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## Final Author Manuscript

### Network Analysis Reveals Multi-Scale Controls on Streamwater Chemistry

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50 **Abstract**

51

52 By coupling synoptic data from a basin-wide assessment of streamwater chemistry with network-  
53 based geostatistical analysis, we show that spatial processes differentially affect biogeochemical  
54 condition and pattern across a headwater stream network. We analyzed a high-resolution dataset  
55 consisting of 664 water samples collected every 100 m throughout 32 tributaries in an entire  
56 fifth-order stream network. These samples were analyzed for an exhaustive suite of chemical  
57 constituents. The fine grain and broad extent of this study design allowed us to quantify spatial  
58 patterns over a range of scales using empirical semivariograms that explicitly incorporated  
59 network topology. Here, we show that spatial structure, as determined by the characteristic  
60 shape of the semivariograms, differed both among chemical constituents and by spatial  
61 relationship (flow-connected, flow-unconnected, or Euclidean). Spatial structure was apparent at  
62 either a single scale or at multiple nested scales, suggesting separate processes operating  
63 simultaneously within the stream network and surrounding terrestrial landscape. Expected  
64 patterns of spatial dependence for flow-connected relationships (e.g., increasing homogeneity  
65 with downstream distance) occurred for some chemical constituents (e.g., dissolved organic  
66 carbon, sulfate, and aluminum) but not for others (e.g., nitrate, sodium). By comparing  
67 semivariograms for the different chemical constituents and spatial relationships, we were able to  
68 separate effects on streamwater chemistry of (1) fine- versus broad-scale processes and (2) in-  
69 stream processes versus landscape controls. These findings provide novel insight on the  
70 hierarchical scaling of local, longitudinal, and landscape processes that drive biogeochemical  
71 patterns in stream networks.

72

73 **Key words:** biogeochemistry, spatial pattern, stream network, connectivity, scale

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75

76 **Significance Statement**

77

78 Headwater streams are important sources of water for downstream ecosystems and human  
79 communities. These streams comprise the vast majority of stream and river kilometers in  
80 watersheds and affect regional water quality. However, the actual spatial variation of water  
81 quality in headwater streams is often unknown. Our study uses an unusually high-resolution  
82 spatial dataset from a headwater stream network and employs a new statistical tool to objectively  
83 describe spatial patterns of streamwater chemistry within a stream network. This approach  
84 provides new insights on how flowing water interacts with vegetation, soil, and geologic  
85 materials in the surrounding landscape. Application of this method may help to identify factors  
86 impairing water quality and to inform strategies for protecting aquatic ecosystems.

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## **Introduction**

Spatial heterogeneity of ecosystems has been a focus of landscape ecology for over two decades, but the linkages between these patterns and underlying processes are still poorly understood (1-3). Quantifying these pattern-process links is largely a problem of scale. Specifically, it is difficult to perform experiments at the landscape scale and measure responses over the range of spatial and temporal scales commensurate with the processes of interest (4, 5).

This problem of scale limits our understanding of both terrestrial and freshwater ecosystems. Effects of landscape pattern on ecosystem response can be evaluated at stream outlets using biogeochemical signals that integrate physical and biological conditions of the catchment (6, 7). However, the spatial complexity of biogeochemical patterns and processes within stream networks has not been fully investigated because it is difficult to quantify such patterns at a grain and extent sufficient for examining spatial heterogeneity and processes across scales (8). Quantifying this variability and linking fine- and broad-scale patterns and processes within the branched topology of stream networks is essential for understanding aquatic ecosystem function and aquatic-terrestrial ecosystem connections, but requires new conceptual and methodological approaches (9, 10).

Major advances in understanding biogeochemical fluxes and cycles in rivers and streams have resulted from increased recognition of how spatial heterogeneity and network topology reflect land–water interactions (e.g., 11, 12). However, our understanding of biogeochemical processes in stream networks is still limited to small-scale experiments (e.g., 13), often with limited spatial extent or replication, and large-scale correlative models (14). Fine-grained observations at intermediate scales (e.g., 1 to 10 km<sup>2</sup>) may be especially powerful for advancing understanding of complex aquatic and terrestrial effects on biogeochemical fluxes throughout stream networks (15-17).

Studies quantifying streamwater chemistry in a spatially intensive manner at intermediate scales have revealed a high degree of spatial structure that cannot be explained by current models of biogeochemical processes (11, 18). Specifically, these results show that traditional, continuum-based models—where conditions are regulated primarily by upstream processes, and thus exhibit gradual downstream gradients—are insufficient for describing the true spatial complexity of biogeochemical patterns and processes in stream networks. This unfamiliar ground between fine and coarse scales of understanding is the crux of field-based science, in which the “preferred modes of explanation...appear to be systematically related to customary human scales of perception of the world” (19). Likewise, obtaining a bird’s-eye view of biogeochemical patterns at fine to coarse scales may be crucial for advancing ecosystem science and explaining the spatial complexity of streamwater chemistry within landscapes.

Recent developments in geostatistical modeling provide a valuable new perspective on stream networks by revealing hydrological and ecological patterns in a spatially continuous manner (20, 21). To date, the relatively few sample points required to generate spatial interpolations have fueled the popularity of these models. However, the increasing use of network-based geostatistical techniques underscores a need to understand the processes from which these

134 patterns arise, or, more broadly, to elucidate ecosystem processes from spatial patterns and  
135 develop new hypotheses about system function (22). Recent theoretical and empirical approaches  
136 show that this is possible using empirical semivariograms and synoptic sampling (e.g., 23).  
137 Specifically, the combination of spatial analysis and synoptic sampling allows one to visualize  
138 how patterns occur across different scales, while providing the empirical foundation needed to  
139 identify the processes that give rise to those patterns. Geostatistics have only recently been used  
140 to describe spatial patterns throughout stream networks (24, 25), even though these tools have  
141 long been used to quantify spatial structure in terrestrial ecology (26).

142  
143 We apply geostatistical techniques to an unusually high-resolution synoptic dataset of  
144 streamwater chemistry collected throughout the Hubbard Brook Valley in New Hampshire to  
145 explore the spatial structure of biogeochemical patterns at multiple scales (18). The dataset  
146 consisted of 664 water samples collected over a three-month period every 100 m throughout all  
147 32 tributaries of the 3600 ha, fifth-order stream network of the Hubbard Brook Valley. We show  
148 previously undescribed patterns of spatial dependence based on three spatial relationships,  
149 revealing biogeochemical determinants occurring across scales, both within the stream network  
150 and surrounding catchment. Stream network patterns were defined by two spatial relationships:  
151 flow-connected and flow-unconnected (*sensu* 20, 21). The straight-line distance between two  
152 points defines Euclidean relationships. Flow-connected and unconnected network relationships  
153 describe distances along the stream network and were considered “connected” if water flows  
154 from one site to another. Thus, all points downstream of other points on the stream network  
155 were considered connected, but points upstream of tributary junctions that do not share flow  
156 were considered “unconnected.”

157  
158 Empirical semivariograms based on these three spatial relationships suggest the importance of  
159 different drivers of spatial variability in streamwater chemistry at multiple scales, e.g., fine  
160 (<1500 m) and broad scales (>3000 m) (Figure 1). For example, semivariograms of flow-  
161 connected relationships indicate whether downstream flow and longitudinal transport exert a  
162 dominant control on streamwater chemistry by showing the level of autocorrelation between  
163 flow-connected samples. Likewise, semivariograms of flow-unconnected relationships provide  
164 information about the similarity/dissimilarity of tributary branches due to influences of landscape  
165 properties (e.g., soils or geology). Semivariograms of streamwater chemistry using Euclidean  
166 relationships reveal interactions or lateral connectivity between the stream network and the  
167 landscape. Therefore, both Euclidean and flow-unconnected network relationships provide  
168 information on how the landscape influences patterns of streamwater chemistry within a single  
169 catchment/network, whereas a flow-connected relationship largely describes the effect of  
170 hydrologic transport and upstream spatial dependence.

171  
172 Extensive work in the Hubbard Brook Ecosystem Study (HBES) over the last five decades  
173 provides the temporal context for understanding biogeochemical processes and landscape change  
174 through ecosystem change revealed by long-term research (27, 28). The current study aims to  
175 provide a spatial context (29) for interpreting how biogeochemical patterns observed from sparse  
176 fixed sites (e.g., outlets of experimental watersheds) fit within the larger stream network. We  
177 expect spatial dependence of streamwater chemistry to be structured by flow directionality and  
178 network topology, especially for constituents that are not strongly biologically cycled in  
179 headwater streams (e.g., base cations,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ). However, patchiness longitudinally in the

180 stream network and across the landscape (i.e., by Euclidean distances) may arise due to the local  
181 influences of landscape features such as seeps and springs, and variation in vegetation, soil, and  
182 geologic materials. Our objectives were to (1) quantify spatial heterogeneity in streamwater  
183 chemistry at multiple scales within the stream network, (2) compare patterns of streamwater  
184 chemistry using different spatial relationships within the stream network and across the  
185 landscape (i.e., using network and Euclidean relationships), and (3) evaluate this approach for  
186 linking biogeochemical patterns and processes by identifying potential drivers of spatial patterns  
187 in streamwater chemistry that bridge scales from tributaries, to the main stem, and throughout the  
188 entire Hubbard Brook Valley.

189

## 190 **Results**

### 191 *Spatial structuring in streamwater chemistry*

192 Streamwater chemistry patterns throughout the Hubbard Brook Valley exhibited spatial  
193 patchiness and gradients at multiple scales (see supplemental information [Figure S1] for a  
194 complete set of distribution maps for all chemical constituents). However, it is difficult to  
195 systematically compare these patterns visually due to the spatial complexity of the data. For  
196 example, patterns of dissolved organic carbon (DOC), sodium, dissolved silica, and specific  
197 conductance were visibly different (Figure 2), but the extent and typology of these differences  
198 cannot be quantified based on visual inspection alone. In contrast, analysis with empirical  
199 semivariograms revealed a high degree of spatial structuring in streamwater chemistry, as  
200 indicated by the overall shape of the semivariograms (Figures 3 and S2). Specifically, some of  
201 the semivariograms showed spatial structure at predominantly one scale of variation (<1500 m)  
202 (cf. Figure 1c, flow-connected semivariograms in Figure 3), whereas other semivariograms  
203 varied substantially among spatial relationships and exhibited spatial structure at multiple scales  
204 (cf. Figure 1d, Figure 3). Semivariograms of the 16 chemical constituents exhibited several of  
205 the theoretical spatial structures described in Figure 1 (Table 1, Figures 3 and S2): (1)  
206 nonstructured, or poorly defined structure ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ; cf. Figure 1a); (2) single-scale  
207 structure (many examples; cf. Figure 1c); and (3) nested structure (many examples; cf. Figure  
208 1d). Scales of variation in streamwater chemistry ranged from 500 to >6000 m for the variables  
209 that showed spatial structure (Table 1). The finest and broadest scales of variation were  
210 associated with semivariograms of the nested type, for which Euclidean and flow-unconnected  
211 relationships had the finest scales of variation, and flow-unconnected relationships had the  
212 broadest scales of variation. Scales of variation for flow-connected network relationships were  
213 less variable compared to the other spatial relationships.

214

### 215 *Effects of network connectivity on patterns of spatial dependence*

216 Patterns of spatial dependence in streamwater chemistry varied not only among chemical  
217 constituents but also depending on how connectivity, or relationships among sample points, was  
218 defined in space. For example, semivariograms of specific conductance differed in shape and  
219 overall variance (i.e., height of the curve with respect to the y-axis) based on the way the spatial  
220 relationship was calculated between sample points (i.e., flow-connected, flow-unconnected, and  
221 Euclidean spatial relationships) (Figure 3d). Specifically, the shape of the flow-connected  
222 semivariogram of specific conductance indicated the presence of spatial structure at one scale  
223 (Figure 3d), whereas the semivariogram of flow-unconnected relationships exhibited pronounced  
224 patterns associated with nested spatial structure at two scales. The semivariogram based on the  
225 Euclidean spatial relationship also exhibited a nested pattern, but was not as clearly defined as

226 the flow-unconnected semivariogram. Overall variance was generally highest for the  
227 semivariogram based on Euclidean relationships and lowest for the flow-connected  
228 semivariograms.

229  
230 The differences described above for semivariograms of specific conductance generally applied to  
231 the majority of chemical constituents that exhibited spatial structure (i.e., monomeric aluminum  
232  $[Al_m]$ ,  $Cl^-$ , dissolved inorganic carbon [DIC], DOC,  $K^+$ , dissolved Si, and  $SO_4^{2-}$ ) (Figure S2), but  
233 there were some notable exceptions. For example, semivariograms of acid-neutralizing capacity  
234 (ANC),  $Ca^{2+}$ , and  $K^+$  were also similar, but only for flow-connected and Euclidean spatial  
235 relationships with distances less than about 4500 m (Figure S2). Semivariograms of  $Mg^{2+}$  and  
236  $Na^+$  exhibited an analogous pattern but at shorter distances (~1500 m). The nugget value (i.e.,  
237 discontinuity at the origin) (e.g., defined in Figure 1c) of semivariograms based on Euclidean  
238 and flow-connected relationships were close to zero for all chemical constituents except for DIC  
239 (Figures 3 and S2), whereas nugget-variance for flow-unconnected semivariograms were  
240 substantially greater than zero for all chemical constituents except  $Al_m$  and  $K^+$ .

## 241 242 **Discussion**

243 Understanding controls on spatial patterns of streamwater chemistry and developing tools for  
244 predicting spatial variation of stream chemistry in headwaters is important for managing water  
245 quality in downstream systems. Headwater streams comprise the vast majority of stream length  
246 in watersheds (30) and perform critical functions for downstream ecosystems, but are still  
247 considered *aqua incognita* in hydrology and ecology (31, 32). We found complex variability in  
248 spatial patterns of streamwater chemistry (multi-scale structure) across the Hubbard Brook  
249 Valley, suggesting that different processes are affecting streamwater chemistry at different scales  
250 and with different spatial relationships. Our results suggest that streamwater chemistry is more  
251 complex than the expected pattern of a single scale of spatial autocorrelation (Figure 1c) or  
252 increasing homogeneity with downstream distance. There is both fine-scale patchiness and  
253 broad-scale trend operating within the stream network and across the landscape. These  
254 observations may provide clues about how streams function and ultimately lead to better models  
255 of aquatic and terrestrial ecosystem interactions in stream networks. Furthermore, the spatial  
256 structure of stream network chemistry that emerges from our analysis is similar to patterns that  
257 have been observed in landscape ecology, where both broad-scale gradients and fine-scale  
258 patchiness are influenced by environmental attributes (33).

259  
260 Semivariograms of water chemistry in the stream network of the Hubbard Brook Valley revealed  
261 spatial structure at multiple scales previously described only in unbranched stream sections (11)  
262 or for a limited suite of chemical constituents examined at much coarser scales (34). Other  
263 pioneering studies of stream networks have examined spatial heterogeneity or developed  
264 predictive models in stream networks (16, 35), but these studies have been too coarse in grain  
265 (low resolution) to detect spatial structure at scales ranging from hundreds to thousands of  
266 meters. Our analysis of the shape and characteristics of semivariograms (Figure 1) of water  
267 chemistry in a stream network provide empirical support for three models of spatial structure in  
268 stream networks (sensu 26): (1) broad-scale heterogeneity with few patches (Figure 1b; e.g., the  
269 Euclidean relationship of  $Na^+$ , dissolved Si, and DIC), (2) fine-scale heterogeneity with many  
270 patches (Figure 1c; e.g., flow-connected  $K^+$ ,  $Cl^-$ , DOC), and (3) nested heterogeneity that

271 contains fine-scale patchiness and broad-scale heterogeneity (Figure 1d; e.g., flow-unconnected  
272  $H^+$ ,  $Al_m$ , DOC).

273  
274 The different spatial relationships permit the examination of heterogeneity dominated by  
275 landscape versus stream network processes. Euclidean and flow-unconnected network  
276 relationships were associated with the nested type of heterogeneity indicative of landscape  
277 influences occurring over multiple spatial scales, such as soil, geology, and vegetation controls  
278 on the chemistry of water sources. In contrast, flow-connected relationships were entirely (with  
279 the exception of  $Na^+$ ) of the single-scale type, suggesting that similarity at large stream distances  
280 in the network was largely controlled by channel-mediated transport and groundwater flow  
281 accumulation, which seemed to stabilize the variance of all chemical constituents at about 2000  
282 m separation distance. This range among the semivariograms for flow-connected relationships  
283 provides an indication of where the hydrologic control on variability begins to overwhelm the  
284 patchiness at the fine-scale (<2000 m). As one would expect, hydrologic transport and  
285 longitudinal gains of groundwater were the main drivers of the spatial pattern among most of the  
286 solutes. At Hubbard Brook, solute chemistry is relatively constant temporally compared to  
287 discharge, which may suggest general persistence in these spatial relationships (17).

288  
289 Euclidean and flow-unconnected semivariograms exhibit higher variance, spatial dependence at  
290 broader scales, and multiple structures (single and nested) compared to flow-connected  
291 semivariograms, suggesting processes other than hydrologic transport were also responsible for  
292 observed patterns of streamwater chemistry. Chemical constituents typically considered to be  
293 controlled by mineral weathering (e.g.,  $Ca^{2+}$ , dissolved Si, DIC,  $Mg^{2+}$ , ANC, and  $Na^+$ ) all show  
294 either broad- or multi-scale heterogeneity with the Euclidean relationship and high nugget values  
295 with the flow-unconnected network relationship, suggesting discontinuity or dissimilarity among  
296 short unconnected distances such as two sites above a confluence residing on different tributaries  
297 (Figure S2). The broad-scale component of variation in the Euclidean relationships may be  
298 explained by either gross changes in bedrock type or glacial till composition/thickness across the  
299 Hubbard Brook Valley. The Valley is underlain by granodiorite in the western portion and  
300 pelitic schist in the eastern portion (36) with an overlying soil parent material composition that  
301 varies with lithologic sources eroded and deposited by the most recent glaciation (37). The most  
302 apparent broad-scale pattern occurs with  $Na^+$  where the Euclidean semivariogram shows a  
303 monotonic increase, which manifests itself spatially with a general increase in concentration  
304 across the Valley from west to east. This pattern is different from chloride suggesting the trend in  
305  $Na^+$  is not due to road-salt contamination in the east part of the basin, which is near an interstate  
306 roadway. Sodium may be geologically controlled; however, the trend is counter to currently  
307 known mineral chemistry differences in the Hubbard Brook Valley (37). Nevertheless, the  
308 comparison between the Euclidean and the flow-connected semivariograms for  $Na^+$  suggests a  
309 strong landscape control on the spatial pattern at the basin-wide scale, and fine-scale patchiness  
310 along the stream. Similar spatial dependence at large Euclidean distance is apparent with  $K^+$ ,  
311  $Ca^{2+}$ , dissolved Si,  $Cl^-$ ,  $SO_4^{2-}$ , ANC, DIC, and specific conductance.

312  
313 The difference between nugget values of mineral weathering-controlled chemistry (i.e.,  $Ca^{2+}$ ,  
314 dissolved Si,  $Mg^{2+}$ , ANC, and  $Na^+$ ) for the two network relationships suggests differences in  
315 landscape character and their potential influence on spatial structure, but over shorter distances.  
316 A higher nugget value for the flow-unconnected metric highlights spatial variability over short

317 distances at tributary junctions and chemical dissimilarities between tributaries. This pattern  
318 shows that sources contributing to streamflow that are not downstream from one another may be  
319 heterogeneous despite close proximity. This same pattern was noted by Likens and Buso (18) in  
320 streams strongly influenced by groundwater seeps and springs. Seeps have been noted  
321 throughout the valley and typically show distinct chemistry (e.g., 17).

322 Streamwater chemistry that exhibited the weakest structure, including  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{PO}_4^{3-}$ ,  
323 may be explained in large part by their low concentrations (i.e., at or near analytical detection  
324 limits [30]). However, there was some indication of spatial dependence over fine scales (<1000  
325 m) in  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  (i.e., linear increases in variation over short flow-connected distances),  
326 suggesting that in-stream uptake may be occurring over very short distances due to biological  
327 demand for these nutrients in the generally nutrient-poor environment (38). Uptake lengths for  
328 ammonium and phosphorus within the Hubbard Brook Valley were shown to vary between 5 to  
329 277 m and 2 to 54 m, respectively (39), suggesting strong in-stream processing influence on  
330 spatial variation over short flow-connected distances.

331  
332 Both landscape and hydrologic drivers influence some chemical constituents. For example,  
333 DOC,  $\text{H}^+$  and  $\text{Al}_m$  show autocorrelation at flow-connected relationships >1500 m, indicating an  
334 influence of flow accumulation on spatial structure. However, these solutes also exhibited  
335 nested structure in flow-unconnected distance at fine (<750 m) and broad (>4500 m) spatial  
336 scales. Thus, two scales of heterogeneity and three different spatial relationships appear to be  
337 important. One is fine-scale, resulting in hotspots of DOC and  $\text{H}^+$  variation, which typically  
338 coincides with  $\text{Al}_m$  variation (40). At large distances that are not flow-connected, such as  
339 headwater regions in different parts of the network, there is also a high degree of variation in  $\text{H}^+$ ,  
340 DOC and  $\text{Al}_m$ . This pattern may occur because headwater and valley bottom regions throughout  
341 the Hubbard Brook Valley contain patches of coniferous forest and distinct soils. Many of these  
342 areas (e.g., ridge tops, north-facing slopes, and along the stream) tend to have shallow, wet,  
343 acidic soils (41) with deep litter layers, and high DOC and Al soil-water concentrations that have  
344 been shown to affect spatial patterns of streamwater DOC and Al (17, 40). It is striking that our  
345 semivariogram analysis provides a quantitative characterization of this large-scale patchiness,  
346 which small-scale, descriptive studies cannot capture.

347  
348 This study shows that network geostatistics combined with high-resolution water chemistry data  
349 can provide insight into dominant processes driving biogeochemical patterns in stream networks  
350 at local, longitudinal, and landscape scales. In the Hubbard Brook Valley, landscape processes  
351 were shown to occur over a wide range of spatial scales (500 to >6000 m), with broad-scale  
352 trends and fine-scale patchiness likely driven by geologic, soil, and vegetation features across the  
353 Valley. Hydrologic transport and flow accumulation in streams were also found to exert  
354 influence on streamwater chemistry at downstream distances of 1400 to 2200 m, where variation  
355 in chemistry tended to stabilize. By revealing the spatial structure of stream biogeochemistry  
356 and scales of underlying drivers, this spatially explicit, network-level analysis is crucial to  
357 refining long-held assumptions about stream structure and function (e.g., 42).

358  
359

## 360 **Methods**

### 361 *Basin-wide survey*



362 Streamwater chemistry was measured by Likens and Buso (18) throughout the 3600 ha Hubbard  
363 Brook Valley in the White Mountains of central New Hampshire (USA) (43°56'N, 71°45'W.  
364 Detailed information on the ecological, hydrological, climatological, and geological setting is  
365 summarized by Likens (43). The field survey of streamwater chemistry ( $Al_m$ , acid-neutralizing  
366 capacity,  $Ca^{2+}$ ,  $Cl^-$ , DIC, DOC,  $K^+$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $NH_4^+$ ,  $NO_3^-$ , pH,  $PO_4^{3-}$ , dissolved Si,  $SO_4^{2-}$ , and  
367 specific conductance) was conducted during October through December 2001 and is described in  
368 Likens and Buso (18). A subset of 664 from the total of 761 samples was selected for network  
369 analysis based on an assessment of hydrography and the ability to delineate catchment areas  
370 using a geographical information system (GIS) derived from 10-m digital elevation models. The  
371 sites left out were almost entirely small tributaries with only a few samples and they were  
372 scattered systematically throughout the Valley, but primarily in headwater areas.

373

### 374 *Analysis of spatial structure with empirical semivariograms*

375 We quantified spatial structure in streamwater chemistry by calculating empirical  
376 semivariograms using distance metrics based on spatial connectivity within the stream network  
377 and across the landscape of the Hubbard Brook Valley (20, 21). Empirical semivariograms  
378 provide a means to describe spatial structure in geographically referenced data by quantifying the  
379 variance (or relatedness) in sample values (e.g.,  $Ca^{2+}$  or specific conductance) as a function of  
380 the distance between sample points in Euclidean space (44) or throughout the stream network  
381 (24, 45). An empirical semivariogram that displays semivariance as a function of stream network  
382 distance separately for flow-connected and flow-unconnected relationships is called a Torgegram  
383 (46). We used Torgegrams and empirical semivariograms based on Euclidean distance as  
384 exploratory tools for visualizing patterns of spatial autocorrelation.

385

386 Empirical semivariograms provide information on patterns of spatial dependence and have  
387 various theoretical forms (Figure 1). We used the typology proposed by Ettema and Wardle (26)  
388 to compare shapes of semivariograms among chemical constituents and spatial relationships.  
389 Because all of the spatial relationships used the same data, standardization of semivariance was  
390 not necessary for comparisons among relationships for a given chemical constituent. Only the  
391 shapes of the semivariograms were compared among chemical constituents, and this approach  
392 made it possible to preserve the original units in the semivariograms to aid interpretation. In  
393 geostatistics, terms used to describe the semivariogram include the range, sill, and nugget, all of  
394 which can be estimated quantitatively and have specific meaning for the purposes of predictive  
395 modeling (47). We did not attempt fit models to the empirical semivariograms because of the  
396 complexity of the structures observed and uncertainty associated with identifying model forms *a*  
397 *priori* to estimate parameters. We determined the approximate range visually by identifying the  
398 inflection point (or points) in variance as a function of separation distance. The approximate  
399 variances at the *y*-intercept (i.e., the nugget) and the inflection point in variance (i.e., the sill)  
400 were also assessed visually. The goal of analysis with semivariograms was to provide a means  
401 to visualize, with the aid of relatively simple geostatistical tools, the full range of spatial  
402 complexity in biogeochemical patterns across scales in a headwater stream network. Specific  
403 elucidation of mechanisms and explanatory variables for individual chemical constituents is the  
404 topic of ongoing work, including the examination of chemical variability at scales finer than that  
405 available from Likens and Buso (18) (see 17).

406

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416 manuscript. Any use of trade, product, or firm names is for descriptive purposes only and does  
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418

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516 **Figure Legends**

517

518 Figure 1. Hypothetical semivariograms and associated maps depicting representative spatial  
519 patterns of water chemistry in a stream network. Nonstructured spatial pattern (a) is indicated in  
520 the semivariogram by no change in semivariance ( $\gamma$ ) ( $y$ -axis) with increasing distance ( $d$ )  
521 between neighbors ( $x$ -axis), as is graphically depicted by the uniform line color in the associated  
522 network map. In the example shown (a),  $\gamma = 0$  for a uniform, nonstructured spatial pattern. Other  
523 potential semivariograms and associated network patterns include (b) spatial dependence at a  
524 broad-scale with a gradient symbolized in the network map by changes in line color from the  
525 upper left (blue) to the lower right (red) of the stream network, (c) fine-scale patchiness or spatial  
526 dependence indicated in the network map as ‘hotspots’, and (d) nested heterogeneity reflecting a  
527 combination of fine-scale patchiness imbedded within a broad-scale gradient (sensu Ettema and  
528 Wardle 2002). Characteristics of the semivariogram (c) are the asymptote or *sill*, which is  
529 roughly equivalent to the total population variance; the variance discontinuity at the  $y$ -intercept  
530 or *nugget*, which represents variance due to sampling error and/or spatial dependence at distance  
531 intervals not explicitly sampled; and the *range*, which defines the distance or scale over which  
532 spatial dependence is expressed. Beyond this range, in a non-nested structure, points are spatially  
533 independent of one another or uncorrelated. Nested semivariograms are hierarchical structures,  
534 each characterized by its own range.

535

536 Figure 2. Spatial patterns of (a) sodium ( $\text{Na}^+$ ; mg/L), (b) dissolved silica (DSi; reported as  $\text{SiO}_2$   
537 mg/L), (c) dissolved organic carbon (DOC; mg/L), and (d) specific conductance (SC;  $\mu\text{S}/\text{cm}$ )  
538 derived from sampling streamwater chemistry at 664 locations throughout the Hubbard Brook  
539 Valley, NH during October–December 2001.

540

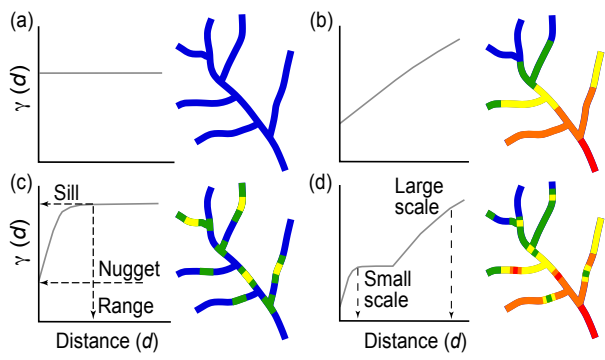
541 Figure 3. Empirical semivariograms for (a) sodium ( $\text{Na}^+$ ; mg/L), (b) dissolved silica (DSi;  
542 reported as  $\text{SiO}_2$  mg/L), (c) dissolved organic carbon (DOC; mg/L), and (d) specific conductance  
543 (SC;  $\mu\text{S}/\text{cm}$ ) based on Euclidian, flow-connected, and flow-unconnected spatial relationships ( $d$ )  
544 in the Hubbard Brook Valley. Visually estimated the ranges (see Table 1) for Euclidean (E)  
545 (yellow and black line), flow-connected (FC) (orange), and flow-unconnected (FU) (blue)  
546 relationships are indicated with vertical lines. Symbols with lighter color shades indicate  
547 semivariance estimates based on  $< 100$  pairs of points.

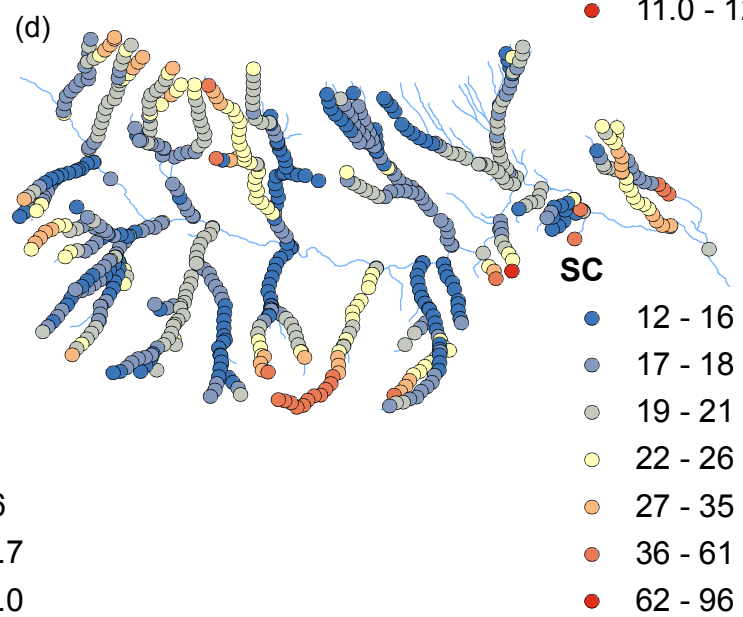
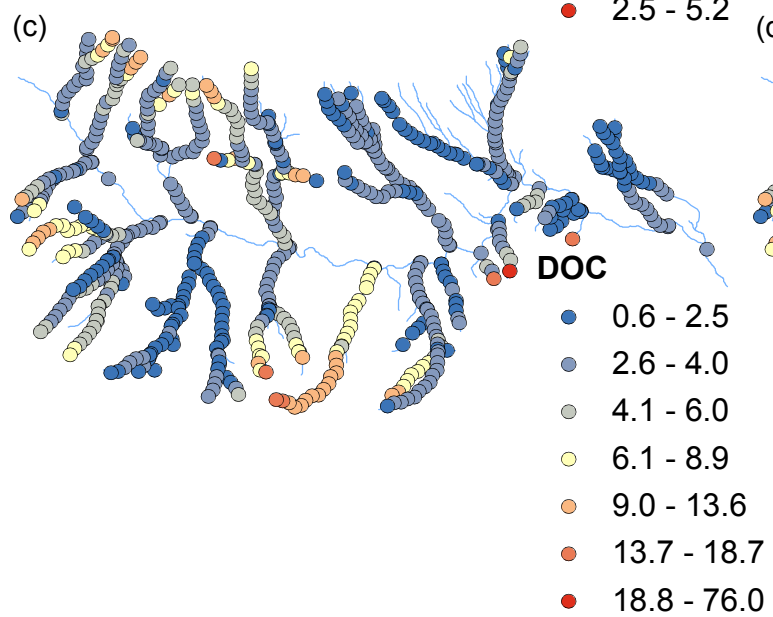
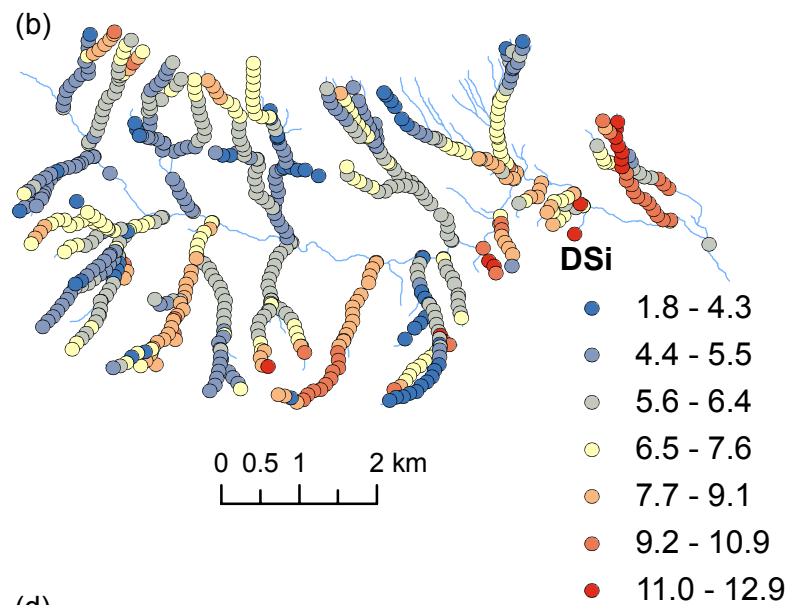
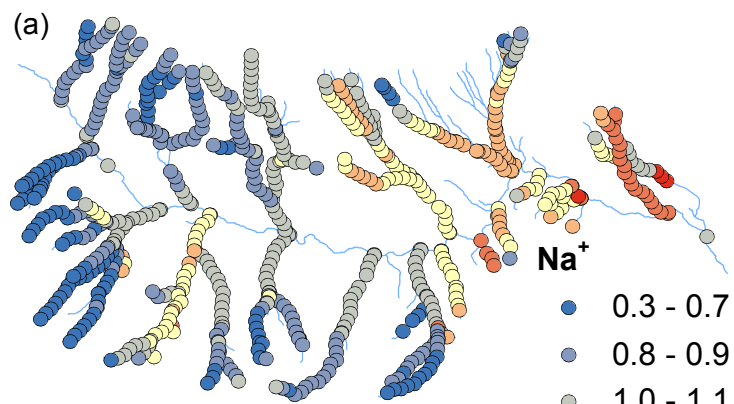
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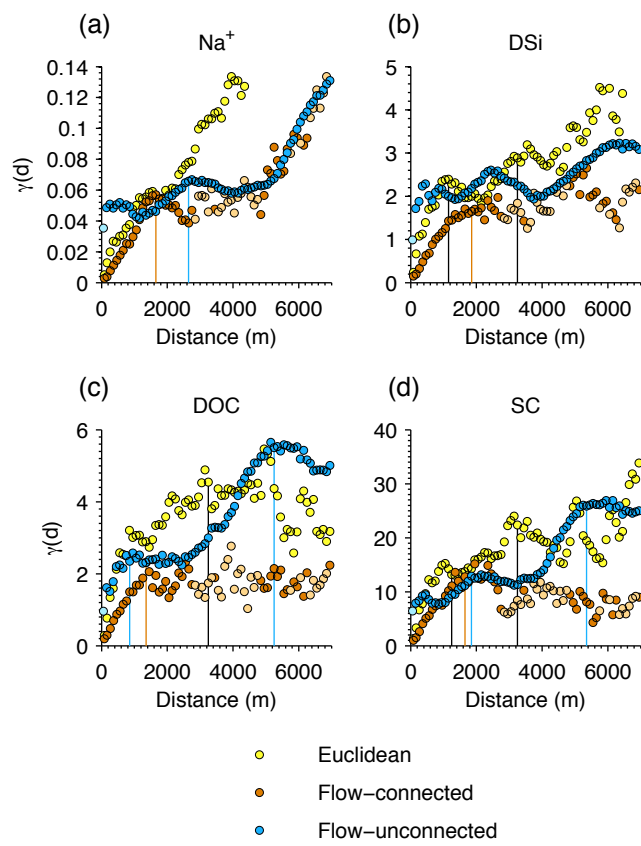
Characteristics of empirical semivariograms for streamwater chemistry based on Euclidean, flow-connected, and flow-unconnected spatial relationships in the Hubbard Brook Valley. Semivariogram type and range for each spatial relationship indicate nested- versus single-scale spatial structure and the distances over which spatial dependence is expressed, respectively.

Solute	Euclidean relationship		Flow-connected network relationship			Flow-unconnected network relationship		
	Type	Scale (m)	Type	Scale (m)	Type	Scale (m)	Type	Scale (m)
H <sup>+</sup>	single	2300 -	single	1500 -	nested	900 4500		
Ca <sup>2+</sup>	nested	1000 ?	single	1800 -	single	2500 -		
Mg <sup>2+</sup>	nested	1100 3700	single	1700 -	nested	2600 ?		
Na <sup>+</sup>	single	? -	nested	1600 ?	nested	2600 ?		
K <sup>+</sup>	nested	1200 5400	single	1700 -	single	1800 -		
NH <sub>4</sub> <sup>+</sup>	-	- -	-	- -	-	- -		
Al <sub>m</sub>	nested	700 3400	single	1700 -	nested	900 4500		
DSi	nested	1100 3200	single	1800 -	single	? -		
SO <sub>4</sub> <sup>2-</sup>	nested	2600 ?	single	1700 -	nested	1100 5900		
Cl <sup>-</sup>	nested	500 3600	single	1500 -	nested	1700 4600		
NO <sub>3</sub> <sup>-</sup>	single	3600 -	-	- -	nested	1100 ?		
PO <sub>4</sub> <sup>3-</sup>	nested	1200 ?	-	- -	single	2100 -		
DOC	single	3200 -	single	1500 -	nested	800 5200		
DIC	nested	1100 ?	single	1400 -	-	- -		
ANC	nested	1300 ?	single	1900 -	nested	500 2600		
SC	nested	1200 3200	single	1600 -	nested	1800 5300		

The dash symbol (-) indicates semivariograms (1) for which the type or range could not be determined due to low chemical concentrations or (2) that are not applicable for the given type. An unknown range is indicated with a question mark (?) for solutes with semivariograms that appear to be nested beyond the maximum separation distance used for the analysis or for ranges that cannot easily be determined visually.









## Supplemental Methods

### *Basin-wide survey*

The study area is located largely within the Hubbard Brook Experimental Forest (HBEF) where biogeochemistry and ecosystem processes have been investigated by the HBES for almost five decades (1). The watershed is vegetated with hardwood and mixed hardwood–conifer forest interspersed with conifer patches. Elevations in the watershed range from 200 m at the outlet to over 1000 m in the headwaters. Detailed information on the ecological, hydrological, climatological, and geological setting is summarized by Likens and Buso (2), Likens (1) and the HBES ([www.hubbardbrook.org](http://www.hubbardbrook.org)). Water samples for this study were collected along the main stem of Hubbard Brook at locations directly upstream of tributary junctions (17 sites along the main stem), whereas samples in the tributaries were collected at 100-m intervals throughout 32 tributaries across the entire fifth-order stream network (total length surveyed = 75 km) (see Likens and Buso [2006] for details on field and analytical methods). Although the density of samples was much higher in the tributaries than in the main stem, longitudinal patterns in the main stem revealed relatively homogeneous solute concentrations and justified a coarser sampling density.

### *Analysis of spatial structure with empirical semivariograms*

Matrices of distances between pairs of points used in the calculation of semivariograms were calculated in a GIS based on Euclidean distance and on stream network distance with software specifically designed for analyzing stream networks (3). The GIS software for stream network analysis created a matrix of downstream-only distances that was manipulated to produce matrices of stream network distances based on flow-connected and flow-unconnected relationships (4). Semivariograms were calculated with customized functions in the S-PLUS statistical package (5, 6).

The classical estimator of the semivariogram is sensitive to outliers and non-normal distributions inherent in ecological data. Therefore, we used the robust estimator of semivariance recommended by Cressie (7). Broad- and fine-scale spatial trends are typically removed from the data by detrending before semivariograms are calculated (8). This approach is particularly important when the semivariograms are used for prediction at unsampled locations or when broad-scale trends are known and, thus, not the focus of analysis (9) (e.g., the effects spatial streamflow accumulation). We investigated potential trends in streamwater chemistry with respect to catchment area as a surrogate for streamflow accumulation and downstream distance (cf. 10) and found only weak relationships with these variables ( $r < |0.13|$  and only 6 out of 16 variables had  $p < 0.05$ ). Moreover, removing these trends had little or no effect on the shape or characteristics of the empirical semivariograms. Therefore, we used the untransformed data in our analyses.

The number of pairs of points for a given distance class in the semivariogram varied as a function of distance and among the various spatial relationships, but was consistent among streamwater chemistry variables. Because low numbers of pairs for a given distance class can complicate the interpretation of the semivariogram, we verified that the number of pairs for each semivariance calculation exceeded the Rossi et al. (11) recommendation of 50 pairs per distance class; the numbers of pairs for flow-connected, flow-unconnected, and Euclidean spatial relationships were 78-679, 62-3433, and 569-3527, respectively. Semivariance was calculated at

100-m intervals with a maximum separation distance between any two points in the stream network of 6950 m. At the maximum separation distance, at least 100 distance pairs were included for all relationships (106, 2396, and 642 for flow-connected, flow-unconnected, and Euclidean relationships, respectively).

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## Legends for Supplemental Figures

Figure S1 (Supplement). Spatial patterns of (a) hydrogen ion (eq/L), (b) acid-neutralizing capacity (ANC;  $\mu\text{eq/L}$ ), (c) calcium ( $\text{Ca}^{2+}$ ; mg/L), (d) magnesium ( $\text{Mg}^{2+}$ ; mg/L), (e) potassium ( $\text{K}^+$ ; mg/L), (f) sulfate ( $\text{SO}_4^{2-}$ ; mg/L), (g) ammonium ( $\text{NH}_4^+$ ; mg/L), (h) nitrate ( $\text{NO}_3^-$ ; mg/L), (i) ortho-phosphate ( $\text{PO}_4^{3-}$ ; mg/L), (j) chloride ( $\text{Cl}^-$ ; mg/L), (k) total monomeric aluminum ( $\text{Al}_m$ ; mg/L), and (l) dissolved inorganic carbon (DIC;  $\mu\text{mol/L}$ ).

Figure S2 (Supplement). Empirical semivariograms for (a) hydrogen ion (eq/L), (b) calcium ( $\text{Ca}^{2+}$ ; mg/L), (c) magnesium ( $\text{Mg}^{2+}$ ; mg/L), (d) potassium ( $\text{K}^+$ ; mg/L), (e) ammonium ( $\text{NH}_4^+$ ; mg/L), (f) total monomeric aluminum ( $\text{Al}_m$ ; mg/L), (g) sulfate ( $\text{SO}_4^{2-}$ ; mg/L), (h) chloride ( $\text{Cl}^-$ ; mg/L), (i) nitrate ( $\text{NO}_3^-$ ; mg/L), (j) ortho-phosphate ( $\text{PO}_4^{3-}$ ; mg/L), (k) dissolved inorganic carbon (DIC;  $\mu\text{mol/L}$ ), and (l) acid-neutralizing capacity (ANC;  $\mu\text{eq/L}$ ) based on Euclidian, flow-connected, and flow-unconnected spatial relationships (*d*) in the Hubbard Brook Valley. Symbols with lighter color shades indicate semivariance estimates based on < 100 pairs of points.

