$ .

497           Regulatory agencies may therefore need to implement a watershed based  
498 management strategy that would preserve forested streams within mined watersheds to  
499 provide appropriate dilution and prevent downstream degradation of aquatic ecosystems.  
500 Such a holistic approach to CWA §401 and §404 permitting is one option for mitigating  
501 potential cumulative effects of increased ion loads downstream of valley fills. Our  
502 deterministic model is one tool that could be used to estimate dilution provided from

503 forested watersheds to reach a targeted conductivity range that is protective of aquatic  
504 life. Elevated TDS that result from valley fillings is however, only one potential adverse  
505 impact and should be considered in concert with other environmental, human health, and  
506 socioeconomic factors.

## 507 **5. Conclusion**

508 In the future, the deterministic model will continue to be tested across other  
509 geographic areas and disturbance types. Furthermore, additional water chemistry  
510 parameters such as nitrate, ammonia, or orthophosphate may be used for testing model  
511 predictions at stream confluences. However, model error may be greater for these  
512 nutrients because they are more bioreactive than the more conserved physiochemical  
513 parameters used here. *Dent and Grimm* [1999] however, successfully modeled spatial  
514 dependence of nutrient concentrations in a desert stream over a 3 km lag distance using  
515 semivariograms. *Strager et al.* [2009] also used a spatially explicit, GIS-based watershed  
516 model to evaluate downstream effects of acid mine drainage in West Virginia. This  
517 demonstrates that no single geostatistical or modeling approach may accurately  
518 characterize downstream influence for all variables or stressors at all spatial scales within  
519 stream networks. Use of such methods, however, requires that investigators expand  
520 beyond the stream reach spatial scales commonly used in lotic research. Choice of the  
521 best modeling approach can also provide unique insight into underlying spatial scale  
522 variation and ecological processes operating in the watershed. Others have studied  
523 spatial variation in streamwater chemistry [e.g., *Dent and Grimm* 1999; *Likens and Buso*,  
524 2006] and have noted the need for understanding ecological patterns at these larger  
525 spatial scales when assessing anthropogenic impacts [*Likens and Buso*, 2006]. Though

526 “significant nexus” was not clearly defined in *Rapanos and Carabell v. United States*  
527 [2006], if use of quantitative tools such as those presented here demonstrate spatial  
528 dependence or substantial influence on downstream water quality, this would likely  
529 constitute a “nexus” and therefore meet the intended criterion.

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688 Table 1. Summary statistics for water chemistry parameters from the Buckhorn Creek, KY watershed in a) spring (May 2006,  
 689 n = 494) and b) summer (Sept. 2005, n = 239). RF = Robinson Forest (unmined), BC = remainder of Buckhorn watershed  
 690 (partially mined).

<b>a)</b>	<b>Parameter</b>	<b>RF (n = 245)</b>			<b>BC (n = 249)</b>				
		<i>Min.</i>	<i>Max.</i>	<i>Median</i>	<i>Range</i>	<i>Min.</i>	<i>Max.</i>	<i>Median</i>	<i>Range</i>
	Conductivity ( $\mu\text{S cm}^{-1}$ )	34	782	50	748	32	3190	871	3158
	Temperature ( $^{\circ}\text{C}$ )	11.37	18.56	14.33	7.19	12.04	25.74	16.69	13.7
	pH (su)	5.13	7.96	6.46	2.83	3.25	8.71	7.28	5.46
	D.O. (mg/l)	5.79	11.27	9.52	5.48	5.05	14.11	9.65	9.06
<b>b)</b>	<b>Parameter</b>	<b>RF (n = 110)</b>			<b>BC (n = 129)</b>				
	Conductivity ( $\mu\text{S cm}^{-1}$ )	20	212	86	192	93	11810	2330	11717
	Temperature ( $^{\circ}\text{C}$ )	14.53	25.02	18.44	10.49	15.70	25.55	19.66	9.85
	pH (su)	5.78	8.15	6.72	2.37	5.05	8.34	7.35	3.29
	D.O. (mg/l)	7.35	13.40	5.50	11.40	3.00	11.71	8.00	8.71

693 Table 2. Root mean square error (RMSE) and mean absolute error (MAE) for predictive  
 694 model results from the Buckhorn Creek, KY watershed, combined data from spring (May  
 695 2006) and summer (Sept. 2005).

<b>Parameter</b>	<b>Summer</b>		<b>Spring</b>	
	<i>RMSE</i>	<i>MAE</i>	<i>RMSE</i>	<i>MAE</i>
Conductivity ( $\mu\text{S cm}^{-1}$ )	267.05	158.18	74.62	34.56
pH	0.28	0.18	0.33	0.18
Temperature ( $^{\circ}\text{C}$ )	1.03	0.68	0.63	0.43

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711 Table 3. Summary water chemistry for observed values and predictive model error (RMSE = root mean square error & MAE = mean  
 712 absolute error) for Little Miami River (LMR)(Clermont Co., OH; Sept. 2006, n = 118 sites) and Twentymile Creek (TMC)(Nicholas  
 713 Co, WV; May 2007, n = 51 sites).

	LMR			TMC		
	Cond. ( $\mu\text{S cm}^{-1}$ )	Temp. ( $^{\circ}\text{C}$ )	pH	Cond. ( $\mu\text{S cm}^{-1}$ )	Temp. ( $^{\circ}\text{C}$ )	pH
Min.	86	18.18	6.98	37	13.34	4.91
Max.	667	23.54	8.81	3970	21.35	8.5
Median	312	20.14	7.71	1483	18.05	7.73
Range	581	5.36	1.83	3933	8.01	3.59
RMSE	37.67	0.45	0.17	188.46	0.42	0.29
MAE	21.79	0.27	0.11	98.20	0.25	0.19

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## LIST OF FIGURES

720 **Figure 1.** Location and course landuse map of the Buckhorn Creek, KY watershed.

721 **Figure 2.** Location and course landuse map of the Little Miami River, OH and the

722 Twentymile Creek, WV watersheds.

723 **Figure 3.** Map of stream conductivity ( $\mu\text{S cm}^{-1}$ ) values for all sites sampled in (a)

724 Summer 2005 (n = 239 sites) and (b) Spring 2006 (n = 439) in the Buckhorn Creek, KY

725 watershed. Delineated area = Robinson Forest boundary (unmined).

726 **Figure 4.** Map of stream temperature ( $^{\circ}\text{C}$ ) values for all sites sampled in (a) Summer

727 2005 (n = 239 sites) and (b) Spring 2006 (n = 439) in the Buckhorn Creek, KY

728 watershed. Delineated area = Robinson Forest boundary (unmined).

729 **Figure 5.** Map of stream pH values for all sites sampled in (a) Summer 2005 (n = 239

730 sites) and (b) Spring 2006 (n = 439) in the Buckhorn Creek, KY watershed. Delineated

731 area = Robinson Forest boundary (unmined).

732 **Figure 6.** Empirical semivariograms for summer temperature in the (a) Clemons Fork

733 (Robinson Forest) and (a) Buckhorn Creek watersheds.

734 **Figure 7.** Influence of major mined (dashed arrows) and unmined (solid arrows)

735 tributaries on stream conductivity ( $\mu\text{S cm}^{-1}$ ) along the mainstem Buckhorn Creek, KY in

736 (a) Spring 2006 and (a) Summer 2005.

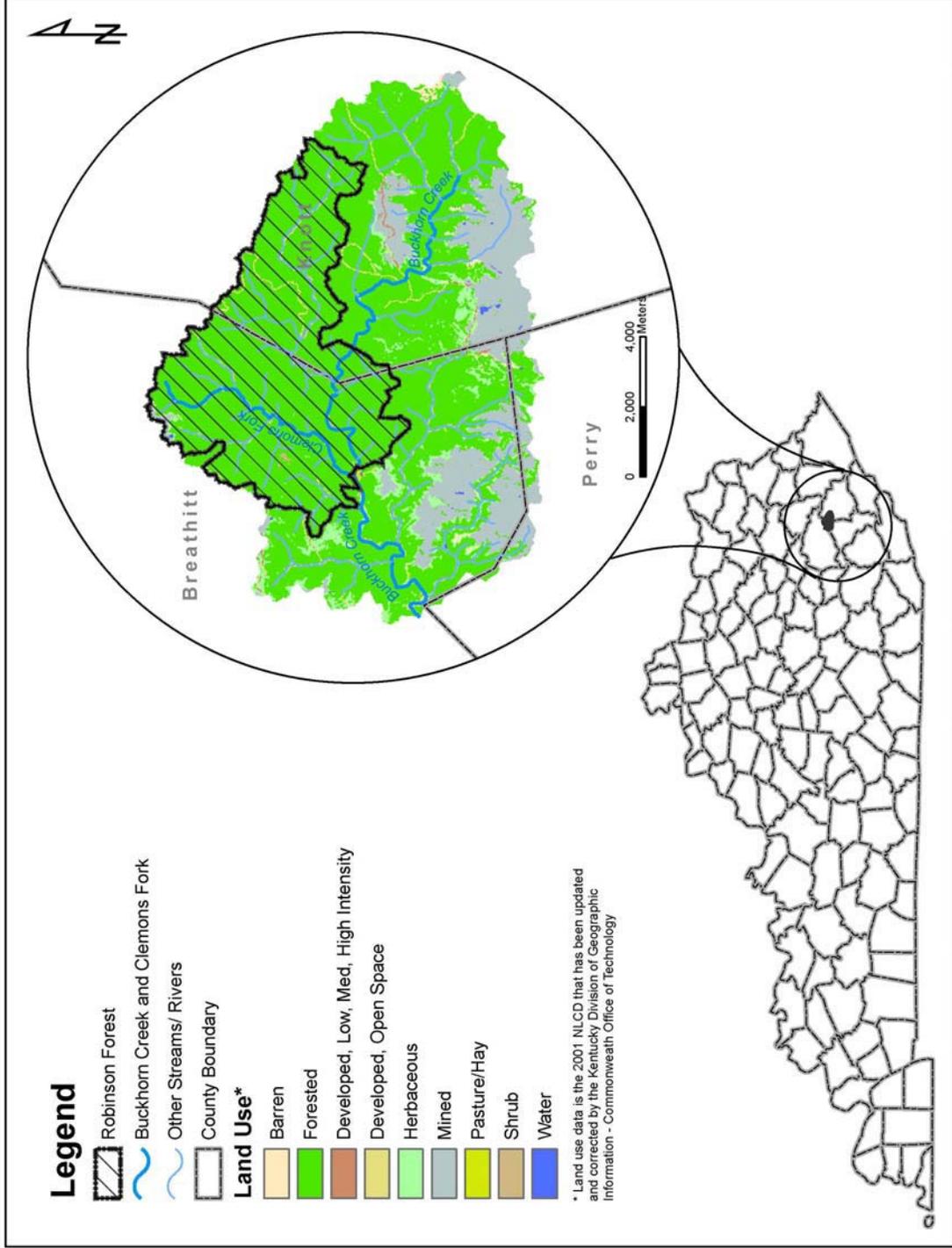
737 **Figure 8.** Predictive results for full model (a) Conductivity ( $\mu\text{S cm}^{-1}$ ), (b) pH, and (c)

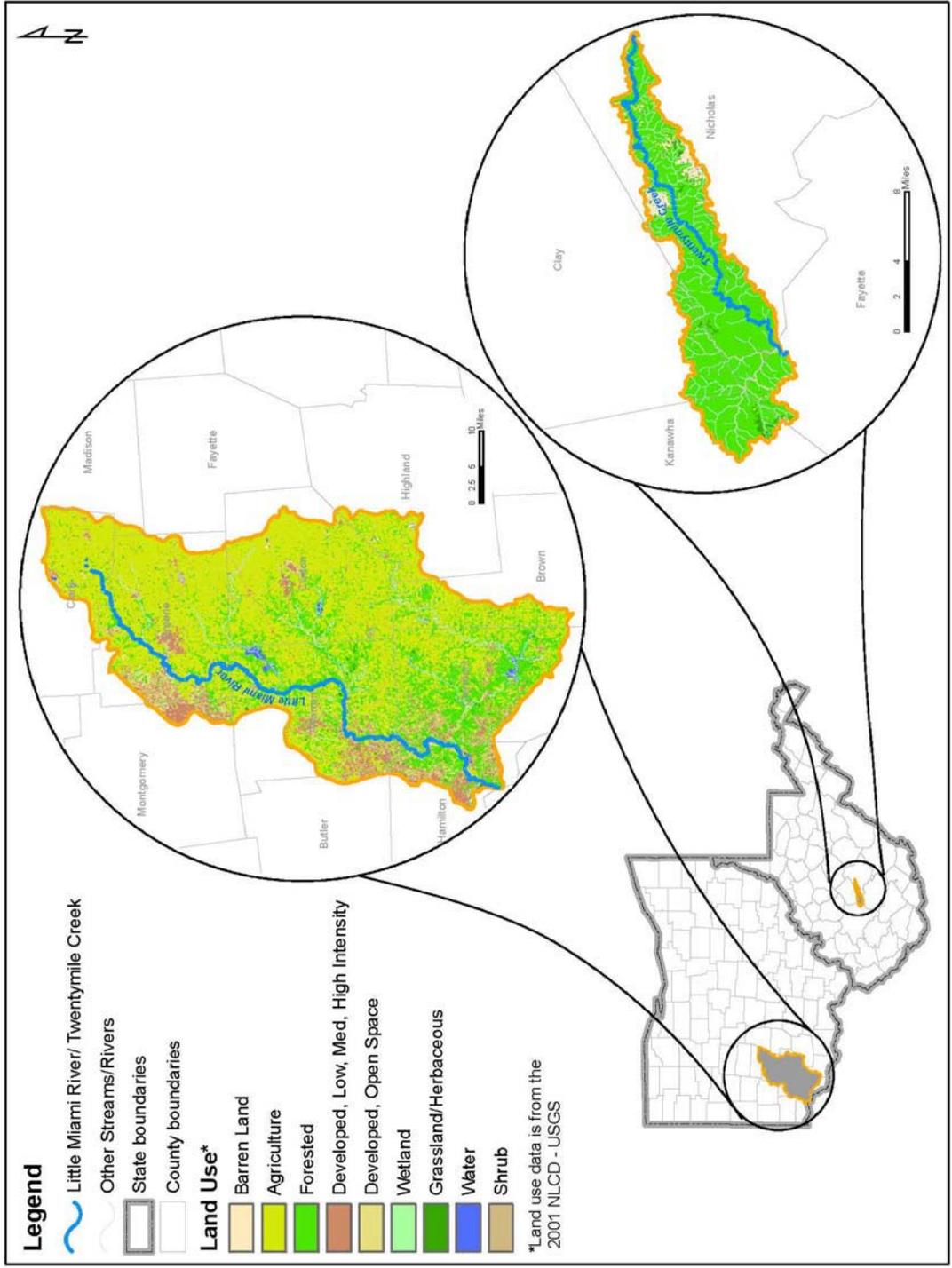
738 Temperature ( $^{\circ}\text{C}$ ) at confluences from Buckhorn Creek, KY (BC) in Summer 2005 and

739 Spring 2006, Twentymile Creek, WV (TMC), and the Little Miami River (LMR)

740 watershed.

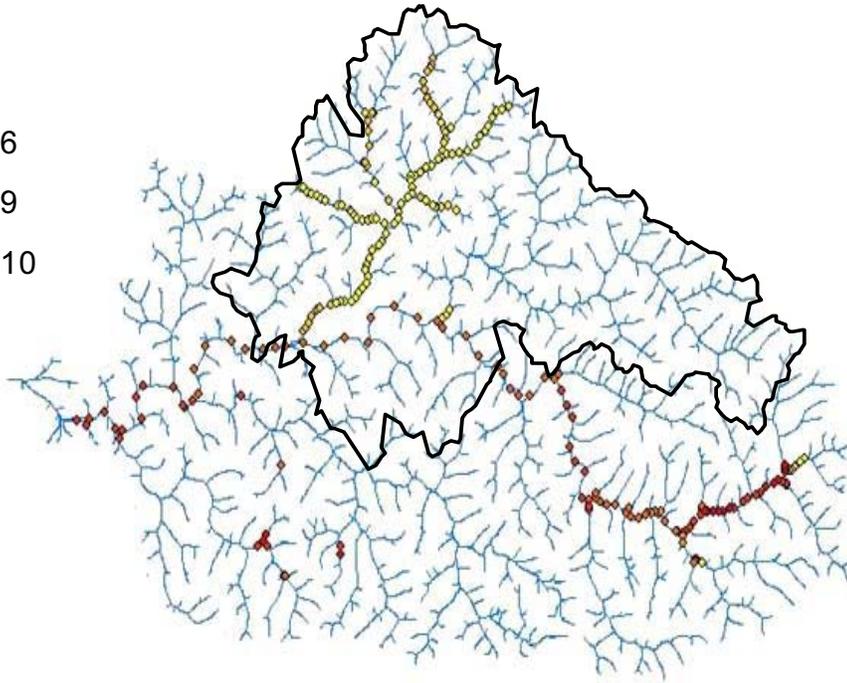
741 **Figure 9.** Predicted conductivity values ( $\mu\text{S cm}^{-1}$ ) downstream of confluences in the  
742 forested Clemons Fork Watershed, Robinson Forest, KY, with hypothetical valley filling  
743 of one (a), two (b), three (c), and four (d) headwater stream tributaries.





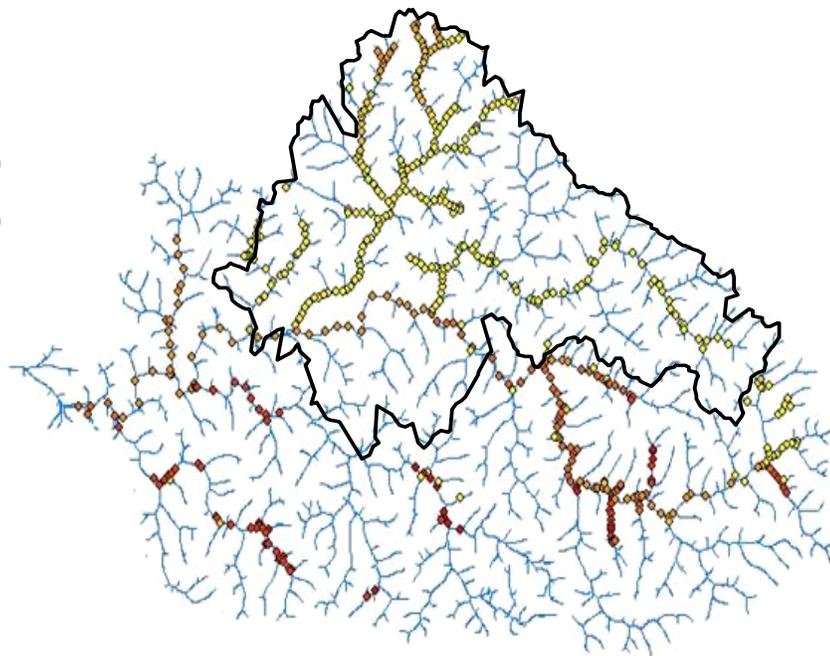
A)

- 20 - 126
- 127 - 266
- 267 - 1809
- 1810 - 2336
- 2337 - 2859
- 2860 - 11810



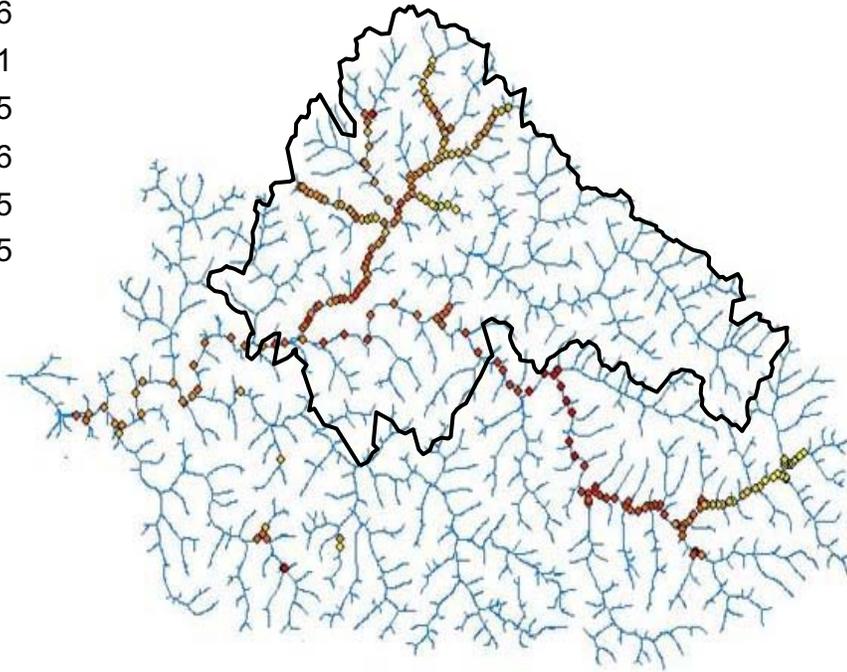
B)

- 32 - 124
- 125 - 323
- 324 - 801
- 802 - 1470
- 1471 - 2310
- 2311 - 3190



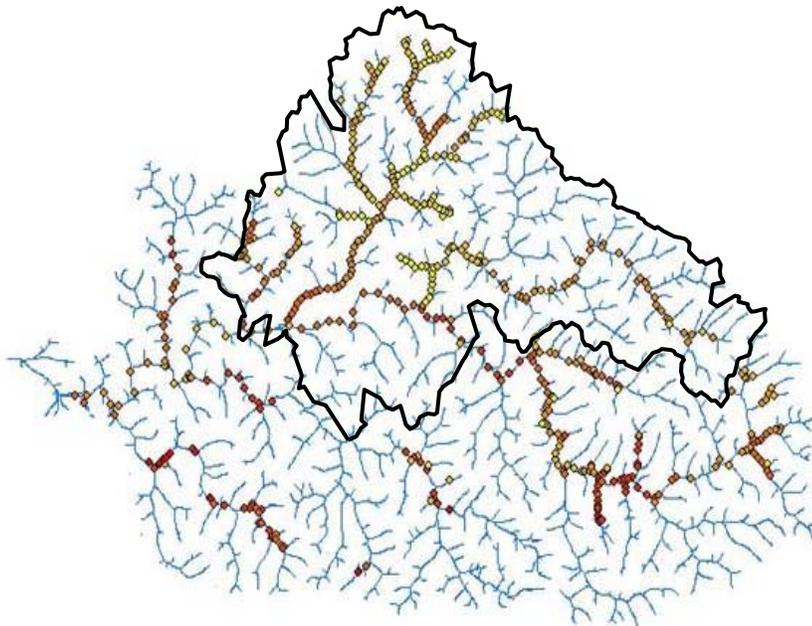
A)

- 14.53 – 16.96
- 16.97 – 18.01
- 18.02 – 18.95
- 18.96 – 20.16
- 20.17 – 21.55
- 21.56 – 25.55



B)

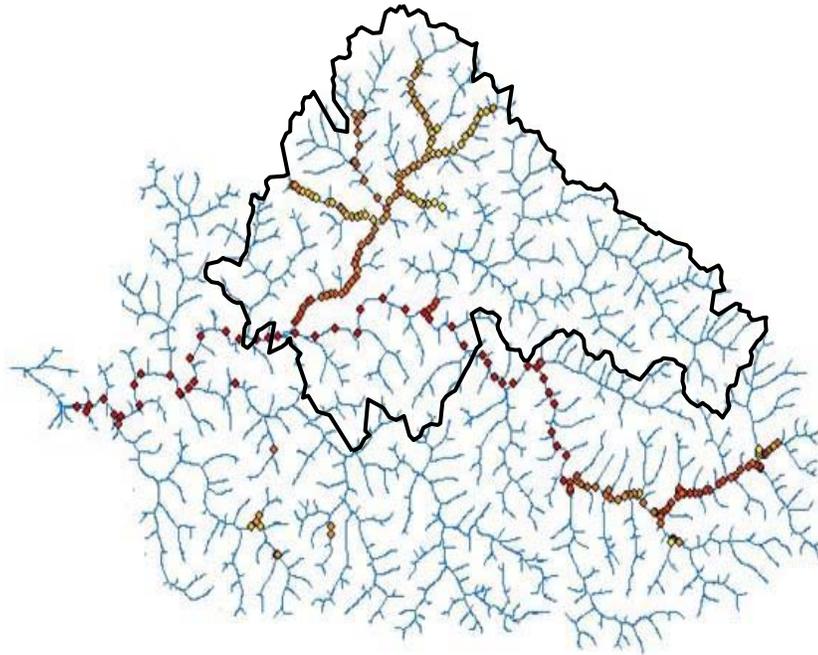
- 11.37 – 13.36
- 13.37 – 14.71
- 14.72 – 16.10
- 16.11 – 17.87
- 17.88 – 20.62
- 20.63 – 25.74



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749  
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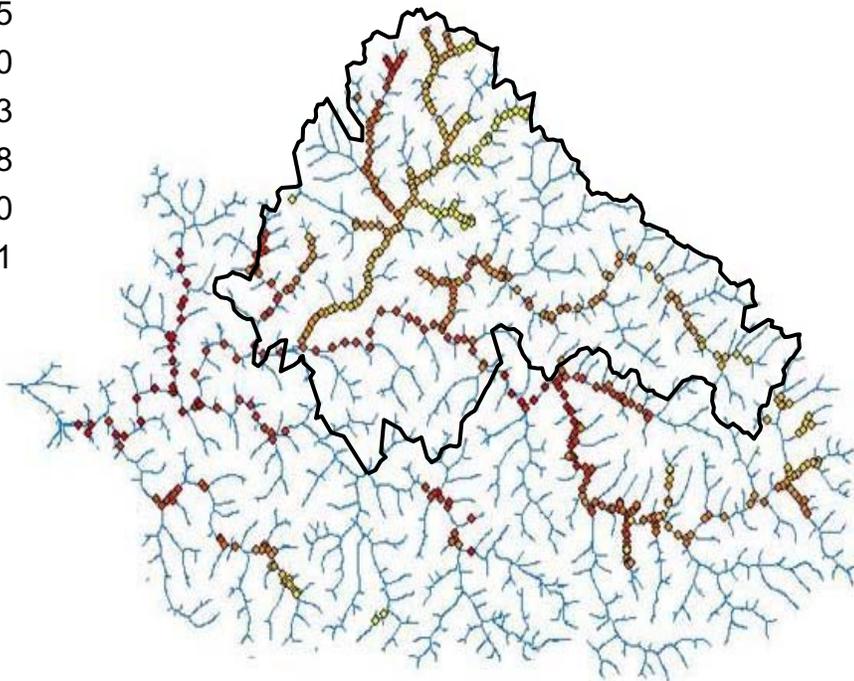
A)

- 5.05 – 6.02
- 6.03 – 6.54
- 6.55 – 6.87
- 6.88 – 7.23
- 7.24 – 7.79
- 7.80 – 8.34



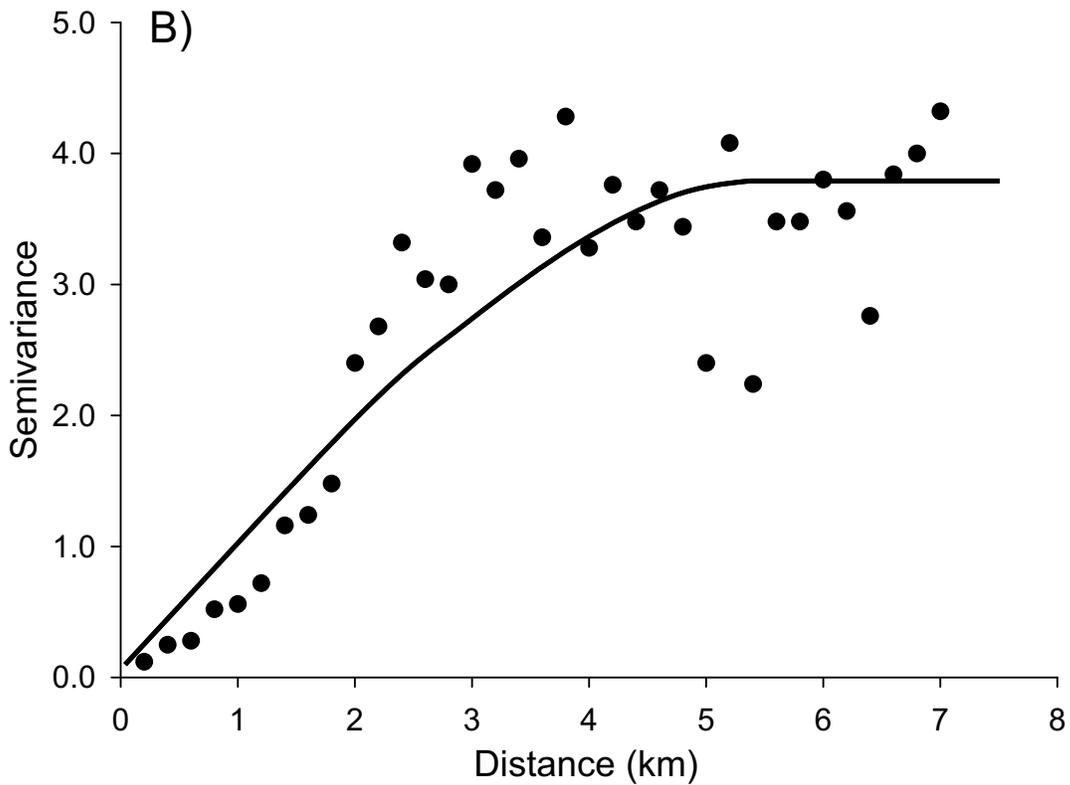
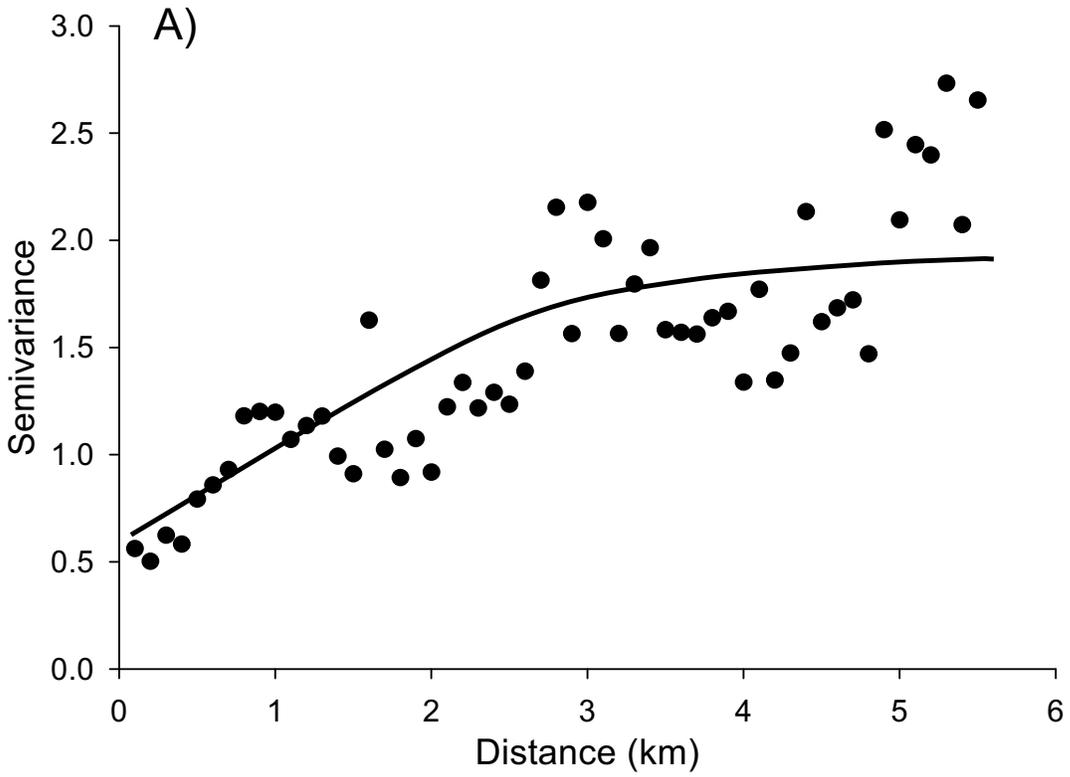
B)

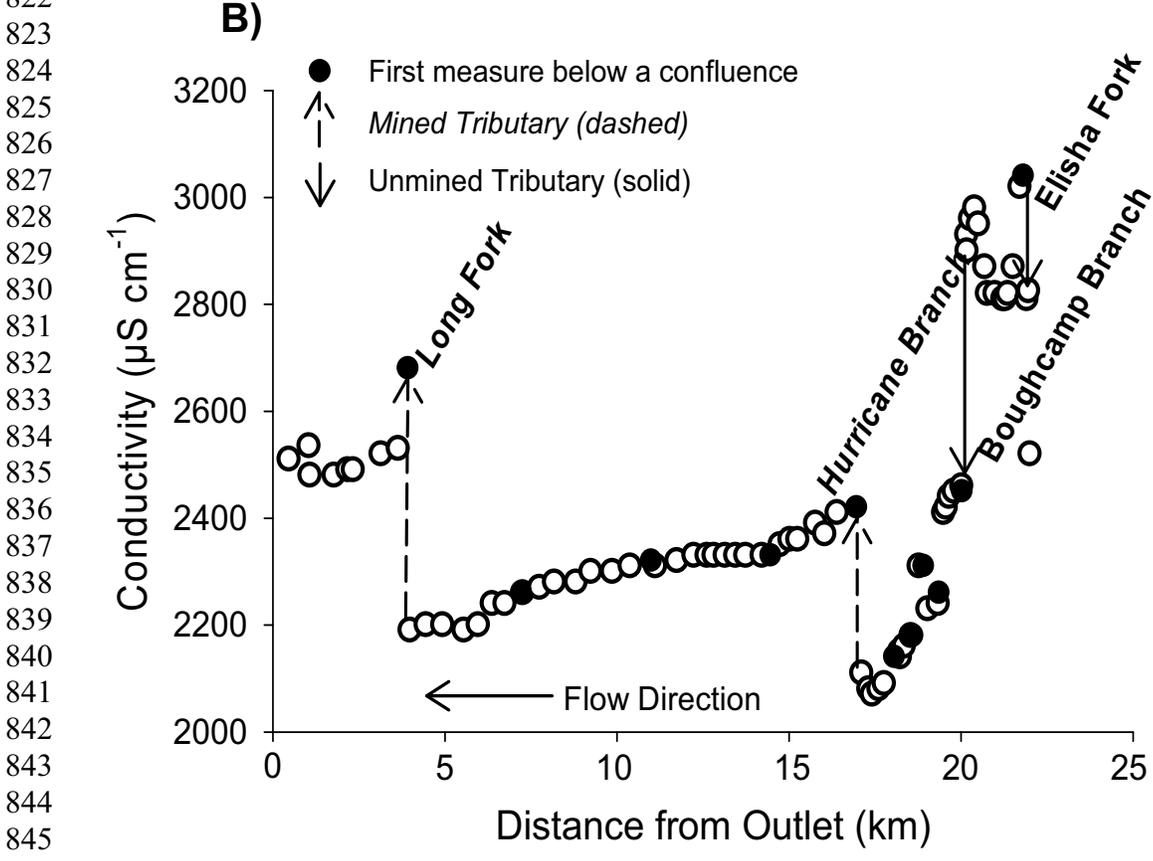
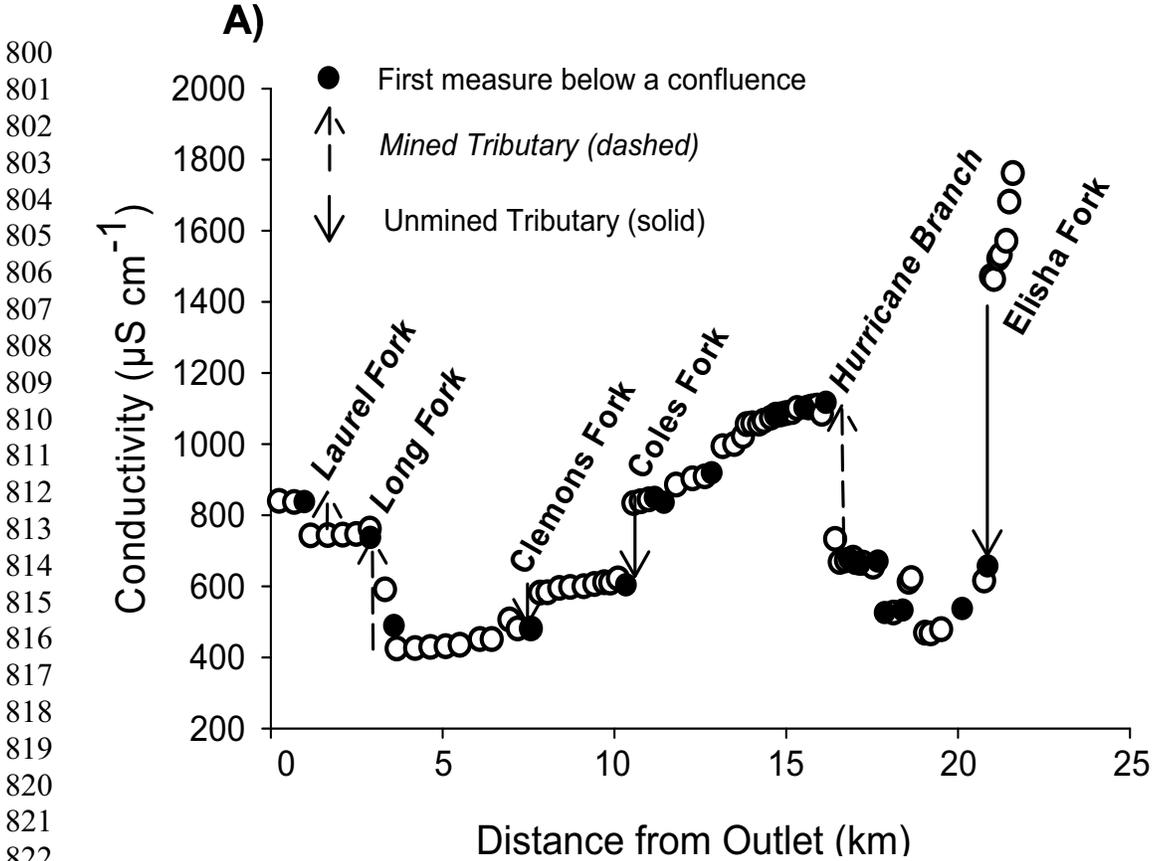
- 3.25 – 5.75
- 5.76 – 6.40
- 6.41 – 6.83
- 6.84 – 7.28
- 7.29 – 7.80
- 7.81 – 8.71



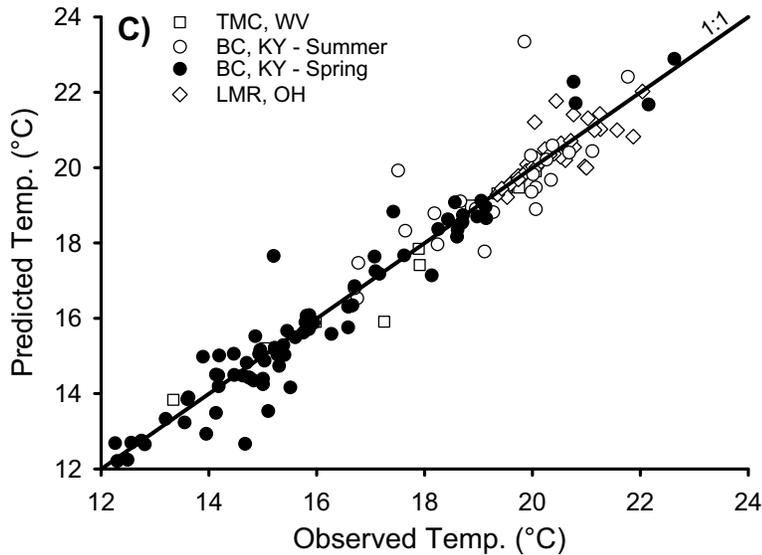
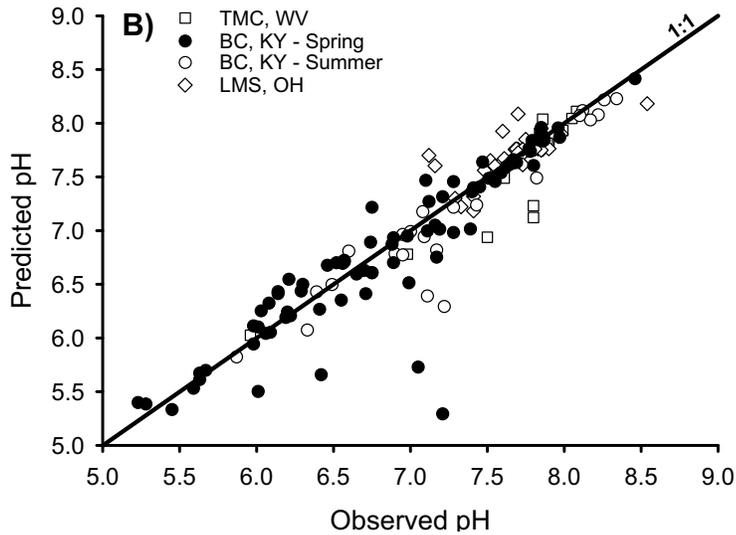
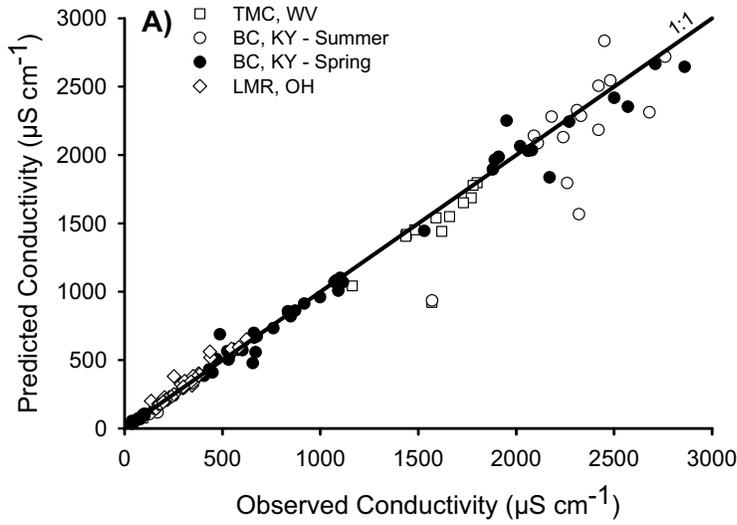
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