GEOCHEMICAL COMPARISON OF KARST AND CLASTIC SPRINGS IN THE APPALACHIAN VALLEY & RIDGE PROVINCE, SOUTHEASTERN WV AND CENTRAL PA

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Abstract

The Appalachian Valley and Ridge (V&R) Province extends over 11 states and is an essential water source for those states and further downstream. The regional geology is complex due to tectonic forces followed by differential erosion. More resistant clastic rocks, typically sandstones and mixed shales, form the ridge tops and mountain flanks while carbonates underlie the valleys. The carbonate units have been the focus of most of the hydrogeologic research in the V&R, although the clastic units are essential in creating headwater streams, recharging the carbonate aquifers, and sustaining base flow. These streams often recharge the more-studied karst aquifers via direct input at sinkholes at the clastic-carbonate contact. Furthermore, the high-quality water from the clastic springs make them valued sources by private landowners, public water supplies, and bottled water companies.

In this study, we compare the geochemistry of different types of springs on and near Peters Mountain in Monroe County, WV along with additional data on clastic springs from central PA and northcentral WV. More than 250 springs have been mapped in the ~225 km^2 study area on and adjacent to Peter's Mountain. Five representative springs are sampled approximately monthly and 13 springs are continuously logged for temperature. Six clastic springs in WV and PA were sampled and monitored for comparison to the Monroe County springs. In general, the sandstone and clastic-sourced springs are smaller and more ephemeral than the limestone springs; their waters have low pH (4.0-6.0), low electrical conductivity (21 to 83 µS/cm), and low concentrations of coliform and E. coli bacteria. These springs flow from sandstones and shales of the Juniata and Tuscarora formations in PA and the Conemaugh Formation in northern WV. Springs flowing from the Martinsburg (Reedsville) Formation on the flanks of Peters Mountain are similar to the other clastic springs but have higher pHs and electrical conductivities due to the presence of interbedded carbonate layers in the shale. Temperatures in these clastic springs range from highly consistent to highly variable. In contrast, the carbonate valley springs have higher pH (6.28 to 8.36), higher electrical conductivity (1,000 to 1,700 µS/cm), and higher concentrations of bacterial indicators. Although the clastic springs along Peter's Mountain have Ca and Mg concentrations similar to the carbonate springs, they can be distinguished by higher Ca/Mg mole ratios.

Introduction

The Valley and Ridge (V&R) physiographic province of the Appalachian Mountains plays a key role in supplying water to downstream users. The province covers <3% of the land area in the contiguous U.S. but extends over 11 states (Figure 1). The streams and springs of the V&R contribute water to downstream communities providing water to more than 13% of the U.S. population. These waters are critical resources for domestic, agricultural, commercial, and industrial use.

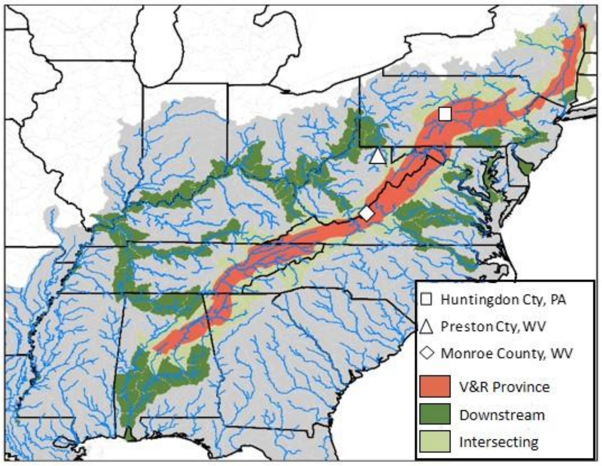

Figure 1. *The V&R (red) with downstream and intersecting USGS HUC8 watersheds (green). The regional locations for the three study sites are indicated.*

The V&R region is structurally and stratigraphically complex; differential erosion has resulted in ridges defined by resistant clastic rocks and valleys underlain by the more soluble carbonate limestones and dolomites. The higher-elevation clastic rocks include fractured sandstones on the ridge tops and mixed-shale units often found on the ridge flanks or in high-elevation valleys. Much of the hydrogeologic research in the V&R has focused on case studies or on the carbonate units. However, clastic rock units also play an essential role in creating headwater streams, recharging the carbonate aquifers, sustaining baseflow, supporting ecosystems, and providing water supplies for private landowners and small towns. The differences between the two spring types also has implication for ecosystems: the different water chemistries support different faunal assemblages (Glazier 1991; Glazier and Gooch 1987).

Although past studies provide critical information and approaches to studying water flow in the V&R, they are almost completely focused on carbonate aquifers (Shuster and White 1971) and pay little attention to the clastic-sourced waters that help recharge the carbonate zones. Jacobson and Langmuir (1974) included the sandstone recharge waters in their study but only near the carbonate formations and with the purpose of illustrating why sinkholes develop when the aggressive waters reach the formational contacts.

Springs and ground water in the clastic units of the V&R have had little attention. Hobba et al. (1979) identified V&R springs issuing from clastic formations but focused on thermal waters. McColloch (1986) inventoried springs in WV but only included larger springs. According to that report, only 31 springs are reported in the study area (27 limestone, 2 shale, and 2 sandstone); although more than 250 springs have now been identified and mapped.

Studies of the hydrogeology in Monroe County WV provide a more detailed background into the distribution of springs relative to rock units. Richards (2006) conducted hydrological and geochemical characterization of clastic springs on the ridge and flanks of Peter’s Mountain plus carbonate springs in the adjacent valley in WV. Over 250 springs have mapped in the region. In general, the lower elevation carbonate springs were less common and had higher discharge. Chemically, the lower springs had much higher specific conductivities (SCs) and concentrations of measured ions. Water flowing from the clastic units was chemically similar to the regional precipitation. In a report to the WV Department of Public Health, Dean and Kulander (1992) mapped the geology, fractures and springs in the Gap Mills area. They concluded that groundwater flow from the clastic units was a critical component to recharging the lower carbonate aquifers and that the upper system is tied to fracture and bedding plane orientations.

The purpose of this study is to compare between the carbonate and clastic springs based on screening parameters, major ion concentrations, and temperature variability.

Methods

Spring Locations

The main study site is the V&R region of eastern Monroe County in southeastern WV, selected because the relief provided by Peters Mountain allows access to springs from all rock units (Table 1, Figure 2). The top of Peters Mountain is formed by the highly resistant Silurian Tuscarora Formation quartzite. The western flanks of the mountain are underlain by the Martinsburg and Juniata Formations and the valley by the Moccasin Limestone, the Black River and St. Paul Limestones, and the Beekmantown series (Dean and Kulander 1992; (McDowell and Schultz 1990). The area is bounded to the west by the St. Clair Thrust Fault. The springs include thermal mineral springs along the thrust fault, carbonate springs in the valley, and clastic-sourced springs on the mountain flanks and near the ridges. The relief over the study area is ~550 meters. The highest elevation spring, APPL, is located near the ridge top and flows from the Tuscarora Fm. Elevations can be used as a local proxy for rock type because strike approximates topographic contour and the most resistant units are found at the highest elevations.

Table 1. *Sample descriptions*

Location	*Geology*	*Sample IDs*
Monroe County WV	Tuscarora Fm sandstone, near ridge-top (illustrated with the WV and PA sandstone springs)	APPL
	Mountain flanks in the Martinsburg Fm (illustrated as clastic springs)	BROY[1], ECH[1], GMILL[2,3], HANCK[2], LUGER[2], OLDU[3], OLSON[1]
	Valley carbonates within or on the contact of the Beekmantown Series (carbonate springs)	CRABT, DROPL, HATCH[3], MEFF, ZEN[1]
	Streams draining valley	QHAN, QIND, QRCH, QSEC, QSWT
Preston County WV	Sandstones and shales, Conemaugh Fm	RBSH, RBWG
Huntingdon County PA	At the contact of the Old Port Fm (sandstone) and the Onondaga Fm (shale)	HCOLD, HDUBB1

[1]Private water supply; [2]Part of a public water supply; [3]Used commercially for bottled water or a fish hatchery. Stratigraphy based on geology maps (Nicholson et al. 2007) and USGS Bulletin 1839-E (McDowell and Schultz 1990).

Additional major ion data was obtained for clastic springs located in northcentral WV and central PA (Figure 2b, c). Two springs are located on a farm in Preston County WV. This is in the High Plateau Province to the west of the V&R and is underlain by the gently-folded sandstones and shales of the Conemaugh group (Nicholson et al. 2007). Two springs from the central PA V&R are included. Both springs are located in Huntingdon County and discharge from a synclinal structure in the along the contact between Old Port (sandstone) and the Onondaga (shale) Formations (Dicken et al. 2008).

The assignment of a spring to a geologic unit is challenging for three reasons: (1) the geologic maps may not have sufficient accuracy at the necessary scale; (2) the location of the spring does not necessarily represent the geology of its entire catchment basin; and, (3) geologic contacts are often located by the springs and therefore selecting the geologic unit for a spring from the map can be a circular process. This is particularly true in areas like the V&R where there is limited rock exposure.

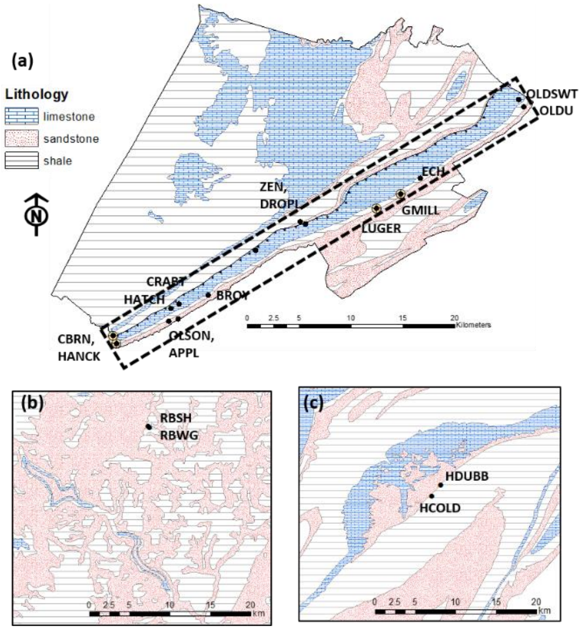

Figure 2. *Locations of sampling sites and bedrock geology. (a) Monroe County WV with the Peters Mountain area boxed; (b) Preston County WV springs; (c) Huntingdon County PA springs.*

Water Quality Measurements

A calibrated YSI Pro multi-meter was used to measure pH, temperature and SC at the field site. Grab samples were collected for alkalinity and major ions. Alkalinity was determined by titration using either a Hach Digital Titrator and calibrated pH meter or a Hanna Instruments autotitration system. A Gran titration with pH endpoints of 4.2 and 3.9 was used. Major elements were measured using an ICP-OES on filtered (<0.45 µm) and acid-preserved samples. Anions Cl, SO_4 and NO_3 were measured using ion chromatography on filtered samples.

Continuous Data Logging

ONSET HOBO U22 data loggers were placed in 13 springs in Monroe County plus 4 additional sandstone springs in Preston and Huntingdon Counties. Temperature is recorded at 10 to 30 minute intervals.

Results and Discussion

Water Chemistry

All of the Monroe County carbonate and Martinsburg Fm clastic springs can be classified as having calcium-carbonate waters (Figure 2). The stream waters fed by Peters Mountain are comparable to and overlap with both the carbonate and clastic spring water chemistries.

The sandstone springs have proportionally higher magnesium and sulfate concentrations than do the other springs and may discharge magnesium-carbonate or magnesium-sulfate waters.

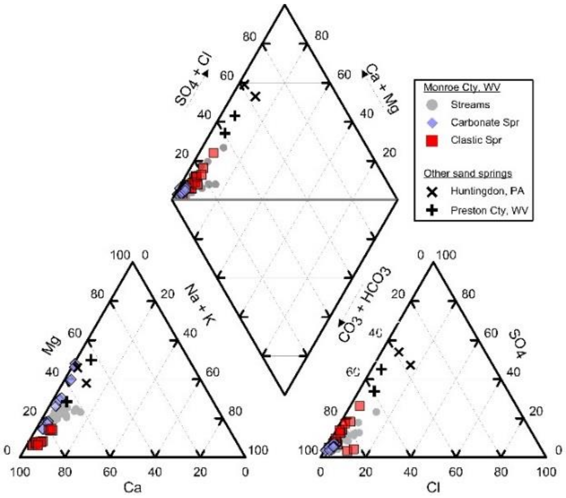

Figure 2. *Piper diagram for all water samples collected*

The Monroe County springs have overlapping pH ranges (Figure 3) but the carbonate spring waters generally have higher average SCs than do the clastic spring waters. The sample with the highest SC (ZEN) is likely to discharge dolomitic water. As expected, the stream water chemistry is more variable than the spring water chemistry.

The sandstone springs have distinctly lower pHs and SCs than the other springs. The three V&R springs (HCOLD, HDUBB, and APPL) have pHs between 4 and 5; the two Plateau springs (RBWG, RBSH) have slightly higher pHs (5-6).

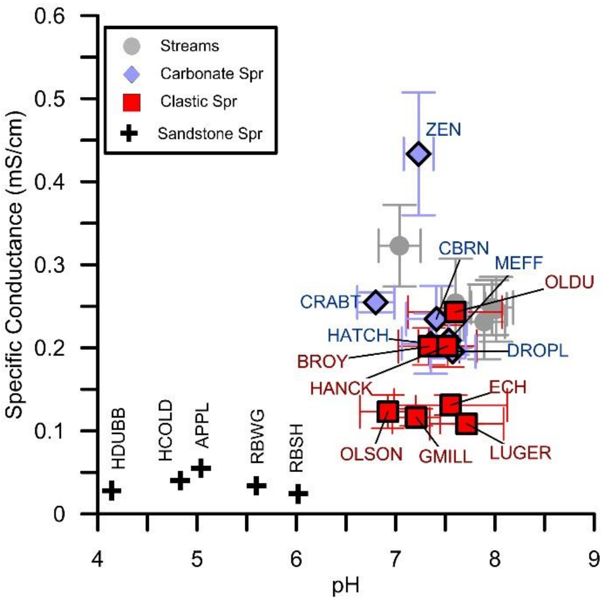

Figure 3. *Field screening parameters measured in springs and stream samples. Error bars are for one standard deviation; there are no error bars for the sandstone springs because they have only been sampled once to date.*

The Ca concentrations in the sandstone spring waters are much lower than detected in the other waters (Figure 4); however, the range of Ca concentrations in the Monroe County carbonate and clastic springs are similar to each other. The similar Ca concentrations between these groups can be attributed to carbonate units in the Martinsburg Fm. In its lower portions, the Martinsburg Fm is a fine-grained limestone that grades upward into interbedded calcareous shales and siltstones; regionally, the lower portion of the Martinsburg Fm is called the Trenton Limestone and the upper portion the Reedsville Shale (McDowell and Schultz 1990).

The Ca/Mg molar ratio is a better indicator of the spring water source than the individual concentrations (Figure 4). The clastic spring waters had higher Ca/Mg ratios (5.66 – 14.9, mean 11.5) than did the carbonate springs (1.12 – 5.65, mean 3.2). Higher ratios indicate the presence of purer limestone while lower ratios indicate dolomite-sourced waters. The spring with lowest ratio (1.1) is Zenith Spring (ZEN) supporting the interpretation that this spring discharges from dolomite.

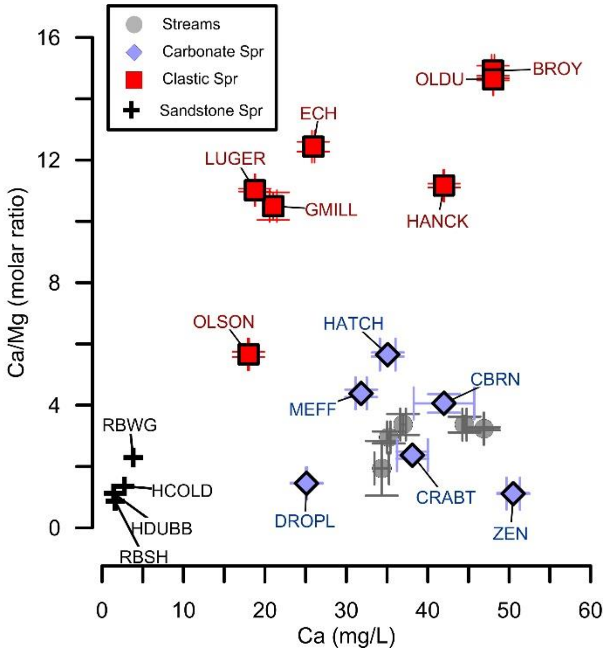

Figure 4. *Ca vs Ca/Mg ratio with error bars for one standard deviation. There are no error bars for the cold springs because they have only been sampled once.*

Temperature Fluctuations

The variability in spring water temperature during storms is an indicator of how rapidly the spring is recharged from rainwater. Based on the available data from 2017, all three groups of springs included had members that were highly consistent and members that varied significantly with storms and/or seasons (Figure 5, Table 2).

Of the sandstone springs, the most variable is RBSH. This spring is located near the top of a sandstone knob and likely has a small catchment area. The nearby spring RBWG is located in an erosional channel at lower elevation. The two springs in Huntingdon County PA (HDUBB and HCOLD) map on the same geologic contact at near the same elevation. Their different thermal responses may be related to the exact location of the contact but there is little nearby rock exposure to evaluate that factor. Given the stream location for the logger at HCOLD, it is possible that the temperature spike may be due to overland flow from a storm.

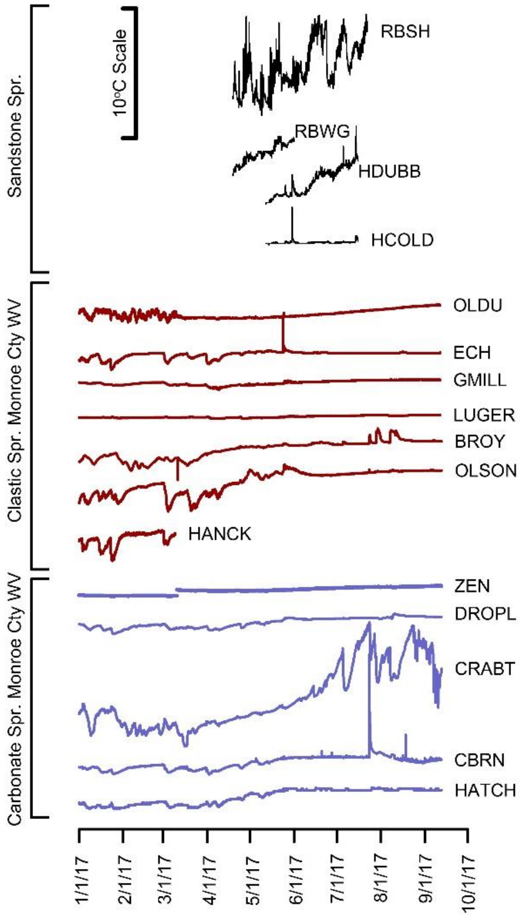

Figure 5. *Temperature logger data. Missing and offset data due to logger problems. Monroe County springs are arranged within each group from northeast (top) to southwest (bottom). All data are plotted using the same scale.*

Both groups of springs in Monroe County include locations with very consistent and much more variable temperatures. For the clastic springs in the Martinsburg Fm, there is a general trend between elevation and the temperature variability in 2017. This may be because the higher elevation maps to the upper layers of the Martinsburg that are less calcareous; however, it is also possible that there is sufficient change in the Martinsburg lithology from northeast to southwest to account for these variations. The clastic springs with the least variable temperatures are located in the northeast or central region of the study area while the most variable springs are located in the southwest region (Figures 2 and 5, Table 2).

Table 2. *Elevation and temperature data for locations illustrated in Figure 5.*

Location	*Site ID*	*Elevation, m*	*Average Temp, C*	*RSD Temp, %*
Clastic Springs Monroe County, WV	BROY	817	11.0	6.2
	ECH	876	10.2	2.5
	GMILL	874	10.1	1.8
	HANCK	782	9.94	5.4
	LUGER	907	10.2	0.8
	OLDU	913	11.3	2.7
	OLSON	847	9.94	8.9
Carbonate Springs Monroe County, WV	CRABT	645	12.0	19.5
	CBRN	583	11.5	5.4
	DROPL	741	10.9	3.5
	HATCH	636	11.3	5.1
	ZEN	667	12.0	0.4
Preston County, WV	RBSH	---	13.5	14
	RBWG	---	10.9	6.6
Huntingdon County, PA	HCOLD	---	10.9	1.2
	HDUBB	---	11.7	8.9

RSD = (standard deviation)/ (mean) expressed as a percent. Data logger lost at MEFF spring. Data for ZEN begin after change in logger on 3/10/17

The ability of each spring system to transmit water needs to be considered in the context of recharge style, the ability to transfer water into and out of storage, and the overall size of the catchment area (Figure 6). The clastic springs in this study, such as RBSH, may not have sinkholes or conduits but the small catchment basin may control the spring response.

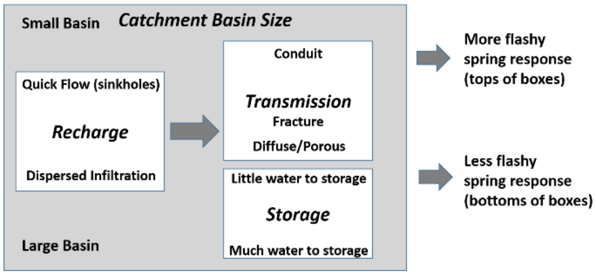

Figure 6. *Conceptual model for spring catchment hydrology.*

Summary

The Appalachian V&R Province hosts a wealth of springs; although most of the research to date has focused on the carbonate springs, the smaller clastic and sandstone springs also play a critical role as headwater sources and for ecosystem support. The clastic springs studied in this project had similar ranges of chemistry and thermal fluctuations as the carbonate springs suggesting that the conceptual framework used for carbonate springs is also useful for these smaller and more ephemeral springs.

Additional data are needed to better understand spring chemistries and storm responses. Better geologic mapping is critical; if springs are used to map geologic contacts then the resulting geologic maps may not be provide independent data about the source of the water. Natural tracers that can “fingerprint” the different water sources need to be identified to be able to distinguish between catchment areas and to quantify the input of the clastic spring waters into the carbonate aquifers.

Acknowledgements

This research is funded by a WVU Community Engagement Grant, an experiment.com crowd-sourcing initiation, and the WVU Appalachian Freshwater Initiative (funded by the National Science Foundation under Award Number 1458952). Additional field support provided by members of the Indian Creek Watershed Association.

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