Network analysis reveals multiscale controls on streamwater chemistry

Kevin J. McGuireb,1, Christian E. Torgersenb, Gene E. Likensc,d,1, Donald C. Buso*, Winsor H. Lowef, and Scott W. Baileyg

*Virginia Water Resources Research Center and Department of Forest Resources and Environmental Conservation, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061; bUS Geological Survey, Forest and Rangeland Ecosystem Science Center, Cascadia Field Station, and School of Environmental and Forest Sciences, University of Washington, Seattle, WA 98195; cCary Institute of Ecosystem Studies, Millbrook, NY 12545; dDepartment of Ecology and Evolutionary Biology, University of Connecticut, Storrs, CT 06269; eCary Institute of Ecosystem Studies, Hubbard Brook Forest Station, North Woodstock, NH 03262; fDivision of Biological Sciences, University of Montana, Missoula, MT 59812; and gUS Forest Service, Northern Research Station, Hubbard Brook Experimental Forest, North Woodstock, NH 03262

Contributed by Gene E. Likens, March 18, 2014 (sent for review September 13, 2012)

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.

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.


Conflict of interest statement: The authors declare no conflict of interest.

To whom correspondence may be addressed. E-mail: kevin.mcguire@vt.edu or likensg@ecostudies.org.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1404820111/-/DCSupplemental.
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\(_2\)-). 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.

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

![Fig. 1. Hypothetical semivariograms and associated maps depicting representative spatial patterns of water chemistry in a stream network. Non-structured spatial pattern (i.e., uniform or random) (A) is indicated in the semivariogram by no change in semivariance ($\gamma$) (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.](https://www.pnas.org/content/early/2014/01/02/1322989111.full.pdf)
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. 1C and flow-connected semivariograms in Fig. 3), whereas other semivariograms varied substantially among spatial relationships and exhibited spatial structure at multiple scales (compare Fig. 1D 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\textsubscript{3}, NO\textsubscript{2}, PO\textsubscript{4}\textsuperscript{3-}; compare to Fig. 1A); (ii) single-scale structure (many examples: compare to Fig. 1C); and (iii) nested structure (many examples: compare to Fig. 1D). 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 generally applied to the majority of chemical constituents except Al\textsubscript{m} and K\textsuperscript{+}. The differences described above for semivariograms of specific conductance can 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. 1C and flow-connected semivariograms in Fig. 3), whereas other semivariograms varied substantially among spatial relationships and exhibited spatial structure at multiple scales (compare Fig. 1D 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\textsubscript{3}, NO\textsubscript{2}, PO\textsubscript{4}\textsuperscript{3-}; compare to Fig. 1A); (ii) single-scale structure (many examples: compare to Fig. 1C); and (iii) nested structure (many examples: compare to Fig. 1D). 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.

The differences described above for semivariograms of specific conductance generally applied to the majority of chemical constituents except Al\textsubscript{m} and K\textsuperscript{+}. The differences described above for semivariograms of specific conductance can 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. 1C and flow-connected semivariograms in Fig. 3), whereas other semivariograms varied substantially among spatial relationships and exhibited spatial structure at multiple scales (compare Fig. 1D 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\textsubscript{3}, NO\textsubscript{2}, PO\textsubscript{4}\textsuperscript{3-}; compare to Fig. 1A); (ii) single-scale structure (many examples: compare to Fig. 1C); and (iii) nested structure (many examples: compare to Fig. 1D). 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.

**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...
(blue) relationships are indicated with vertical lines. Symbols with lighter 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.

Fig. 3. Empirical semivariograms for sodium (Na⁺; mg/L) (A), dissolved silica (DSi; reported as SiO₂, 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.

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. 1C) 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. 1B; e.g., the Euclidean relationship of Na⁺, dissolved silica, and DIC); (ii) fine-scale heterogeneity with many patches (Fig. 1C; e.g., flow-connected K⁺, Cl⁻, DOC); and (iii) nested heterogeneity that contains fine-scale patchiness and broad-scale heterogeneity (Fig. 1D; e.g., flow-unconnected H⁺, Al₃⁺, 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).

Unconnected and flow-unconnected semivariograms exhibit higher variance, spatial dependence at broader scales, and multiple structures (single and nested) compared with flow-connected

| Table 1. Characteristics of empirical semivariograms for streamwater chemistry based on Euclidean, flow-connected, and flow-unconnected spatial relationships in the Hubbard Brook Valley |
|------------------|------------------|------------------|------------------|
| Solute           | Euclidean        | Flow-connected   | Flow-unconnected |
|                  | Type             | Scale, m         | Type             | Scale, m         | Type             | Scale, m         |
| H⁺               | Single           | 2,300            | Single           | 1,500            | Nested           | 900              |
| Ca²⁺             | Nested           | 1,000            |                |                 |                 |                  |
| Mg²⁺             | Nested           | 1,100            | Single           | 1,700            | Nested           | 2,600            |
| Na⁺              | Single           |                | Nested           | 1,600            | Nested           | 2,600            |
| K⁺               | Nested           | 1,200            | Single           | 1,700            |                | 1,800            |
| NH₄⁺             | Nested           | 700              | Single           | 1,700            | Nested           | 900              |
| Al₃⁺             | Nested           | 1,100            | Single           | 1,800            |                |                  |
| SO₄²⁻            | Nested           | 2,600            |                |                 | Nested           | 1,100            |
| Cl⁻              | Nested           | 500              | Single           | 1,500            | Nested           | 1,700            |
| NO₃⁻             | Single           | 3,600            |                |                 | Nested           | 1,100            |
| PO₄³⁻             | Nested           | 1,200            |                |                 | Single           | 2,100            |
| DOC              | Single           | 3,200            | Single           | 1,500            | Nested           | 800              |
| DIC              | Nested           | 1,100            | Single           | 1,400            |                |                  |
| ANC              | Nested           | 1,300            |                | 1,900            | Nested           | 500              |
| SC               | Nested           | 1,200            | Single           | 1,600            | Nested           | 1,800            |

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.

McGuire et al. | PNAS | May 13, 2014 | vol. 111 | no. 19 | 7033
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 portion (36) with an overlying soil parent material composition.

Gross changes in bedrock type or glacial till composition/thickness variation in the Euclidean relationships may be explained by either distance at fine (750 m) and broad (4,500 m) spatial 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 reviewing the spatial structure of stream geochemistry 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\(_{\text{soil}}\), acid-neutralizing capacity, Ca\(^{2+}\), Cl\(^{−}\), DIC, DOC, K\(^{+}\), Mg\(^{2+}\), Na\(^{+}\), NH\(_{4}\), NO\(_{3}^{−}\), pH, PO\(_{4}^{3−}\), dissolved silica, SO\(_{2}^{−}\), 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, and semivariograms can be estimated empirically and theoretically. The 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).

ACKNOWLEDGMENTS. P. Likens is thanked for help with submission of the manuscript. Financial support for data collection was provided by the National Science Foundation (NSF), including the Long Term Research in Environmental Biology and Long Term Ecological Research programs, and The A.W. Mellon Foundation. Support for K.J.M. and S.W.B. was provided by NSF Grant EAR 1014507. Support for W.H.L. was provided by NSF Grant DEB 1050459. The US Forest Service (Northern Research Station, Newtown Square, PA) operates and maintains the Hubbard Brook Experimental Forest. This manuscript benefited greatly from discussions with the Spatial Statistics for Streams Working Group supported by NCEAS (NSF Grant EF 0553768), University of California Santa Barbara, and the State of California. Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the US Government.

Supporting Information

McGuire et al. 10.1073/pnas.1404820111

SI 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 Hubbard Brook Ecosystem Study (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 more than 1,000 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). 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 (2) 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 geographical information system (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 nonnormal distributions inherent in ecological data. Therefore, we used the robust estimator of semivariance recommended by Cressie (7). Broad-scale 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 (compare ref. 10) and found only weak relationships with these variables ($r < 0.13$), and only 6 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, 62–3,433, and 569–3,527, respectively. Semivariance was calculated at 100-m intervals with a maximum separation distance between any two points in the stream network of 6,950 m. At the maximum separation distance, at least 100 distance pairs were included for all relationships (106, 2,396, and 642 for flow-connected, flow-unconnected, and Euclidean relationships, respectively).

Fig. 51. Spatial patterns of hydrogen ion (eq/L) (A), acid-neutralizing capacity (ANC; μeq/L) (B), calcium (Ca$^{2+}$; mg/L) (C), magnesium (Mg$^{2+}$; mg/L) (D), potassium (K$^+$; mg/L) (E), sulfate (SO$_4^{2-}$/CO$_3^{3-}$; mg/L) (F), ammonium (NH$_4^+$; mg/L) (G), nitrate (NO$_3^-$; mg/L) (H), ortho-phosphate (PO$_4^{3-}$/CO$_3^{3-}$; mg/L) (I), chloride (Cl$^-$; mg/L) (J), total monomeric aluminum (Al$_{m}$; mg/L) (K), and dissolved inorganic carbon (DIC; μmol/L) (L).
Fig. S2. Empirical semivariograms for hydrogen ion (eq/L) (A), calcium (Ca$^{2+}$; mg/L) (B), magnesium (Mg$^{2+}$; mg/L) (C), potassium (K$^+$; mg/L) (D), ammonium (NH$_4^+$; mg/L) (E), total monomeric aluminum (Al$_{m}$; mg/L) (F), sulfate (SO$_4^{2-}$; mg/L) (G), chloride (Cl$^-$; mg/L) (H), nitrate (NO$_3^-$; mg/L) (I), ortho-phosphate (PO$_4^{3-}$; mg/L) (J), dissolved inorganic carbon (DIC; μmol/L) (K), and acid-neutralizing capacity (ANC; μeq/L) (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.