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Chapter 33

Black shale weathering contribution to stream chemistry using end-member mixing analysis

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Abstract

A mathematical approach known as end-member mixing analysis (EMMA) was applied to determine the end-member components (overland/shallow subsurface, runoff, and groundwater) contributing to the surface water chemistry of two first-order headwater tributaries of the Little Red River in Arkansas. Binary mixing between two end-members explained only a portion of the variance in major anion and cation chemistry of the surface waters. Therefore, ternary mixing was investigated using the EMMA method. Previous studies using EMMA have involved first- and second-order streams of various bedrock types. This study is unique in that it is the first, to our knowledge, to apply this approach to the study of first-order streams draining black shales. The tributaries we investigated (Cove Creek and Begley Creek) are underlain mainly by metal-rich Mississippian Fayetteville Shale. Weathering of this bedrock could affect water quality. Where surface waters are in intimate contact with these shales, it is necessary to determine the extent to which these waters contribute to the chemistry of the stream as a first approximation to the significance of black shale weathering to the catchment.

The mixing analysis results suggest that the contributions from overland/shallow subsurface flow, runoff from the black shale outcrop, and groundwater play a major role in making up the surface water chemistry of Begley and Cove Creeks under both storm and base flow conditions. The relative contribution of these end-members varies with flow. As expected, the mixing results showed that groundwater dominates during base flow. During storm flow the surface water chemistry represents a mix of overland/shallow subsurface flow and black shale runoff. We found that during storm flow groundwater and overland/shallow subsurface flow were, in general, indistinguishable across storm hydrographs resulting in storm flow chemistries represented by binary mixtures of two chemically distinct end-members. Ion concentration ratios are similar for overland/ shallow subsurface flow and groundwater because of the lithologic similarities of the rocks in contact with these waters. Runoff from the black shale outcrop does contribute to the surface water chemistry.

33.1. Introduction

Water flowing through a stream channel is composed of water from a variety of sources also known as end-members. These end-members include precipitation, runoff, shallow subsurface (e.g., bank storage), and groundwater that may be further influenced by atmospheric deposition, biological activity, chemical weathering, and the geology of the area. As a result, the chemistry of streams is highly variable. Geochemical hydrograph separation and modeling of hydrochemistry can provide insights into the temporal variability in stream chemistry and the relative contributions of end-member components.

This study focused on black shale weathering as a non-point source of dissolved metals to surface waters of headwater tributaries of the Little Red River. Major ion concentrations were used to identify the major contributing end-members to the surface waters. K^+, Ca^{2+}, Mg^{2+}, Na^+, Cl^-, NO_3^-, alkalinity, acid neutralizing capacity, and silica are among the most commonly used parameters (Pinder and Jones, 1969; DeWalle and Poinke, 1994; Elsenbeer et al., 1995; Jarvie et al., 2000; LaDouche et al., 2001). Many models have been developed to assess the interactions between physical and chemical hydrology. However, when conservative binary mixing fails to explain the observed variation in surface water chemistry, a least-squares mathematical approach called end-member mixing analysis (EMMA) can be used to explain variation under ternary-mixing conditions. Using this approach, we identified the dominant end-member components influencing surface water chemistry in the headwaters of the Little Red River. If waters of the end-members determined by EMMA are in contact with shales, we can use this as our first approximation of the significance of black shale weathering and the potential of weathering of this metal-rich bedrock as a non-point source of dissolved metals to the system. Further analysis of black shale weathering products and trace metal chemistry can then be used to more precisely assess the significance of black shale weathering in influencing the metal chemistry of the surface waters and sediments in black shale draining systems.

EMMA has the advantage of using directly measured solute concentrations to generate verifiable information about the mixing patterns making up the stream chemistry (Christophersen et al., 1990; Hooper et al., 1990). This method simultaneously uses multiple solutes as tracers and relies on binary or ternary component mixing. It utilizes conservation of mass to explain the variation in solute concentration based on the relative composition of the end-members that contribute to the waterway. The end-members chosen must have solute concentrations that are distinct from the stream water and they should bind the stream water data in a mixing diagram. The model assumes that the source solutions are invariant in time and space but it is often difficult to sufficiently sample stream component compositions either spatially or temporally. However, the model can be validated by the linear fit of EMMA predicted versus observed solute concentration and an evaluation of the hydrological patterns predicted. Even if EMMA fails to sufficiently predict the observed stream chemistry the information obtained can be used as a guide for future studies.

This study used EMMA to explore the dissolved chemistry of surface waters draining Mississippian Fayetteville Shale bedrock of first-order streams (Cove Creek and Begley Creek) in the headwaters of the Little Red River in central Arkansas. Previous studies utilizing EMMA have focused on both first- and second-order streams that drain various common bedrock types (e.g., granite, sandstone, limestone) but none have studied surface water draining black shale bedrock (Christophersen et al., 1990; Christophersen and Hooper, 1992; Hooper et al., 1990; Jarvie et al., 2000; Burns et al., 2001; Hannigan and Bickford, 2003). Black shales are metal-rich and sedimentary rocks that are easily weathered. In watersheds dominated by these shales, their presence is often reflected in increased metal loading of waterways and sediments/soils (Chon et al., 1996; Loukola-Ruskeeniemi et al., 1996, 1998; Petsch et al., 2000; Tuttle et al., 2001; Ogendi et al., 2004a). Regions of central and southeastern USA are particularly affected as weathering of shales may be a significant source of pollution in small creeks and streams (Foley et al., 2001). Increases in dissolved metal concentrations may have a negative impact on living organisms including deficiency and toxicity symptoms in plants and livestock such as restricted growth, incomplete cell wall development and gastrointestinal disorders (Kim and Thorton, 1993; Loukola-Ruskeeniemi, 1994, 1996; Ogendi et al., 2004a,b).

In areas where surface or groundwaters are in intimate contact with metal-rich bedrock, it is necessary to determine the extent to which these waters contribute to the chemistry of the stream. Using EMMA to identify the major end-member components contributing to the surface water chemistry of the headwater tributaries of the Little Red River as a guide to the significance of black shale weathering to the chemistry of the stream is a novel approach.

33.2. Methods

33.2.1. Study site

Sampling sites were located on Devil's Backbone, Cove Creek, Begley Creek, and Middle Fork. The streams are first-order streams that are part

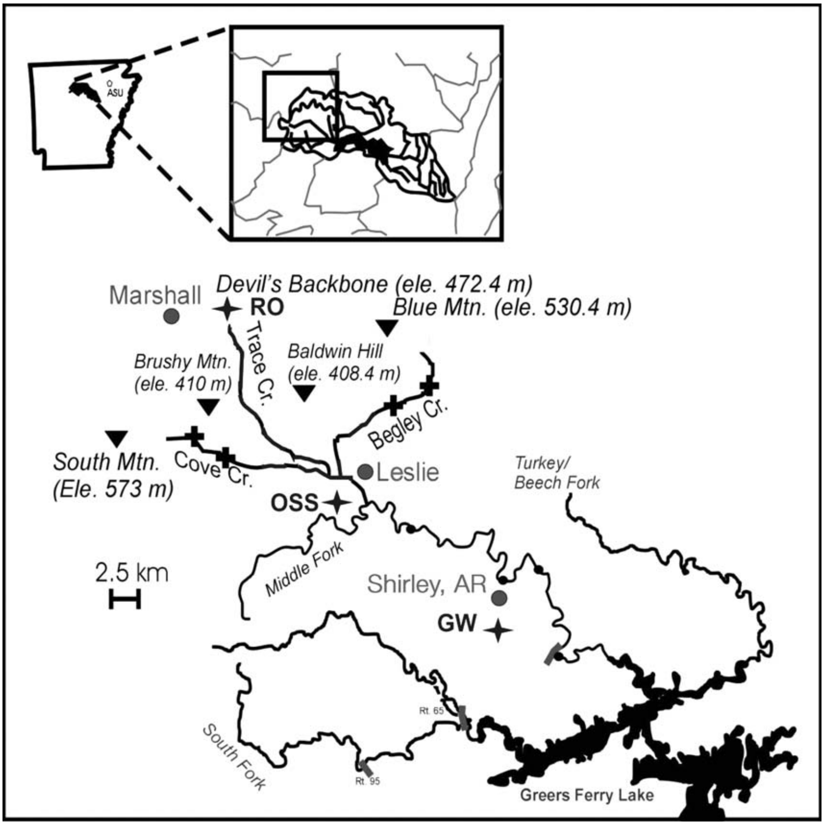

Figure 33.1. Schematic diagram of the study site showing sampling locations. Surface water was collected at Begley Creek and Cove Creek. Runoff from black shales was collected from outcrop and shale seeps at Devil's Backbone during a storm event. Overland/shallow subsurface samples were collected from bank soils along the Middle Fork. Groundwater was collected from a well near Shirley AR. Surface water sampling subsites are indicated by black crosses. End-members are noted as stars (GW, groundwater; OSS, overland/shallow subsurface; RO, runoff). Adapted from Ogendi et al. (2004a).

of the Little Red River watershed (HUC 11010014) in Arkansas, USA (Fig. 33.1). The Little Red River has a total watershed area of 2901.75 km^2 and a total river length of 4882.67 km. The streams drain the northern portion of the Little Red River watershed that is >75% forest riparian and ~20% agricultural/urban riparian. The study focused on the unpopulated upper reaches of the streams. Details on the geology of the study area are given elsewhere in this book (Ogendi et al., 2007) as well as Renken (1998). In summary, the Devil's Backbone, Cove Creek, and Begley Creek flow over the Mississippian Fayetteville Shale (~350 mya), which according to Hudson et al. (2001) rests conformably on the Batesville Sandstone. The Fayetteville Shale is in intimate contact with surface as well as groundwaters of Devil's Backbone, Cove Creek, and Begley Creek (Ogendi et al., 2004b). The Middle Fork drains over the Mississippian Pitkin Limestone that rests conformably on the Mississippian Fayetteville Shale. The mineralogy of the Fayetteville Shale as well as that of the Pitkin Limestone is described in Murthy (2003). The most abundant clay minerals in the Fayetteville Shale are kaolinite, illite, and smectite, whereas micas, quartz, and feldspars form the main mineral constituents of this rock. Calcite and illite dominate the mineral composition of the Pitkin Limestone. The Fayetteville Shale contains a significantly higher organic carbon (5–8wt% than the Pitkin Limestone (⩽1wt %) (Murthy, 2003; Ogendi et al., 2004b).

Water flowing off the face of the Devil's Backbone shale outcrop was collected during a storm event and represents the runoff end-member. Surface waters drain southward from the Blue Mountain catchment into Begley Creek. Begley and Cove Creeks have surface water in direct contact with Fayetteville Shale in the streambed; surface water was collected from both these streams to make up the stream water dataset for EMMA. We did not attempt to model the chemistry of Trace Creek because chloride was non-conservative suggesting an additional end-member in this region such as shallow or deep saline groundwater or saline soil water (Bethke and Marshak, 1990; Winter, 1999; Davis et al., 2003). Middle Fork near Marshall drains an area of limestone. Surface water collected here serves as our overland flow end-member because the major ion chemistry of the overland flow in this region was found to be indistinguishable from the soil water and bank storage fluids of Cove and Begley Creeks. Given that it is easier to collect sufficient quantities of surface waters at Middle Fork than the shallow subsurface fluids at Cove or Begley we selected this option, although less than ideal. Surface waters from Cove and Begley Creeks mix with Middle Fork. Groundwater data from Middle Fork near Shirley represents our groundwater end-member because the region shares a common aquifer. Groundwater data were obtained from Earthinfo Inc. USGS Quality of Water for Central USA (http://www.earthinfo.com/).

The end-members were determined by the availability of data and the likelihood of them contributing to the stream. The runoff from Devil's Backbone, overland flow/shallow subsurface (Middle Fork) and groundwater are potential end-members because of the geology and hydrology of the area. The shales of the northern Little Red River watershed are non-permeable but they are highly fractured allowing the upflow of groundwater through the more permeable limestone aquifer into the streambeds.

33.2.2. Sample collection

Stream water samples were collected during storm and base flow at various times during the year in nitric acid-washed high-density polyethylene bottles at randomly determined subsites. Samples were filtered using a 0.45 μm Gelman in-line filter with the fraction passing through the filter operationally defined as dissolved. 125 ml was acidified with nitric acid for analysis of cations, and 125 ml was left unacidified for analysis of anions. All samples were stored at ~4°C prior to analysis.

Water quality parameters such as temperature, pH, electrical conductivity, dissolved oxygen, and stream flow were measured in the field using various meters. Discharge was calculated from stream velocity. Major ion concentrations were measured by ion-chromatography (Dionex DX 120). Major anion concentrations were measured within 24 h of collection and major cation concentrations were measured within 48 h of collection. Alkalinity was determined by titration.

33.2.3. End-member mixing analysis

Alkalinity/HCO_3^-, Cl^-, K^+, Mg^{2+}, Ca^{2+}, Na^+, and SO_4^{2-} concentrations and water quality parameters for Begley and Cove Creeks stream water are summarized in Tables 33.1 and 33.2. Binary mixing plots of the various solutes were generated to show variation in solute concentrations and to perform a simple two-component mixing analysis as in Jarvie et al. (2000). A principal component analysis (PCA) was performed on a standardized correlation matrix of the stream water dataset and a model was generated that accounted for the most variance (~97%) in the dataset. The number of end-members needed to complete the model is equal to the number of principal components plus one. The end-member solute compositions were then standardized against the stream water data and multiplied by the eigenvalues of the matrix for the stream water values then projected onto a mixing diagram. The mixing diagram consisted of

Table 33.1. Physical water quality parameters for the stream samples used in this study

Date	Site	T (°C)	pH	DO	Conductivity (μS)	Discharge ($m^3 s^{-1}$)
May-04	BC	24.0	6.05	6.30	260.50	0.118
May-04	BC	24.0	6.04	6.38	258.50	0.130
May-04	CC	24.1	6.80	6.80	224.50	0.115
May-04	CC	24.2	6.8	6.70	221.50	0.0975
Jan-04	BC	4.0	7.12	11.40	237.75	0.213
Jan-04	BC	4.1	7.09	10.40	233.00	0.190
Jan-04	CC	7.9	7.60	10.80	245.50	0.180
Jan-04	CC	8.5	7.50	10.60	249.50	0.145
Nov03	BC	22.5	5.80	6.40	212.00	0.298
Nov-03	BC	22.4	5.78	6.30	211.00	0.343
Nov-03	CC	22.1	6.80	6.70	203.25	0.290
Nov-03	CC	22.0	6.75	6.80	205.50	0.313
Sep-03	BC	25.1	7.89	8.16	372.17	0.0550
Sep-03	BC	25.1	7.75	8.24	369.17	0.0550
Sep-03	CC	24.9	8.11	8.17	361.67	0.0425
Sep-03	CC	25.0	8.22	8.13	366.67	0.0450
Aug-03	BC	24.0	6.30	6.40	205.75	0.325
Aug-03	BC	23.9	6.10	6.30	197.50	0.333
Aug-03	CC	25.2	7.10	6.70	195.50	0.303
Aug-03	CC	25.0	7.00	6.70	196.25	0.315
June-03	BC	21.3	6.52	9.54	165.50	0.798
June-03	BC[a]	–	–	–	169.50	0.828
June-03	CC	20.8	6.57	9.24	161.25	0.768
June-03	CC[a]	–	–	–	156.00	0.775

BC, Begley Creek; CC, Cove Creek.
[a] Sample split.

the principal components of stream water determined from EMMA and the end-member values. The end-member proportions were tested within the model to derive the fraction of each end-member contributing to stream chemistry. The model resulted in the predicted percentage frequency of various end-member contribution combinations that best explain stream chemistry and provided details about the relative contributions of the end-members used.

33.3. Results

Alkalinity/HCO_3^-, Cl^-, K^+, Mg^{2+}, Ca^{2+}, and SO_4^{2-} were chosen for EMMA because the concentration of these solutes were available from USGS Quality of Water Data for the end-members being tested. The solute concentrations for overland/shallow subsurface, runoff, and

Table 33.2. Solute concentrations in stream water samples from the Little Red River. Concentrations of bicarbonate in mg l^{-1} all others in meq l^{-1}

Date	Site	HCO_3^- (mg l^{-1})	Cl^-	K^+	Mg^{2+}	Ca^{2+}	Na^+	$SO4^{2-}$
May-04	BC	220.00	0.11	0.14	0.89	3.95	0.04	1.07
May-04	BC	224.00	0.11	0.14	0.89	3.95	0.05	1.09
May-04	CC	230.00	0.18	0.16	1.09	3.28	0.10	0.27
May-04	CC	235.00	0.18	0.15	1.08	3.36	0.09	0.28
Jan-04	BC	296.59	0.15	0.19	1.20	5.33	0.06	1.44
Jan-04	BC	301.99	0.14	0.19	1.20	5.34	0.06	1.47
Jan-04	CC	336.77	0.27	0.23	1.58	4.75	0.15	0.40
Jan-04	CC	344.09	0.26	0.22	1.56	4.87	0.14	0.41
Nov03	BC	177.54	0.09	0.16	0.99	4.39	0.05	0.86
Nov-03	BC	180.77	0.09	0.16	0.99	4.40	0.05	0.88
Nov-03	CC	206.20	0.16	0.16	1.08	3.24	0.10	0.25
Nov-03	CC	210.68	0.16	0.15	1.07	3.32	0.09	0.25
Sep-03	BC	459.34	0.23	0.28	1.76	7.84	0.09	2.23
Sep-03	BC	467.69	0.22	0.28	1.76	7.85	0.10	2.27
Sep-03	CC	480.22	0.38	0.32	2.16	6.50	0.20	0.57
Sep-03	CC	490.66	0.37	0.30	2.14	6.67	0.19	0.58
Aug-03	BC	182.09	0.09	0.15	0.97	4.33	0.05	0.88
Aug-03	BC	185.40	0.09	0.16	0.97	4.33	0.05	0.90
Aug-03	CC	201.23	0.16	0.20	1.35	4.05	0.13	0.24
Aug-03	CC	205.61	0.15	0.19	1.33	4.15	0.12	0.24
June-03	BC	117.87	0.06	0.07	0.44	1.97	0.02	0.57
June-03	BC	120.01	0.06	0.07	0.44	1.97	0.02	0.58
June-03	CC	153.67	0.12	0.08	0.52	1.56	0.05	0.18
June-03	CC	157.01	0.12	0.07	0.51	1.60	0.05	0.19

BC, Begley Creek; CC, Cove Creek.

groundwater are summarized in Table 33.3. A PCA reduced the six major ions used in two principal components that explained 98% of the variability of the dataset. The first component, U1, explained 79% of the variability and the second component, U2, explained 19%. The mixing diagram of these two principal components along with the end-member components is shown in Fig. 33.2. The surface water samples did not fall within the end-member mixing triangle. Although the graphic fit to the stream data was poor, the EMMA model did not fail to identify the end-member contributions. The relation between observed solute concentration and EMMA predicted concentration showed strong correlation (Fig. 33.3; Alkalinity/HCO_3^- $r^2 = 0.90$; Mg^{2+} $r^2 = 0.91$; Ca^{2+} $r^2 = 0.98$; Cl^- $r^2 = 0.75$; SO_4^{2-} $r^2 = 0.83$; K^+ $r^2 = 0.93$). Since the predictions were linearly correlated with the observed concentrations we examined which combinations of the sampled end-members EMMA predicted as comprising the surface water chemistry.

Table 33.3. End-member solute concentrations from USGS water quality data used in EMMA in meq l^{-1} unless otherwise indicated

	HCO_3^- (mg l^{-1})	Cl^-	K^+	Mg^{2+}	Ca^{2+}	SO_4^{2-}
Overland/shallow subsurface	517	0.231	0.285	1.8	8.1	2.44
Black shale runoff	345	0.02	0.054	0.197	0.6	0.1
Groundwater	29.00	0.275	0.203	1.241	2.74	0.05

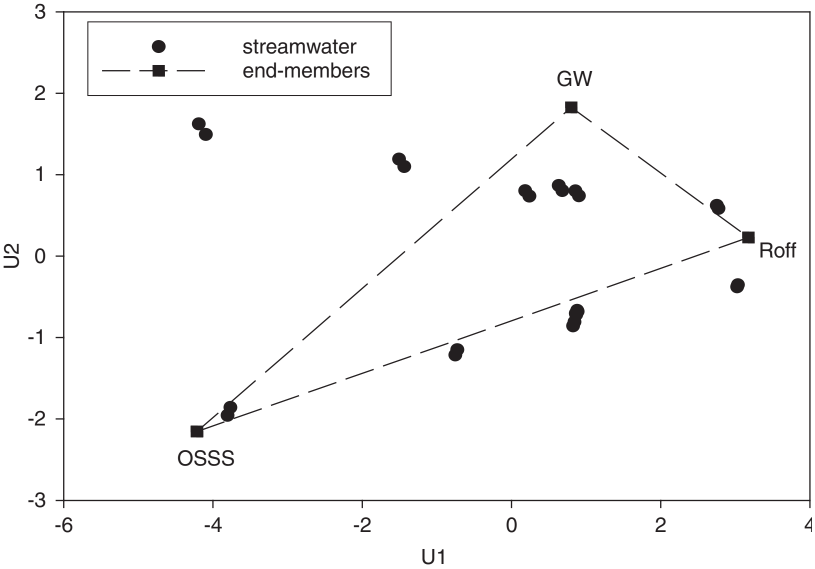

Figure 33.2. Mixing diagram of the principal components U1 and U2 of the stream water and end-member data for the Little Red River. The end-members do not adequately bind the stream water chemistry. The model did yield insights into the presence of three end-members but variance related to discharge needs to be isolated from the variance associated with end-member mixing.

The most frequent combination of end-members that explained the majority of the variance in stream water chemistry was a combination of the overland/subsurface flow and runoff (Fig. 33.4; 41.67%). The combination of the overland/subsurface flow, runoff, and groundwater end-members had a frequency of 33.33%, overland/subsurface flow and groundwater 16.67%, and the runoff and groundwater combination 8.33%. No single end-member accounted for the mixing pattern is

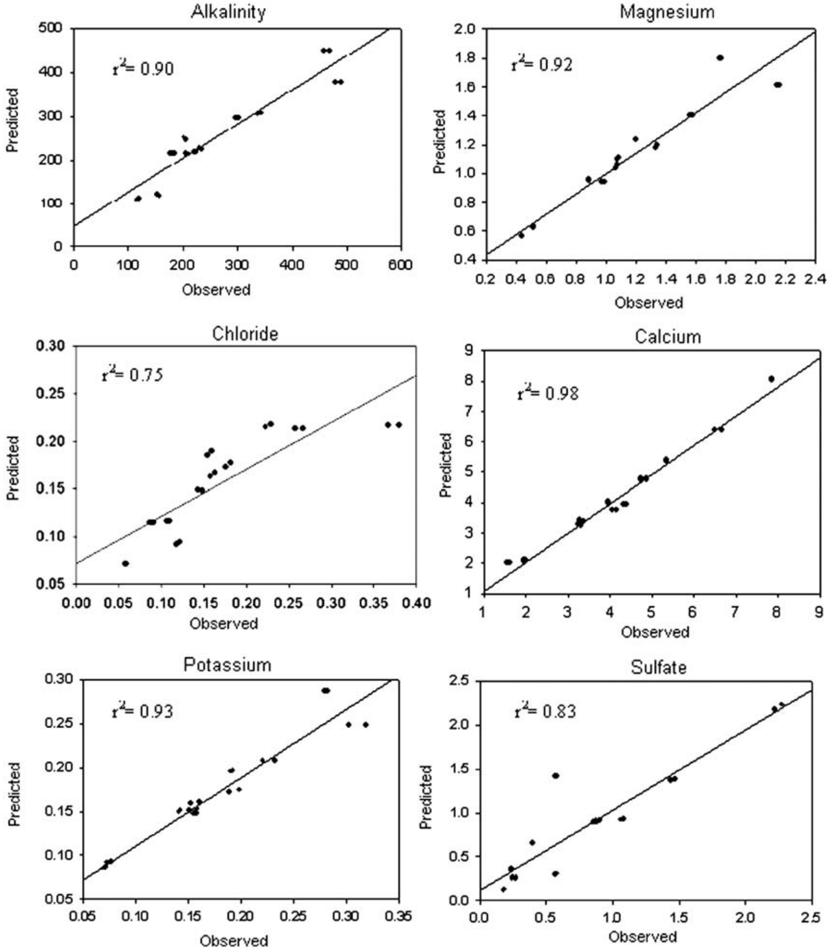

Figure 33.3. Observed stream water chemistry versus EMMA predicted solute concentrations. These results indicate that EMMA has not failed in identifying the contributing end-members to stream chemistry.

observed. As expected, major solute concentrations were lowest during storm flow (Fig. 33.5).

Binary mixing plots of the various solutes show two distinct mixing patterns. Simple binary mixing best describes the relation between surface water concentrations of Cl^- and Mg^{2+}, and HCO_3^- and Mg^{2+} (Fig. 33.6a). Ternary mixing is suggested by the relation between other solutes (Fig. 33.6b).

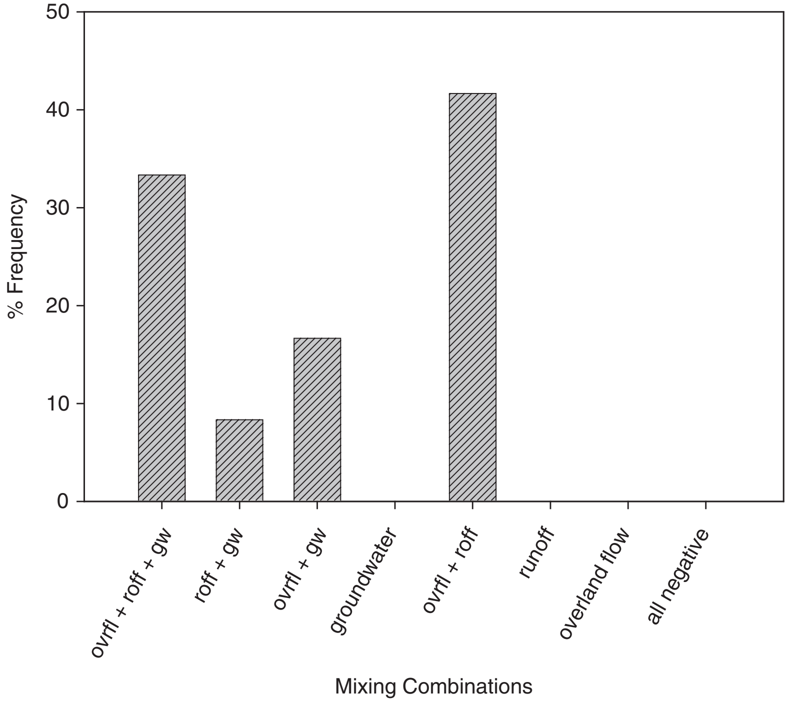

Figure 33.4. Histogram shows the relative contributions of various end-members to stream water chemistry. The percentage frequency at which the variation in the stream water dataset could be explained by a particular end-member or end-member combinations is plotted. A combination of overland/shallow subsurface water and black shale runoff was determined to be the dominant combination of end-member sources (41.67%). A combination of the three end-members, groundwater, overland/shallow subsurface, and black shale runoff had a frequency of 33.33%. This suggests stream chemistry is mainly controlled by these two end-members (ovrfl, overland/shallow subsurface flow; roff, runoff; gw, groundwater).

33.4. Discussion

The stream water sample data did not fit with the mixing triangle of the end-members. Although the graphic fit to the stream data was poor, the EMMA model did not fail to identify the end-member contributions. The poor graphic fit may have been due to seasonal variability within the end-member dataset. The end-member solute concentrations were obtained from USGS data and the seasonal variability could not be adequately captured. The EMMA model assumes that the source solutions are invariant in time and space. Although this assumption is often violated, the

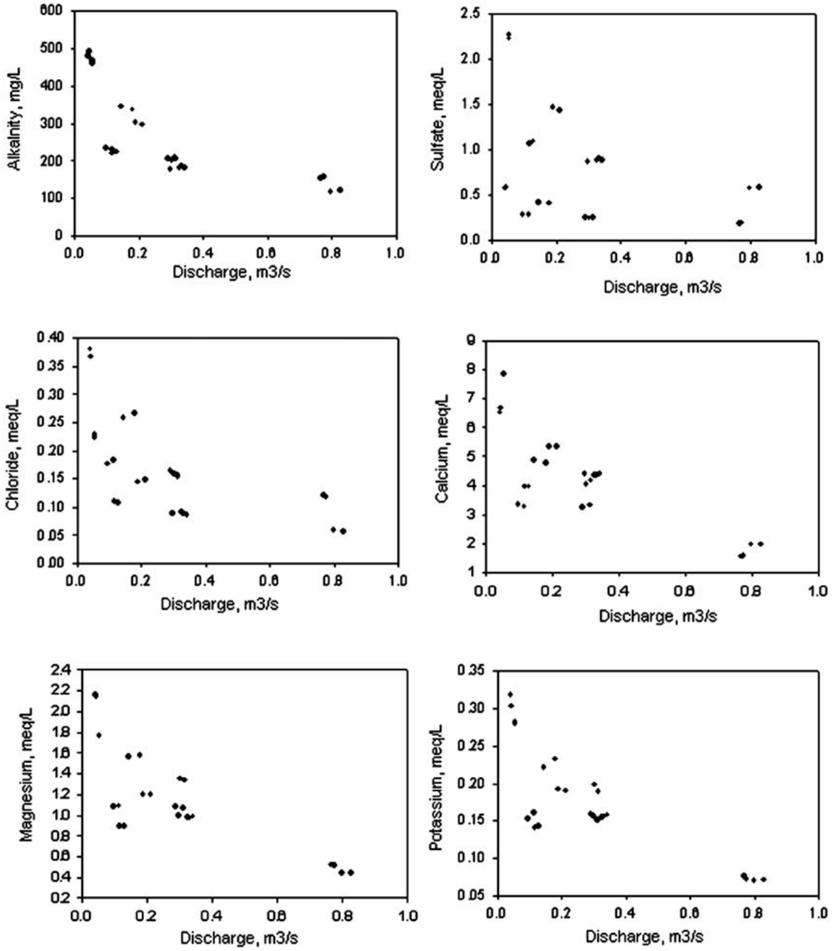

Figure 33.5. Total stream discharge versus major solute concentration used in EMMA. Solute concentrations dilute with increase flow suggesting changes in source waters making up stream chemistry during high flow or dilution of solute concentration.

linear fit of EMMA predicted versus observed stream water data validates the model. The seasonal variability in the dataset is also apparent in the stream water data but the sampling frequency gives a seasonal average of solute concentrations.

The PCA determined that mixing of two components accounts for the majority of variation in the surface water chemistry data (~98%). Given the results of the EMMA model a combination of the two dominant

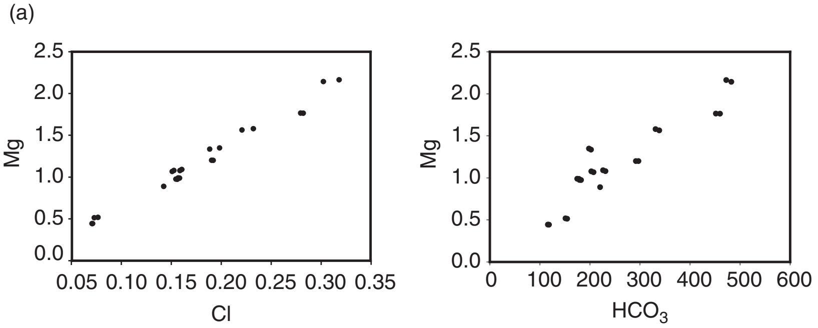

Figure 33.6. (a) Binary mixing plots of the solutes employed in EMMA. The relations between Mg^{2+} and Cl^- and Mg^{2+} and HCO_3^- are simple binary mixing between two end-members as shown by the straight-line relationship. The primary source of these solutes remains the same across the hydrograph. (b) The relation between the other solutes is not binary as shown by the lack of linearity between the solute pairs with several showing two distinct mixing patterns. The dilute effect of storm flow is evidenced at lower stream concentrations such that one of the end-members is present throughout the hydrograph. This is supported by the EMMA model.

end-members, overland/shallow subsurface flow and runoff, were determined to be the dominant end-members accounting for the majority of the variance in stream water chemistry (Fig. 33.4). The solute-mixing relations show that the dissolved surface water Cl^- and Mg^{2+}, and HCO_3^- and Mg^{2+} chemistries are best explained by mixing of two discrete end-members (Fig. 33.6a). Major ion chemistry across the hydrograph is best explained by binary mixing of end-member components with different base flow and storm flow chemistries (Fig. 33.5). Since ion concentrations decrease as discharge increases, a mixing pattern where ion concentrations are low most likely occurs at storm flow and vice versa. The differences in chemistries may result from changes in the flowpaths of water during precipitation events or from dilution of source water inputs. EMMA determined these end-member components to be overland/subsurface flow that includes both soil water and pre-event bank storage water with a chemical signature similar to the surface waters in the limestone draining Middle Fork. The second end-member, runoff from black shale, mixes with the overland/subsurface waters during and just after precipitation events leading to the development of a dissolved chemistry distinct from base flow.

Two end-member components mixing explain 98% of stream water chemistry variability in the dataset, but to explain 100% of the variance a third end-member must be included. Binary mixing plots of HCO_3^- versus

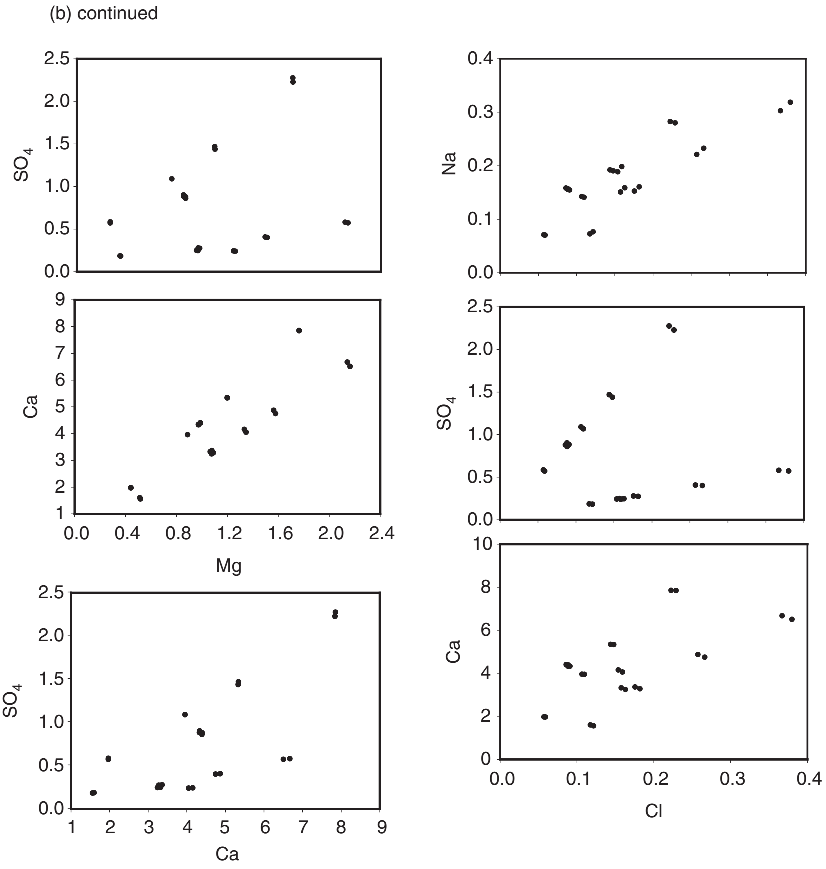

Figure 33.6. Continued

SO_4^{2-}, Ca^{2+}, Na^+, Cl^-; Na^+ versus SO_4^{2-}, Ca^{2+}, Mg^{2+}; Mg^{2+} versus Ca^{2+}, SO_4^{2-}; Cl^- versus Na^+, SO_4^{2-}, Ca^{2+}, and Ca^{2+} versus SO_4^{2-} show a ternary-mixing pattern (Fig. 33.6b). Mixing lines converge at low-ion concentrations pointing to a common storm flow end-member component where the ion concentrations are more dilute but two distinct base flow end-members where the ion concentrations are higher.

Single straight-line binary-mixing plots for Mg^{2+} and Cl^- and Mg^{2+} and HCO_3^- show that there is one base flow and one storm flow end-member components; binary-mixing plots for the other solutes show that there are two base flow components and one storm flow component. This is best explained by the flushing of pre-event (old) water into the stream after a rain event. The binary mixing relations are best explained as two

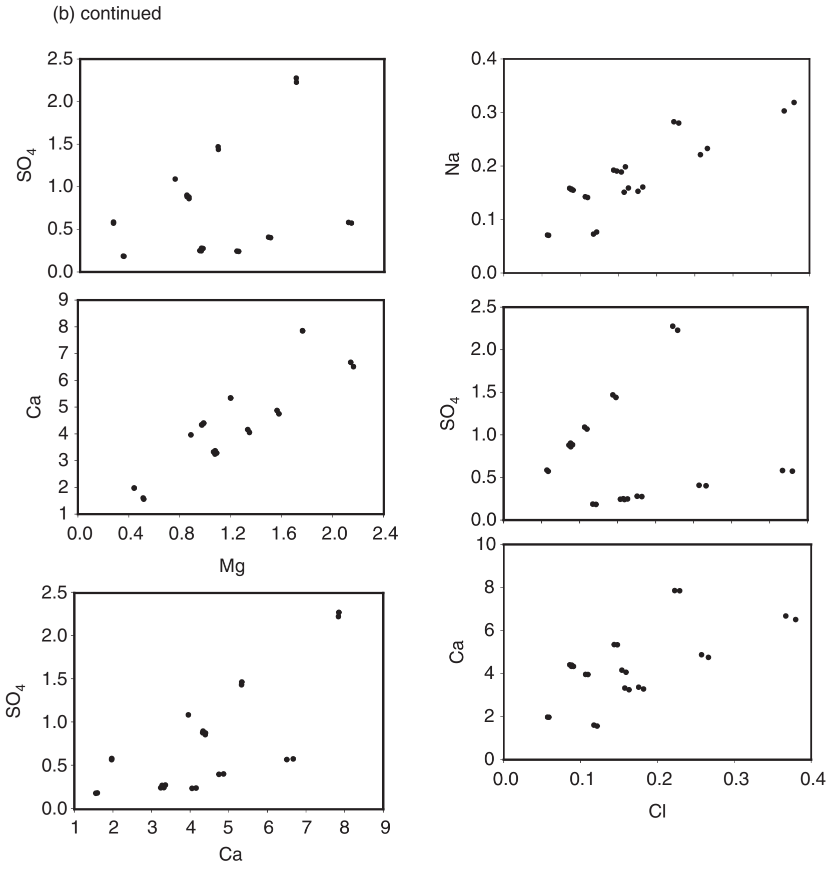

Figure 33.6. Continued

end-members (overland/shallow subsurface and runoff) being present during both storm and base flows with a third end-member, groundwater, only influencing stream water chemistry during true base flow. Ion concentration ratios are similar for overland/shallow subsurface flow and groundwater because of the lithologic similarities where these waters flow. This would also explain why the frequency percentage of the three end-members combination (33.33%) was close to the percentage of the overland/shallow subsurface flow and runoff end-member combinations (41.67%). Although the spring from which groundwater collected was not as close to the headwaters as the other end-members, its chemistry must be similar to the overland/shallow subsurface flow closer to the headwaters for it be identified by EMMA as a discrete end-member.

Runoff from the shales is a significant contributor to the chemistry of the surface water during storm flow. This means that weathering products from black shales are being contributed to the surface waters of the Begley Creek and Cove Creek.

33.5. Conclusion

The PCA determined that two principal components can account for the majority but not all of the variation in the surface water chemistry data. Given that the number of end-members is equal to the number of principal components plus one means that mixing of three discrete end-member sources are required to explain the mixing patterns observed (ternary mixing). Major ion relationships and discharge data suggest that the majority of variation in stream water chemistry of the black shale draining streams can be explained by binary conservative mixing of two end-member components; however, the identity of these end-members change between storm and base flow. During storm flow, the surface water chemistry represents mixing of runoff and overland/shallow subsurface waters. During base flow, groundwater and overland/shallow subsurface waters mix resulting in chemistries distinct from storm flow. In this way, three end-members are required to explain the mixing pattern observed. The individual contributions of these end-members vary between storm and base flow conditions. Runoff from the black shale outcrop does contribute to the surface water chemistry but it is lessened during base flow. The contribution of black shale runoff to surface water chemistry through the hydrograph has implications regarding the potential loading of metals and organic matter into the streams from mechanical and chemical weathering.

The end-members used in this study are not ideal in that runoff water samples contain precipitation as well black shale runoff. Overland/shallow subsurface waters included a mixture of pre-event soil water and hyporheic water. Since waters in intimate contact with shales have been determined to be significant contributors to surface water chemistry future studies will elucidate the role of the hyporheic zone and soil water in the delivery of metals to the streams. Future studies to determine how rock-weathering products, especially metals, are transformed in the hydrograph are warranted. This involves resolving the end-member components determined here and quantifying the contributions of increased precipitation, changes in storm runoff and how metal species are transformed as they move through the stream.

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