Geologic Analyses for Evaluating Watershed Heterogeneity: Implications for Otolith Chemistry Studies

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Abstract: Studies using otolith chemistry to distinguish fish stocks in fresh waters have suggested that spatial heterogeneity in basin geology determines the scale of stock discrimination possible with this approach. However, no studies have illustrated an association between spatial variation in fish otolith chemistry and watershed geology. We consider this relationship in the context of a recent study describing within- and between-river variation in trace element chemistry of otoliths from YOY smallmouth bass (*Micropterus dolomieu*) from the Maury and James rivers (Virginia). Cluster analysis of multivariate geologic data for discrete river segment basins illustrates a phenomenological association between geologic heterogeneity and our ability to discriminate spatial groupings of fish from their otolith chemistry. This analysis provides two significant results: 1) a starting point for considering the mechanistic relationship between watershed geology and fish otolith chemistry; and, 2) a framework for assessing basin heterogeneity prior to designing studies that use otolith chemistry to distinguish fish stocks in river-tributary networks. The latter can be used *a priori* to determine the efficacy of otolith chemistry comparisons and to guide sample collection over large spatial areas.

Key words: Otolith, geology, land use, water chemistry, GIS

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In approximately the last decade, significant advances were made in analysis of fish "hard parts" (e.g., bones, scales, and spines) as records of water chemistry in areas inhabited by fish during their lifetimes (Campana 1999, Kennedy 2000, Campana and Thorrold 2001). This method has demonstrated potential for stock identification (Campana et al. 1999), reconstructing migration history (Secor et al. 1995, Kennedy et al. 2002), and identifying natal origins of fishes (Thorrold et al. 2001, Wells et al. 2003) among other spatial aspects of fish population ecology. Application of otolith chemistry to the study of exclusively inland species is growing, and recent investigations in lotic fisheries have successfully discriminated fish origins across a variety of spatial scales using trace element chemistry of otoliths (Wells et al. 2003, Bickford and Hannigan 2005, Muhlfeld et al. 2005). These researchers suggested that the spatial scale of variation in water chemistry—and in turn the statistically separable "signature" chemistry in otoliths—was ultimately determined by heterogeneity in bedrock geology across the basin of interest. This is an intuitive conclusion since the trace elements analyzed in these studies are presumed to be lithologic in origin (Wells et al. 2003); however, it has yet to be supported by analyses of geologic data.

Our objective in this paper is to determine if differences in basin geology correspond with successful discrimination of fish origins in a recent study of otolith chemistry in riverine smallmouth bass (*Micropterus dolomieu*) populations. Trace element concentrations were used to successfully discriminate natal origins of age-0 smallmouth bass spawned in the James River or its tributary Maury River. The analysis was further able to differentiate among fish collected from different segments of the Maury River based on otolith chemistry. Here we compare the spatial resolution of fish origin discrimination in this previous study (summarized below for context) with patterns of land attribute variation across the study area as a first-order attempt to illustrate an association between otolith chemistry and basin geology. Using readily available spatial data analyzed in a GIS, we present a framework for characterizing geology of river segment basins and for quantifying dissimilarity among basins in the study area. We then use cluster analysis to group segment basins with similar geologic compositions, and compare results of clustering with our ability to distinguish fish origins among basins by otolith chemistry. We discuss our results in the context of applying these methods to guide experimental design and collection effort in future studies of otolith chemistry in river systems.

Study Area and Otolith Chemistry Study

The James River is a large (fifth order) river that runs from the Ridge and Valley physiographic province through the Coastal Plain. The Maury River is a smaller (fourth order) river that originates in the Ridge and Valley and terminates in the James River at the edge of the Blue Ridge province. The James River and its tributary Maury River converge in west-central Virginia near the western edge of the Blue Ridge Mountains (Fig. 1). The original study sought to distinguish between fish spawned in either river based on trace element concentrations of otoliths.

For otolith chemistry analyses, 135 smallmouth bass fry (15 per reach) 2–5 weeks old were collected from five experimental reaches of roughly equal length along approximately 60 river kilometers (rkm) of the Maury below its high-gradient headwaters (reaches MR1–MR5, numbered sequentially downstream) and from four reaches along the James River covering roughly 20 rkm upstream and 10 rkm downstream of the Maury River confluence (reaches JR1–JR3 and Confluence). Whole saggitae were cleaned in a class-100 clean room prior to dissolution in ultrapure nitric acid for solution-based analysis by inductively coupled plasma-mass spectrometry (e.g., Dorval et al. 2005); 128 otoliths produced viable data. Molar concentrations of Ba, Sr, Mg, Mn, Rb, Y, and P were standardized to Ca concentration as element-to-calcium ratios and transformed to univariate normality using Box-Cox methods prior to statistical analysis. Linear discriminant function analysis (LDFA) was used to assess discrimination between rivers and among reaches based on transformed chemistry data.

Discriminant analysis was able to distinguish natal reach of individuals with 60% accuracy in jackknife cross-validation. Overall, 90% of all fish were classified to either their correct natal reach or a reach within the same river (i.e., 90% between-river discrimination accuracy). Patterns in classification suggested that there were

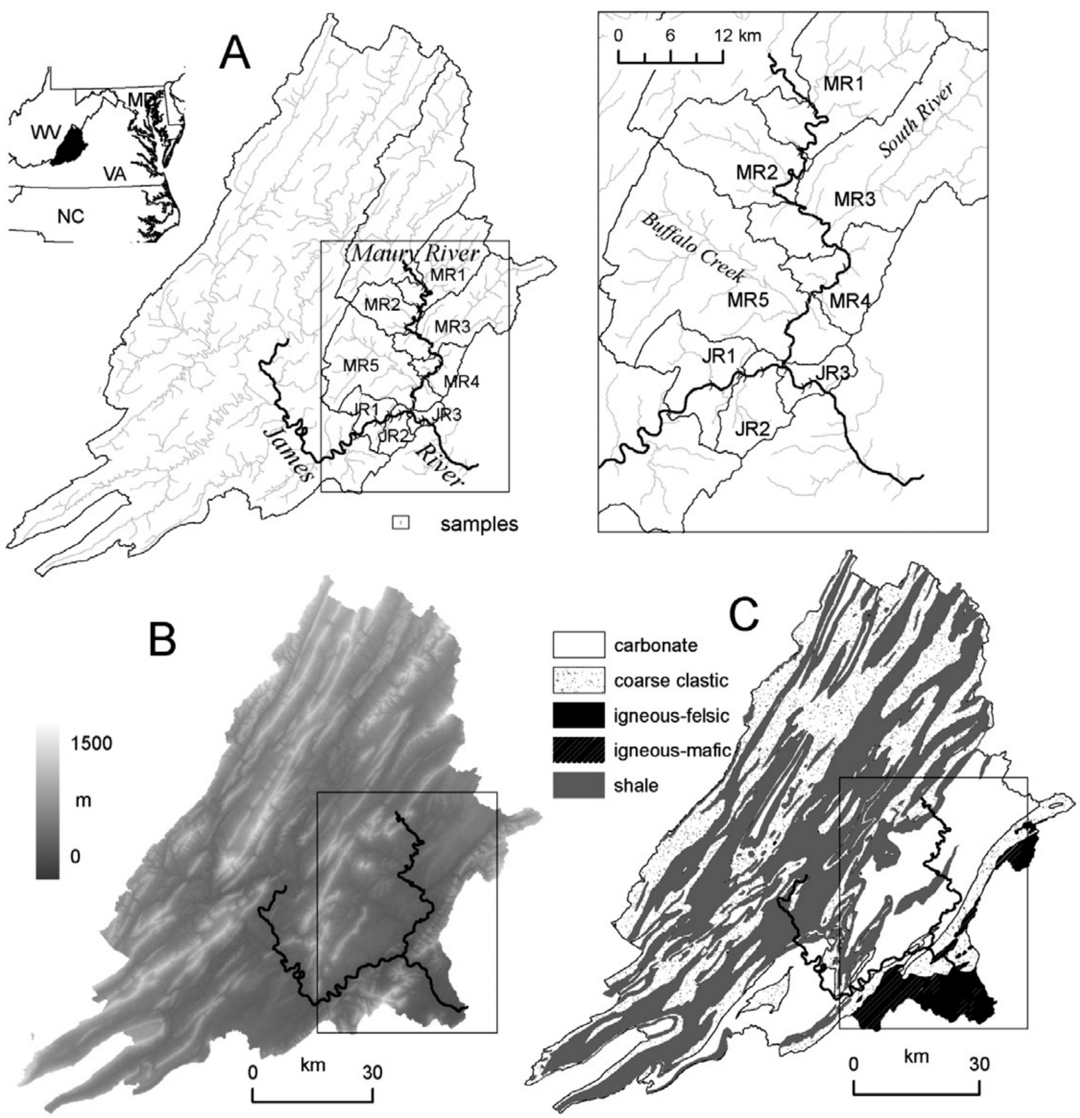

Figure 1. Location of the study rivers and fish sampling locations within the upper James River basin (A) with topography (B) and bedrock geology (C).

four distinct 'regions' in these two rivers from which fish origins could be accurately identified (Table 1): a) the upstream reaches of the Maury River, MR1–MR2; b) the middle reaches of the Maury River, MR3–MR4; c) the downstream reach of the Maury River, MR5; and, d) the James River, JR1–JR3, including the section at the confluence. Aggregate classification accuracy within each of these distinct regions equals or exceeds 80%. We designed the following basin-attribute analysis to determine if underlying heterogeneity in basin geology reflects the spatial pattern of discrimination accuracy among river reaches based on otolith chemistry.

Methods

Geologic Analysis and Data Synthesis

We derived the two types of digital data from sources and at a scale that should be available for most watersheds in the nation with the intent that the method could be directly transferable.

DEM, Watersheds, and Streams.—The watershed boundaries, sub-basins, and river network for the Maury and James Rivers were interpreted from a DEM (digital elevation model). We downloaded these data from the U. S. Geological Survey (1999) at a resolution of ⅓ arc second. We then projected into metric spatial coordinates (UTM) using bilinear resampling, which resulted in a spatial resolution of approximately 27.3 m. We interpreted these data into watersheds using ESRI ArcGIS9.1 hydrology tools that remove "pits" and locate channels when drainage area exceeded 5 km^2. We digitized fish sampling reach endpoints and snapped them to the rasterized channel location, then calculated watershed boundaries for areas upstream from these locations. The "Confluence" fish sampling location was absorbed as the downstream endpoint of reach JR2. The sampling point on the south bank of the James River where the Maury River enters on the left bank was configured to exclude cells in the Maury basin. For analysis of the land attribute changes along each river, we expanded the study area to consider the length of each river from their respective headwaters to a point 24 rkm below their confluence. We converted the raster stream network to a vector and separated the longest channel into 2 rkm segments. We derived the drainage basin for each incremental channel length from the rasterized endpoints of each channel segment.

Geology.—We summarized the dominant lithology from the Virginia State Geologic Map (Virginia Division of Mineral Resources, 2003), which is sufficient in detail for a synoptic analysis (Fig. 1). We rasterized the data to a 90-m resolution, clipped the data to each of the basins derived from the DEM, and tallied the areal percentage as carbonate, coarse clastic, igneous mafic, igneous felsic, or shale. These tallies were made in downstream order for both the sample site basins and the 2-km incremental basins.

Table 1. Results of linear discriminant function analysis classifying fish to their natal reach based on trace element chemistry in otoliths. Entries indicate the percentage of individuals classified to each reach in cross-validation. Cells sharing superscripts indicate general 'regions' of similar otolith chemistry suggested by patterns of misclassifications between adjacent reaches.

	Cross-validation accuracy (%)								
Reach of origin	**MR-1**	**MR-2**	**MR-3**	**MR-4**	**MR-5**	**Confluence**	**JR-3**	**JR-2**	**JR-1**
MR-1 ($N = 12$)	50.0[a]	33.3[a]	0.0	16.7	0.0	0.0	0.0	0.0	0.0
MR-2 ($N = 14$)	35.7[a]	57.2[a]	0.0	0.0	0.0	0.0	0.0	0.0	7.1
MR-3 ($N = 13$)	0.0	0.0	92.3[b]	7.7[b]	0.0	0.0	0.0	0.0	0.0
MR-4 ($N = 14$)	7.1	0.0	7.1[b]	78.7[b]	0.0	0.0	0.0	0.0	7.1
MR-5 ($N = 15$)	6.7	0.0	0.0	0.0	80.0[c]	0.0	0.0	13.3	0.0
Confluence ($N = 14$)	0.0	0.0	0.0	7.1	0.0	35.8[d]	7.1[d]	28.6[d]	21.4[d]
JR-3 ($N = 15$)	0.0	6.7	0.0	0.0	0.0	13.3[d]	66.7[d]	0.0[d]	13.3[d]
JR-2 ($N = 15$)	6.7	0.0	0.0	0.0	13.3	20.0[d]	26.7[d]	33.3[d]	0.0[d]
JR-1 ($N = 15$)	0.0	0.0	6.7	0.0	6.7	6.7[d]	20.0[d]	6.7[d]	53.2[d]

Both igneous categories contain a significant percentage of metamorphic rocks of similar composition.

Statistical Analyses of Basin Data

We analyzed similarity in basin geology using hierarchical agglomerative cluster analyses (SPSS v14.0 software) to identify basins with similar geologic composition. Cluster analyses proceeded in two phases, distinguished by their respective delineation of basins and watershed boundaries. In Phase 1 analyses, basins correspond only to sampling reaches of the otolith chemistry study; subsequently, Phase 2 clustered basins of each 2-rkm increment over the expanded study area (see above). This allowed us to compare clustering at different spatial resolutions and evaluate the validity of experimental reach delineations. Total area of land attribute categories are analogous to count (i.e., species abundance) data; statistical distance between multivariate observations is therefore best characterized using chi-square or similar distance (dissimilarity) measures (Legendre and Legendre 1998). We used the phi-square (ϕ^2) measure of distance, which normalizes the chi-square distance by the square root of the combined frequency, resulting in values ranging from 0.0 (identical) to 1.0 (completely dissimilar; e.g., Norton and Hannon 1997). We used the unweighted pair groups method using averages (UPGMA, or between-groups linkage method) to determine distance between clusters.

Phase I Cluster Analysis.—Following Wells et al. (2003) we compared the clustering of sampling reach basins (based on geologic composition) with the spatial pattern suggested in fish otolith LDFA classification (Table 1). We used the four-region distinction in otolith chemistry described earlier (MR1–2, MR3–4, MR5, and JR1–3) as a benchmark for evaluating basin groupings in the cluster analysis. At the point in hierarchical agglomeration where clustering of basins most closely matched reach grouping in fish origin discrimination, distance between the two nearest clusters determined the "minimum ϕ^2 distance" required between basins for discrimination in fish otolith chemistry.

Phase II Cluster Analysis.—Next we analyzed basins of each 2-rkm section of these rivers using the same clustering method as above on geologic data. Using the agglomeration schedule we determined the step at which the nearest clusters were separated by the minimum distance for discrimination defined in Phase I analysis. All clusters separated by this nominal distance were identified and assumed to contain river segments with potentially distinct otolith chemistry. Concentrations of trace elements in otoliths from river sections in a single cluster would be similar, yet they would be distinct from otoliths in river segments from other clusters. We first applied this approach to Maury River data, testing the prediction that clustering of 2-rkm segments would reflect grouping of reaches in Phase I analysis. If this prediction is supported, an identical analysis of the expanded James River (2-rkm) data could identify sections of the James with distinguishable otolith chemistry.

Table 2. Generalized geologic composition of reach basins and clustering of basins (three- and four-cluster solutions) in Phase I analysis.

Reach	Basin area (km^2)	Carbonates	Coarse clastic	Igneous-felsic	Igneous-mafic	Shale	Four-cluster membership	Three-cluster membership
MR1	287.1	87.1%	0.9%	0.0%	0.0%	12.0%	1	1
MR2	139.1	62.2%	4.1%	0.0%	0.0%	33.7%	1	1
MR3	397.0	58.2%	25.1%	7.9%	5.1%	3.7%	2	2
MR4	88.9	51.6%	36.5%	1.5%	10.4%	0.0%	2	2
MR5	397.0	62.9%	12.2%	0.0%	0.3%	24.6%	1	1
JR3	36.1	0.9%	75.1%	0.0%	24.0%	0.0%	3	3
JR2	64.1	21.2%	47.5%	0.1%	31.2%	0.0%	3	3
JR1	101.2	58.3%	13.8%	0.0%	11.6%	16.3%	4	2

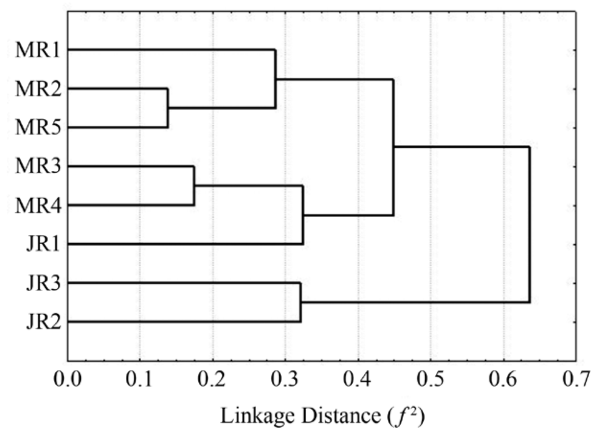

Figure 2. Dendrogram illustrating results from hierarchical cluster analysis of reach basins based on geologic composition.

Results

Geology

Geology varies greatly in the James and Maury River watersheds, which include portions of three physiographic provinces. Relief is highest at the margins of the Blue Ridge igneous region, and along the sandstone ridges of the western headwaters (Fig. 1). Three separate sections of both river basins are quite evident; headwater reaches have shale valley floors with very little carbonate bedrock or agriculture, the Great Valley section is dominated by carbonate with carbonaceous shale under significant agricultural use, and the terminal reach is a complex mix of igneous and sedimentary tributary basins. Water originating in the high-relief western ridges and in the Blue Ridge is developed under mixed deciduous and coniferous forest. For the Maury River below the headwater-valley transition (at MR1), significant additions of new water types come from South River (~42 rkm), which includes igneous terrain, and from Buffalo Creek (~62 rkm), which reinserts a shale influence.

Cluster Analysis

Phase I Results.—The four-group clustering solution for reach basins based on geology (Table 2, Fig. 2) was fairly similar to the four-region grouping in natal reach discrimination (Table 1), with two exceptions: a) reach MR5, which clustered closely with MR1 and MR2 geology but was relatively distinct in LDFA analysis of otolith chemistry; and, b) reach JR1, which was separated from the cluster of James River reaches JR2 and JR3. Given that no single James River reach was distinguishable in otolith chemistry discrimination analyses, we conservatively focused on the three-cluster arrangement in the subsequent agglomeration. The ϕ^2 distance between the two closest clusters (i.e. Cluster 2 and Cluster 3) in this analysis was 0.45 (Fig. 2).

Geologic features contributing to reach clusters are readily apparent. Reaches MR1 and MR2 are distinct from areas upstream by the sudden dominance of carbonates in the basin (Fig. 3), along with the nearly ubiquitous (though chemically heterogeneous) shale. Reaches MR3 and MR4 are distinguished by the first appearance of igneous geology, including the only igneous-felsic formations in the entire river catchment. Reach MR5 is relatively unique, perhaps most like its upstream neighbors MR3 and MR4 in containing igneous-mafic geology but also similar to MR1 and MR2 in that it lacks igneous-felsic features.

Phase II Results.—Analysis of 2-rkm segment basin geology was restricted to examining cluster solutions separated by greater than 0.45 ϕ^2 distance based on reach basin analysis. This led to 4 discernable clusters among Maury River basins, which generally represented contiguous series of river segments (Fig. 3). Upstream and downstream boundaries of these clusters very nearly matched delineation of reaches in Phase I analysis, but importantly they identify specific geologic features and breakpoints that influence their distinction. In particular, clustering of segments upstream from experimental reaches (cluster 1, ~0–8 rkm) suggests that bass spawned in these segments could be distinguishable by otolith chemistry.

Identical analysis of James River 2-rkm segment basin geology indicated six different clusters were separated by at least 0.45 ϕ^2 distance units (Fig. 4). Half of these clusters (4–6) include segments downstream of the Maury River confluence. Clustered segments are often not contiguous in stream sequence and therefore are of questionable utility in delineating larger scale "reaches" for sampling design. However, there do appear to be distinctions of note: a) the first 30 rkm of the James appear to be geologically distinct from most areas downstream; b) cluster 3 first appears 72 rkm downstream, suggesting potential for reach distinction in this area; c) from 112 rkm downstream there appears a strong clustering of segments (cluster 6) driven by shared predominance of igneous-felsic formations.

Discussion

Our analysis reveals a coarse, phenomenological association between variation in basin geology and the distinction of trace element signatures in otoliths of smallmouth bass spawned within and between rivers. Clustering of reach basins using geologic data did not correspond perfectly with grouping in fish origin discrimination using otolith trace element chemistry, but this is hardly surprising. A number of biotic and abiotic factors act as dynamic, interacting filters in the pathway between bedrock geochemistry, stream water chemistry, and subsequently trace element incorporation into otolith material (hydrology, temperature, dissolved oxygen, organismal uptake, etc; Campana 1999, Elsdon and Gillanders 2004). Therefore, we would not expect perfect correlation between the spatial scales of heterogeneity in basin geology

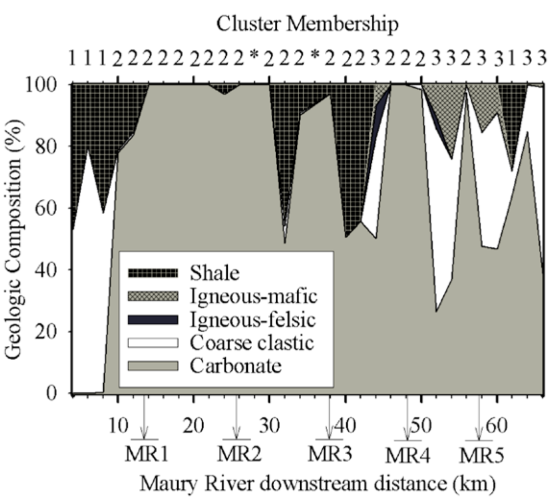

Figure 3. Geologic composition of Maury River 2-rkm segment basins from the headwaters (0 rkm) to the James River confluence (62 rkm). Cluster membership from hierarchical cluster analysis of each 2-rkm basin is indicated on the upper abscissa, where all clusters are separated by a minimum distance of 0.45 (ϕ^2 units; see text for details). The starting points of river reaches designated in fish/otolith collections are indicated along the lower abscissa.

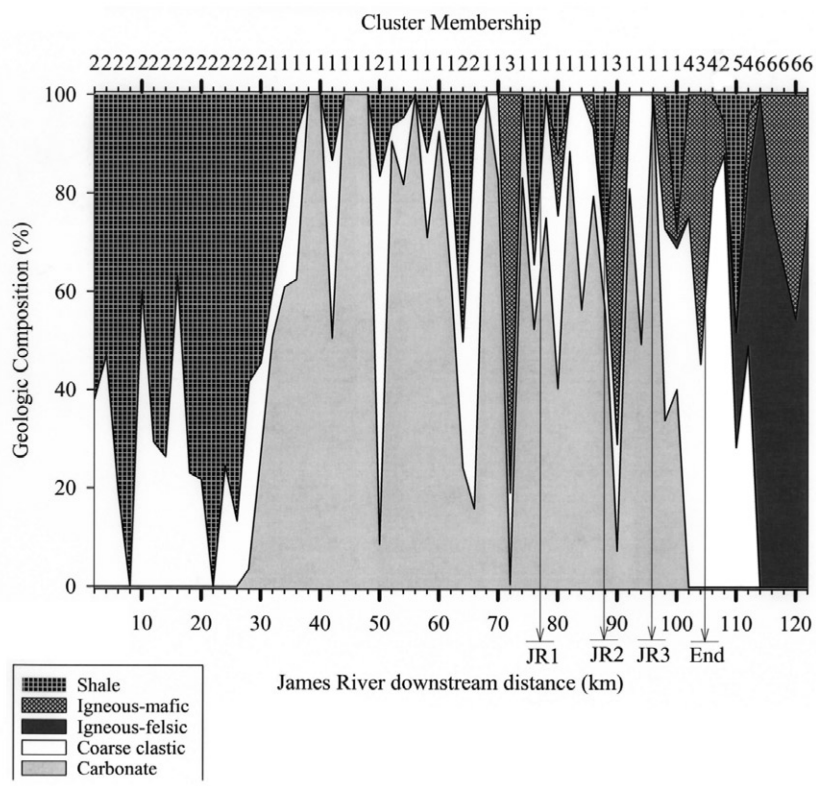

Figure 4. Geologic composition of James River 2-rkm segment basins from the headwaters (0 rkm, confluence of Cowpasture and Jackson Rivers) 122 rkm, or approximately 26 rkm downstream of the Maury River confluence. Cluster membership from hierarchical cluster analysis of each 2-rkm basin is indicated on second (top) abscissa, where clusters are separated by a minimum distance of 0.45 (ϕ^2 units). The starting points of river reaches designated in fish/otolith collections are indicated by vertical lines with labels extending below the lower abscissa.

and variation in fish otolith chemistry; however, we would expect coarse similarities in spatial patterns. Lacking a formal test for correlation between cluster and LDFA results, our assessment of agreement is admittedly a subjective measure. We therefore tried to err on the side of conservatism in selecting a cluster solution that most closely matched discrimination results. In doing so, two of eight reaches were clustered with reaches from which they were otherwise "distinguishable" in LDFA of otoliths. However, the remaining agreement supports the hypothesis that fish origin discrimination via otolith chemistry over relatively fine spatial scales (<15 rkm) reflects heterogeneity in basin geology underlying freshwater systems.

Several challenges and decisions in the design of our multivariate statistical analysis should be addressed here briefly. Selecting the correct measure of distance or similarity in cluster analyses is an important but challenging first step. In this analysis, this was made more difficult by our requirements: a) the measure needed to simultaneously capture variation in basin composition and total area of each categorical attribute; and, b) the statistic needed to have transferable meaning in subsequent comparison of other river basins. While the ϕ^2 measure does not meet these requirements completely, it offers a strong compromise. A review of distance measures appropriate for ecological study (Legendre and Legendre 1998) supports this decision. We chose to define clusters by the method of UPGMA or between-groups linkage because the clustered objects (reaches or segments) were arbitrarily defined—i.e., they have no physical or ecological delineations—and do not represent independent units per se. While nearest-neighbor (single linkage) distance has a more intuitive meaning for separating clusters, our analysis was interested in identifying grouping in a linear series of river segments to determine where any possible boundaries exist. In other words, our primary objective was to identify similar, contiguous segments as clusters; the group average distance more accurately represents the distance between clusters when the cluster itself is the object of interest but its boundaries are not captured in the data. If a similar analysis were used to compare geology of different rivers and tributaries in a watershed—where each system was a management unit of interest, for example—then the single linkage method of clustering would likely be more appropriate (e.g., Wells et al. 2003). This would suggest that the single-linkage method might be more appropriate for analyzing reach basin data than for analyzing the 2-rkm segment data, and indeed the clusters resulting from single-linkage analysis of reach data compare favorably with UPGMA clustering.

It is likely that land use patterns contribute to the correlation between basin geology and stream water chemistry. For example: urban development in a watershed would affect patterns of infiltration and percolation, thereby altering the relationship between precipitation, hydrology, and geochemistry within a stream basin. We did include data on land use in our initial analysis in combination with geologic data and independently. We saw no evidence that these data enhanced agreement between reach basin clusters and spatial grouping in fish otolith discrimination and therefore excluded these results from this report.

Finally, our decision to analyze discrete basin composition as opposed to cumulative basin composition was based on lack of information describing residence time of trace elements in river systems. Clearly, biological uptake and settling out of ions due to particulate binding would eventually degrade signals from upstream basin geology on some critical spatial scale. This scale would be influenced by myriad spatiotemporally dynamic biotic and abiotic factors in both aquatic and riparian terrestrial ecosystems. We lack data to define this scale; first principles suggest that the cumulative basin composition is less meaningful over the length of these rivers for predicting water and otolith trace element composition.

Clustering tended to "absorb" some ambiguous reaches; for example, reach MR5 and clustered with MR1 and MR2. Basin composition data (Figure 3) reveals that this association is largely driven by dominance of carbonate and coarse clastic geology and the general lack of igneous-mafic formations in these basins. Misclassifications in otolith discriminant analysis suggest there is some overlap in trace element composition of otoliths collected from these areas; however these signals are not strong enough to be separated from background variation (noise). These results suggest that these analyses are best applied in concert with visual assessment of pattern in basin composition data to identify contiguous segments of stream as reaches likely to yield distinct trace element concentrations in otoliths. Discontinuities in segment clustering can be evaluated on an individual basis to determine if they warrant specific collections. For example, we could designate the first 30 rkm of the James River as a single sampling unit for fish collections, from 30–60 rkm as a second individual unit, and from 112–122 rkm as a third unit. The remainder of the river appears highly variable, and results from the reach basin clustering (Phase I) suggest that igneous-mafic formations in a basin contribute significantly to trace element chemistry in otoliths. We would therefore expect high variation and subsequent ambiguity among otoliths collected from these reaches. We plan to test these predictions with more collections and analyses in the future.

As this last point illustrates, these analyses would be strengthened by a mechanistic understanding of the biotic and abiotic factors that filter the correlation between basin lithology and trace element chemistry of water and (subsequently) fish otoliths. There are numerous factors affecting correlations between water and otolith chemistries (Campana 1999), and these are currently the subject of significant research effort (Elsdon and Gillanders 2002, 2003, 2004, 2005; Kraus and Secor 2003; Dorval et al. 2005; Walther and Thorrold 2006). Likewise, there are numerous factors which affect the manner in which a river reach's water chemistry will reflect the geologic composition of its watershed. River water chemistry is strongly related to bedrock geology (Puckett and Bricker 1992, Liu et al. 2000), which reflects the release from rock weathering—both in shallow and deep flow paths—but also uptake by lithologically hosted organic matter or hydrous iron and manganese oxides (Drever 1982, Jenne 1995). The latter are particularly prominent in this study area as ores mined in the previous century; deep leaching of the igneous rocks produces ores at the base of the Blue Ridge while leaching of Devonian age black shales produces simlar ores in the headwater basins. The black shale of the western valleys and mafic rocks of the Blue Ridge are the most chemically distinct (Puckett and Bricker 1992), especially in terms of trace elements, with the exception of Sr, Mg, and Y. Due to the adsorptive properties of clay, metals like nickel, copper and zinc are high in the black shale of headwater basins. Barite nodules in the Devonian shale in the headwaters (Clark and Mosier 1989) match the high introduction of barium in the igneous rocks of the Blue Ridge. The carbonate rich shale associated with the valley carbonates is a less likely host for abundant trace elements, especially metals (Goldstein and Jacobsen 1988) with the exception of those substituting for calcium in the crystal lattice (e.g., Sr). The coarse clastic sediments are comparatively low in effect on stream chemistry (Martin and Maybeck 1979).

Distinguishing natal origins of fish in lotic populations is of use in identifying stock structure, determining recruitment sources and sinks, tracking dispersal, and describing metapopulation dynamics (among other possibilities). The methods we present for synthesizing and analyzing land attribute data offer a useful framework for assessing study areas prior to initiating research using otolith chemistry for natal origin discrimination. We sought to follow the excellent example of Wells et al. (2003) who demonstrated that dissimilarity in water chemistry could be used as an initial indicator of potential for otolith / stock discrimination based on trace element chemistry. Their results illustrated that simple water chemistry comparisons could provide a useful tool a preliminary study site assessment prior to otolith chemistry research: one that did not require sacrifice of fish, or costly and labor-intensive otolith chemistry analysis. Our analysis reveals an association between basin geologic heterogeneity and variation in fish otolith chemistry, and our methods employ readily available data and analysis tools that can be applied previous to initiating fieldwork on a study site. We feel it has significant potential for use in designing experiments, guiding water and fish sample collections, and assessing the efficacy of otolith chemistry methods for studying spatial dynamics of fish stocks in lotic ecosystems. Future developments in this area will benefit from a more complete understanding of the causal mechanisms linking elemental composition of waters with basin geology. We present this paper as a first step toward understanding how variation in basin geology can lead to discernable signatures in the trace element concentration of otoliths in river fisheries.

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