Network analysis reveals multiscale controls on streamwater chemistry

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

biogeochemistry | hydrologic connectivity | watershed | autocorrelation | heterogeneity

Spatial heterogeneity of ecosystems has been a focus of landscape ecology for more than 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 by 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-scale 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., refs. 11 and 12). However, our understanding of biogeochemical processes in stream networks is still limited to small-scale experiments (e.g., ref. 13), often with limited spatial extent or replication, and large-scale correlative models (14). Fine-grained observations at intermediate scales (e.g., 1–10 km^2) 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

Significance

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

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

We apply geostatistical techniques to an unusually high-resolution synoptic dataset of streamwater chemistry collected throughout the Hubbard Brook Valley in New Hampshire to explore the spatial structure of biogeochemical patterns at multiple scales (18). The dataset consisted of 664 water samples collected over a 3-mo period every 100 m throughout all 32 tributaries of the 3,600-ha, fifth-order stream network of the Hubbard Brook Valley. We show previously undescribed patterns of spatial dependence based on three spatial relationships, revealing biogeochemical determinants occurring across scales, both within the stream network and surrounding catchment. Stream network patterns were defined by two spatial relationships: flow connected and flow unconnected (in the sense of refs. 20 and 21). The straight-line distance between two points defines Euclidean relationships. Flow-connected and unconnected network relationships describe distances along the stream network and were considered "connected" if water flows from one site to another. Thus, all points downstream of other points on the stream network were considered connected, but points upstream of tributary junctions that do not share flow were considered "unconnected."

Empirical semivariograms based on these three spatial relationships suggest the importance of different drivers of spatial variability in streamwater chemistry at multiple scales, e.g., fine (<1,500 m) and broad scales (>3,000 m) (Fig. 1). For example, semivariograms of flow-connected relationships indicate whether downstream flow and longitudinal transport exert a dominant control on streamwater chemistry by showing the level of autocorrelation between flow-connected samples. Likewise, semivariograms of flow-unconnected relationships provide information about the similarity/dissimilarity of tributary branches due to influences of landscape properties (e.g., soils or geology). Semivariograms of streamwater chemistry using Euclidean relationships reveal interactions or lateral connectivity between the stream network and the landscape. Therefore, both Euclidean and flow-unconnected network relationships provide information on how the landscape influences patterns of streamwater chemistry within a single catchment/network, whereas a flow-connected relationship largely describes the effect of hydrologic transport and upstream spatial dependence.

Extensive work in the Hubbard Brook Ecosystem Study (HBES) over the last five decades provides the temporal context for understanding biogeochemical processes and landscape change through ecosystem change revealed by long-term research (27, 28). The current study aims to provide a spatial context (29) for interpreting how biogeochemical patterns observed from sparse fixed sites (e.g., outlets of experimental watersheds) fit within the larger stream network. We expect spatial dependence of streamwater chemistry to be structured by flow directionality and network topology, especially for constituents that are not strongly biologically cycled in headwater streams (e.g., base cations, Cl^-, SO_4^{2-}). However, patchiness longitudinally in the stream network and across the landscape (i.e., by Euclidean distances) may arise because of the local influences of landscape features such as seeps and springs, and variation in vegetation, soil, and geologic materials. Our objectives were to (*i*) quantify spatial heterogeneity in streamwater chemistry at multiple scales within the stream network, (*ii*) compare patterns of streamwater chemistry by using different spatial relationships within the stream network and across the landscape (i.e., using network and Euclidean relationships), and (*iii*) evaluate this approach for linking biogeochemical patterns and processes by identifying potential drivers of spatial patterns in streamwater chemistry that bridge scales from tributaries, to the main stem, and throughout the entire Hubbard Brook Valley.

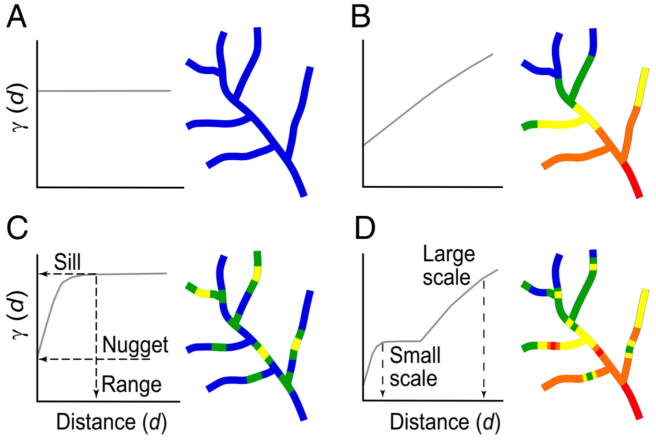

Fig. 1. Hypothetical semivariograms and associated maps depicting representative spatial patterns of water chemistry in a stream network. Nonstructured spatial pattern (i.e., uniform or random) (*A*) is indicated in the semivariogram by no change in semivariance (γ) (*y* axis) with increasing distance (*d*) between neighbors (*x* axis), as is graphically depicted by the uniform line color in the associated network map. In the example shown (*A*), $\gamma = 0$ for a uniform, nonstructured spatial pattern. Other potential semivariograms and associated network patterns include spatial dependence at a broad-scale with a gradient symbolized in the network map by changes in line color from the upper left (blue) to the lower right (red) of the stream network (*B*), fine-scale patchiness or spatial dependence indicated in the network map as "hotspots" (*C*), and nested heterogeneity reflecting a combination of fine-scale patchiness imbedded within a broad-scale gradient (*D*) (in the sense of ref. 26). Characteristics of the semivariogram (*C*) are the asymptote or "sill," which is roughly equivalent to the total population variance; the variance discontinuity at the *y* intercept or "nugget," which represents variance due to sampling error and/or spatial dependence at distance intervals not explicitly sampled; and the "range," which defines the distance or scale over which spatial dependence is expressed. Beyond this range, in a nonnested structure, points are spatially independent of one another or uncorrelated. Nested semivariograms are hierarchical structures, each characterized by its own range.

Results

Spatial Structuring in Streamwater Chemistry. Streamwater chemistry patterns throughout the Hubbard Brook Valley exhibited spatial patchiness and gradients at multiple scales (see Fig. S1 for a complete set of distribution maps for all chemical constituents). However, it is difficult to systematically compare these patterns visually because of the spatial complexity of the data. For example, patterns of dissolved organic carbon (DOC), sodium, dissolved silica, and specific conductance were visibly different (Fig. 2), but the extent and typology of these differences cannot be quantified based on visual inspection alone. In contrast, analysis with empirical semivariograms revealed a high degree of spatial structuring in streamwater chemistry, as indicated by the overall shape of the semivariograms (Fig. 3 and Fig. S2). Specifically, some of the semivariograms showed spatial structure at predominantly one scale of variation (<1,500 m) (compare Fig. 1*C* and flow-connected semivariograms in Fig. 3), whereas other semivariograms varied substantially among spatial relationships and exhibited spatial structure at multiple scales (compare Fig. 1*D* and Fig. 3). Semivariograms of the 16 chemical constituents exhibited several of the theoretical spatial structures described in Fig. 1 (Table 1, Fig. 3, and Fig. S2): (*i*) nonstructured, or poorly defined structure (NH_4^+, NO_3^-, PO_4^{3-}; compare to Fig. 1*A*); (*ii*) single-scale structure (many examples: compare to Fig. 1*C*); and (*iii*) nested structure (many examples: compare to Fig. 1*D*). Scales of variation in streamwater chemistry ranged from 500 to >6,000 m for the variables that showed spatial structure (Table 1). The finest and broadest scales of variation were associated with semivariograms of the nested type, for which Euclidean and flow-unconnected relationships had the finest scales of variation, and flow-unconnected relationships had the broadest scales of variation. Scales of variation for flow-connected network relationships were less variable compared with the other spatial relationships.

Effects of Network Connectivity on Patterns of Spatial Dependence. Patterns of spatial dependence in streamwater chemistry varied not only among chemical constituents but also depending on how connectivity, or relationships among sample points, was defined in space. For example, semivariograms of specific conductance differed in shape and overall variance (i.e., height of the curve with respect to the *y* axis) based on the way the spatial relationship was calculated between sample points (i.e., flow-connected, flow-unconnected, and Euclidean spatial relationships) (Fig. 3*D*). Specifically, the shape of the flow-connected semivariogram of specific conductance indicated the presence of spatial structure at one scale (Fig. 3*D*), whereas the semivariogram of flow-unconnected relationships exhibited pronounced patterns associated with nested spatial structure at two scales. The semivariogram based on the Euclidean spatial relationship also exhibited a nested pattern, but was not as clearly defined as the flow-unconnected semivariogram. Overall, variance was generally highest for the semivariogram based on Euclidean relationships and lowest for the flow-connected semivariograms.

The differences described above for semivariograms of specific conductance generally applied to the majority of chemical constituents that exhibited spatial structure [i.e., monomeric aluminum (Al_m), Cl^-, dissolved inorganic carbon (DIC), DOC, K^+, dissolved silica, and SO_4^{2-}) (Fig. S2), but there were some notable exceptions. For example, semivariograms of acid-neutralizing capacity (ANC), Ca^{2+}, and K^+ were also similar, but only for flow-connected and Euclidean spatial relationships with distances less than approximately 4,500 m (Fig. S2). Semivariograms of Mg^{2+} and Na^+ exhibited an analogous pattern but at shorter distances (~1,500 m). The nugget value (i.e., discontinuity at the origin) (e.g., defined in Fig. 1*C*) of semivariograms based on Euclidean and flow-connected relationships were close to zero for all chemical constituents except for DIC (Fig. 3 and Fig. S2), whereas nugget-variance for flow-unconnected semivariograms were substantially greater than zero for all chemical constituents except Al_m and K^+.

Discussion

Understanding controls on spatial patterns of streamwater chemistry and developing tools for predicting spatial variation of stream chemistry in headwaters is important for managing water quality in downstream systems. Headwater streams comprise the vast majority of stream length in watersheds (30) and perform critical functions for downstream ecosystems, but are still considered *aqua incognita* in hydrology and ecology (31, 32). We found complex variability in spatial patterns of streamwater chemistry (multiscale structure) across the Hubbard Brook Valley, suggesting that different

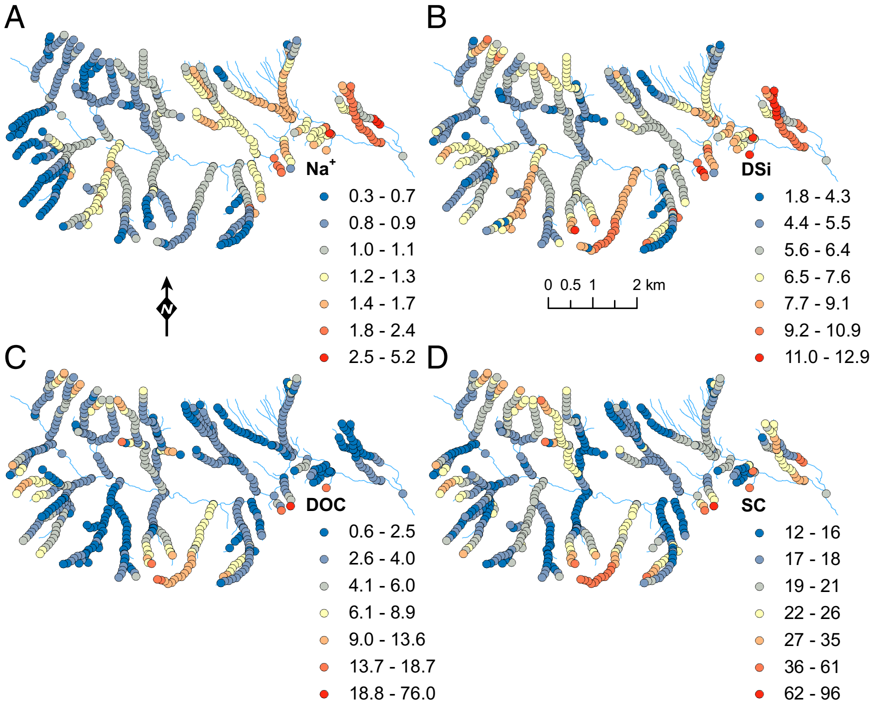

Fig. 2. Spatial patterns of sodium (Na^+; mg/L) (*A*), dissolved silica (DSi; reported as SiO_2 mg/L) (*B*), dissolved organic carbon (DOC; mg/L) (*C*), and specific conductance (SC; μS/cm) (*D*) derived from sampling streamwater chemistry at 664 locations throughout the Hubbard Brook Valley, NH, during October–December 2001.

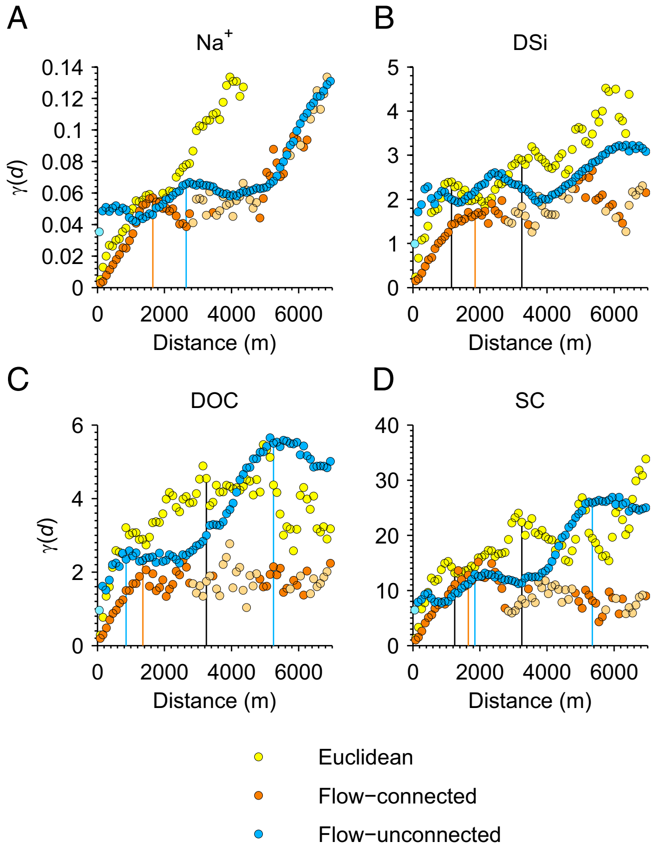

Fig. 3. Empirical semivariograms for sodium (Na$^+$; mg/L) (*A*), dissolved silica (DSi; reported as SiO$_2$ mg/L) (*B*), dissolved organic carbon (DOC; mg/L) (*C*), and specific conductance (SC; μS/cm) (*D*) based on Euclidian, flow-connected, and flow-unconnected spatial relationships (*d*) in the Hubbard Brook Valley. Visually estimated ranges (Table 1) for Euclidean (E) (yellow and black line), flow-connected (FC) (orange), and flow-unconnected (FU) (blue) relationships are indicated with vertical lines. Symbols with lighter color shades indicate semivariance estimates based on <100 pairs of points.

Table 1. Characteristics of empirical semivariograms for streamwater chemistry based on Euclidean, flow-connected, and flow-unconnected spatial relationships in the Hubbard Brook Valley

	Euclidean relationship			Flow-connected network relationship		Flow-unconnected network relationship		
Solute	Type	Scale, m		Type	Scale, m	Type	Scale, m	
H$^+$	Single	2,300	—	Single	1,500	Nested	900	4,500
Ca^{2+}	Nested	1,000	?	Single	1,800	Single	2,500	—
Mg^{2+}	Nested	1,100	3,700	Single	1,700	Nested	2,600	?
Na$^+$	Single	?	—	Nested	1,600	Nested	2,600	?
K$^+$	Nested	1,200	5,400	Single	1,700	Single	1,800	—
NH$_4^+$	—	—	—	—	—	—	—	—
Al$_m$	Nested	700	3,400	Single	1,700	Nested	900	4,500
DSi	Nested	1,100	3,200	Single	1,800	Single	?	—
SO$_4^{2-}$	Nested	2,600	?	Single	1,700	Nested	1,100	5,900
Cl$^-$	Nested	500	3,600	Single	1,500	Nested	1,700	4,600
NO$_3{}^-$	Single	3,600	—	—	—	Nested	1,100	?
PO$_4^{3-}$	Nested	1,200	?	—	—	Single	2,100	—
DOC	Single	3,200	—	Single	1,500	Nested	800	5,200
DIC	Nested	1,100	?	Single	1,400	—	—	—
ANC	Nested	1,300	?	Single	1,900	Nested	500	2,600
SC	Nested	1,200	3,200	Single	1,600	Nested	1,800	5,300

Semivariogram type and range for each spatial relationship indicate nested-scale (i.e., multiple-scale) versus single-scale spatial structure and the distances over which spatial dependence is expressed, respectively. The dash symbol (—) indicates semivariograms (*i*) for which the type or range could not be determined because of low chemical concentrations or (*ii*) 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.

processes are affecting streamwater chemistry at different scales and with different spatial relationships. Our results suggest that streamwater chemistry is more complex than the expected pattern of a single scale of spatial autocorrelation (Fig. 1*C*) or increasing homogeneity with downstream distance. There is both fine-scale patchiness and broad-scale trend operating within the stream network and across the landscape. These observations may provide clues about how streams function and ultimately lead to better models of aquatic and terrestrial ecosystem interactions in stream networks. Furthermore, the spatial structure of stream network chemistry that emerges from our analysis is similar to patterns that have been observed in landscape ecology, where both broad-scale gradients and fine-scale patchiness are influenced by environmental attributes (33).

Semivariograms of water chemistry in the stream network of the Hubbard Brook Valley revealed spatial structure at multiple scales previously described only in unbranched stream sections (11) or for a limited suite of chemical constituents examined at much coarser scales (34). Other pioneering studies of stream networks have examined spatial heterogeneity or developed predictive models in stream networks (16, 35), but these studies have been too coarse in grain (low resolution) to detect spatial structure at scales ranging from hundreds to thousands of meters. Our analysis of the shape and characteristics of semivariograms (Fig. 1) of water chemistry in a stream network provide empirical support for three models of spatial structure in stream networks (in the sense of ref. 26): (*i*) broad-scale heterogeneity with few patches (Fig. 1*B*; e.g., the Euclidean relationship of Na$^+$, dissolved silica, and DIC); (*ii*) fine-scale heterogeneity with many patches (Fig. 1*C*; e.g., flow-connected K$^+$, Cl$^-$, DOC); and (*iii*) nested heterogeneity that contains fine-scale patchiness and broad-scale heterogeneity (Fig. 1*D*; e.g., flow-unconnected H$^+$, Al$_m$, DOC).

The different spatial relationships permit the examination of heterogeneity dominated by landscape versus stream network processes. Euclidean and flow-unconnected network relationships were associated with the nested type of heterogeneity indicative of landscape influences occurring over multiple spatial scales, such as soil, geology, and vegetation controls on the chemistry of water sources. In contrast, flow-connected relationships were entirely (with the exception of Na$^+$) of the single-scale type, suggesting that similarity at large stream distances in the network was largely controlled by channel-mediated transport and groundwater flow accumulation, which seemed to stabilize the variance of all chemical constituents at approximately 2,000-m separation distance. This range among the semivariograms for flow-connected relationships provides an indication of where the hydrologic control on variability begins to overwhelm the patchiness at the fine scale (<2,000 m). As one would expect, hydrologic transport and longitudinal gains of groundwater were the main drivers of the spatial pattern among most of the solutes. At Hubbard Brook, solute chemistry is relatively constant temporally compared with discharge, which may suggest general persistence in these spatial relationships (17).

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

The difference between nugget values of mineral weathering-controlled chemistry (i.e., Ca^{2+}, dissolved silica, Mg^{2+}, ANC, and Na^{+}) for the two network relationships suggests differences in landscape character and their potential influence on spatial structure, but over shorter distances. A higher nugget value for the flow-unconnected metric highlights spatial variability over short distances at tributary junctions and chemical dissimilarities between tributaries. This pattern shows that sources contributing to streamflow that are not downstream from one another may be heterogeneous despite close proximity. This same pattern was noted by Likens and Buso (18) in streams strongly influenced by groundwater seeps and springs. Seeps have been noted throughout the valley and typically show distinct chemistry (e.g., ref. 17).

Streamwater chemistry that exhibited the weakest structure, including NH_4^{+}, NO_3^{-}, and PO_4^{3-}, may be explained in large part by their low concentrations (i.e., at or near analytical detection limits; ref. 30). However, there was some indication of spatial dependence over fine scales (<1,000 m) in $NO_3{}^{-}$ and PO_4^{3-} (i.e., linear increases in variation over short flow-connected distances), suggesting that in-stream uptake may be occurring over very short distances because of biological demand for these nutrients in the generally nutrient-poor environment (38). Uptake lengths for ammonium and phosphorus within the Hubbard Brook Valley were shown to vary between 5 and 277 m and between 2 and 54 m, respectively (39), suggesting strong in-stream processing influence on spatial variation over short flow-connected distances.

Both landscape and hydrologic drivers influence some chemical constituents. For example, DOC, H^{+}, and Al_m show autocorrelation at flow-connected relationships >1,500 m, indicating an influence of flow accumulation on spatial structure. However, these solutes also exhibited nested structure in flow-unconnected distance at fine (<750 m) and broad (>4,500 m) spatial scales. Thus, two scales of heterogeneity and three different spatial relationships appear to be important. One is fine scale, resulting in hotspots of DOC and H^{+} variation, which typically coincides with Al_m variation (40). At large distances that are not flow connected, such as headwater regions in different parts of the network, there is also a high degree of variation in H^{+}, DOC, and Al_m. This pattern may occur because headwater and valley bottom regions throughout the Hubbard Brook Valley contain patches of coniferous forest and distinct soils. Many of these areas (e.g., ridge tops, north-facing slopes, and along the stream) tend to have shallow, wet, acidic soils (41) with deep litter layers, and high DOC and Al soil-water concentrations that have been shown to affect spatial patterns of streamwater DOC and Al (17, 40). It is striking that our semivariogram analysis provides a quantitative characterization of this large-scale patchiness, which small-scale, descriptive studies cannot capture.

This study shows that network geostatistics combined with high-resolution water chemistry data can provide insight into dominant processes driving biogeochemical patterns in stream networks at local, longitudinal, and landscape scales. In the Hubbard Brook Valley, landscape processes were shown to occur over a range of spatial scales (500 to >6,000 m), with broad-scale trends and fine-scale patchiness likely driven by geologic, soil, and vegetation features across the valley. Hydrologic transport and flow accumulation in streams were also found to exert influence on streamwater chemistry at downstream distances of 1,400–2,200 m, where variation in chemistry tended to stabilize. By revealing the spatial structure of stream biogeochemistry and scales of underlying drivers, this spatially explicit, network-level analysis is crucial to refining long-held assumptions about stream structure and function (e.g., ref. 42).

Methods

Basin-Wide Survey. Streamwater chemistry was measured by Likens and Buso (18) throughout the 3,600-ha Hubbard Brook Valley in the White Mountains of central New Hampshire (US) (43°56′N, 71°45′W). Detailed information on the ecological, hydrological, climatological, and geological setting is summarized by Likens (43). The field survey of streamwater chemistry (Al_m, acid-neutralizing capacity, Ca^{2+}, Cl^{-}, DIC, DOC, K^{+}, Mg^{2+}, Na^{+}, NH_4^{+}, NO_3^{-}, pH, PO_4^{3-}, dissolved silica, SO_4^{2-}, and specific conductance) was conducted during October through December 2001 and is described in Likens and Buso (18). A subset of 664 from the total of 761 samples was selected for network analysis based on an assessment of hydrography and the ability to delineate catchment areas by using a geographical information system derived from 10-m digital elevation models. The sites left out were almost entirely small tributaries with only a few samples, and they were scattered systematically throughout the Valley, but primarily in headwater areas.

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

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

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