GEOCHEMICAL COMPARISON OF KARST AND CLASTIC SPRINGS IN THE APPALACHIAN VALLEY & RIDGE PROVINCE, SOUTHEASTERN WEST VIRGINIA AND CENTRAL PENNSYLVANIA

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Abstract

The Appalachian Valley and Ridge (V&R) Province extends over 11 states and is an essential water supply. The regional geology consists of more resistant clastic rocks, typically sandstones and mixed shales, which form the ridge tops and mountain flanks, and carbonate rocks that underlie the valleys. In this study, we report the geochemistry of different types of springs on and near Peter's Mountain in Monroe County, WV. More than 250 springs have been mapped in the ~225 km² study area on and adjacent to Peter's Mountain. These data are compared with preliminary data collected from sandstone-sourced springs from central PA and northcentral WV. Six sandstone springs in WV and PA were sampled and monitored for comparison to the Monroe County springs. Springs were grouped by geologic and geomorphologic location: Group 1: sandstone-sourced springs in WV and PA; Group 2: springs in the Martinsburg Formation on the western flank of Peter's Mountain; and, Group 3: springs in the carbonate valley west of Peter's Mountain. In general, Group 1 springs are smaller and more ephemeral than the other groups; their waters have low pHs (4.1–6.0), low specific conductivities (24 to 55 $\mu\text{S}/\text{cm}$), and low concentrations of dissolved ions. Group 2 springs are also small and ephemeral but have higher pHs (6.7–8.4) and specific conductivities (73–308 $\mu\text{S}/\text{cm}$) due to the mixture of shales and carbonates in the source formation. Temperatures in these springs range from highly consistent to highly variable. Although the Group 2 springs along Peter's Mountain have Ca and Mg concentrations similar to the Group 3 carbonate springs, they can be distinguished by higher Ca/Mg mole ratios.

In contrast, Group 3 springs have higher pHs (6.6–8.4) and higher specific conductivities (144–750 $\mu\text{S}/\text{cm}$).

Introduction

The Valley and Ridge (V&R) physiographic province of the Appalachian Mountains plays a key role in supplying water to downstream users. This province spans from Alabama to Vermont and contains abundant springs and streams throughout its extent (Figure 1). The springs of the V&R are critical resources for domestic, agricultural, commercial, and industrial use.

The V&R region is structurally and stratigraphically complex; differential erosion has resulted in ridges

Figure 1. The V&R (shaded green) with locations of the three study sites.

defined by resistant clastic rocks and valleys underlain by more soluble carbonate limestones and dolomites. The clastic rocks include fractured sandstones on the ridge tops and mixed shale-carbonate units typically 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, other rock units also play an essential role in creating headwater streams, recharging the carbonate aquifers of the lower valleys, sustaining baseflow, and supporting ecosystems. Furthermore, the high-quality water from the ridge and flank springs make them valued sources by private landowners, public water supplies, and bottled water companies. The differences between the 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; Herman et al., 2009; Loran and Reisch, 2012) and pay little attention to other spring types that contribute to recharge of 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 sandstone and shale 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 large springs. According to that report, only 31 springs are reported in the Monroe County study area (27 limestone, 2 shale, and 2 sandstone); although more than 250 springs have now been identified and mapped (Indian Creek Watershed Association, 2017; Richards, 2006).

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 springs on the ridge and flanks of Peter's Mountain plus carbonate springs in the adjacent

valley in WV. In general, the valley carbonate springs were less common and had higher discharge. Chemically, the valley springs had much higher specific conductivity (SC) and concentrations of measured ions. Water flowing from the ridge and flank units had lower SCs and fewer dissolved ions. 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 ridge and flank 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 springs based on screening parameters, major ion concentrations, and temperature variability. The data reported are based on an ongoing watershed study in Monroe County, WV (Bausher, in progress); these results are compared with a limited set of preliminary data collected from sandstone springs outside of Monroe County.

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). The top of Peter's 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). According to McDowell and Shultz (1990), the Martinsburg Formation/Series consists of the Trenton limestone at the base that grades upward into the interbedded shale, calcareous siltstone and sandstones of the Reedsville shale. The exact location of the springs relative to the lithologic contact is unknown; Monroe County is currently being remapped by the U.S. Geological Survey (Doctor, USGS, pers. comm.). The Monroe County study area is bounded to the west by the St. Clair Thrust Fault. The relief over the study area is ~550 meters.

Springs and streams are grouped for this study based on geologic location and follow the scheme used by Richards (2006) in Monroe County (Table 1, Figure 2):

Location and Group		Description of Location	Sample IDs
Monroe County WV (Western side of Peters Mountain)	1	Tuscarora Fm sandstone, near the ridge-top	APPL
	2	On the flanks of Peters Mountain in the Martinsburg Fm	BROY1, ECH1, GMILL2,3, HANCK2, LUGER2, OLDU3, OLSON1
	3	Valley carbonates within or on the contact of the Beekmantown Series	CRABT, DROPL, HATCH3, MEFF, ZEN1
	Stream	Streams draining the valley at the base of Peters Mountain	QHAN, QIND, QRCH, QSEC, QSWT
Preston County, WV	1	Underlain by the gently-folded sandstones and shales of the Conemaugh group in the Appalachian Plateau (Nicholson et al. 2007).	RBSH, RBWG
Huntingdon County PA	1	In a synclinal structure along the contact between Old Port (sandstone) and the Onondaga (shale) Formations (Dicken et al. 2008).	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). Location coordinates are not included to protect the security of the public and private water supplies.			

Table 1. Sample location descriptions.

- Group 1 springs flow from sandstone units; Two of the springs (RBSH, RBWG) are located on the Appalachian Plateau and are provided for comparison with V&R springs.
- Group 2 springs flow from the mixed carbonate and siliciclastic units of the Martinsburg Formation on the western flanks of Peter's Mountain in Monroe County.
- Group 3 springs flow from the Ordovician carbonate units located within the valley west of Peters Mountain in Monroe County.
- Stream includes the five streams that drain the valley at the base of Peter's Mountain in Monroe County.

The assignment of a spring to a geologic unit is challenging for several 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.

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 Ca, Mg, Na, and K were measured using an ICP-OES on filtered (<0.45 µm) and acid-preserved samples. Anions Cl, SO₄ and NO₃ were measured using ion chromatography on filtered samples. More elements were analyzed but are not included in this paper. Only data with charge balance errors of <10% were included in this study. The proportions of major ions are illustrated on a Piper Diagram (Figure 3).

Continuous Data Logging

ONSET HOBO U22 data loggers were placed in 12 springs in Monroe County plus 4 additional sandstone springs in Preston and Huntingdon Counties. Data loggers in Monroe County were installed in the fall of 2015 while loggers in Preston and Huntingdon Counties were installed in April 2017. Monroe County data were truncated for compatibility with the Preston and Huntingdon County data. Temperature is recorded at 10 to 30 minute intervals.

Results and Discussion

Water Chemistry

Average values for field parameters and water chemistry were used to compare the springs (Table 2). Group 1 springs have proportionally higher magnesium and sulfate concentrations than do the other springs and may discharge magnesium-carbonate or magnesium-sulfate waters (Figure 3). Group 2 and Group 3 springs can be classified as having calcium-carbonate waters (Figure 3). The stream waters fed by Peter's Mountain are comparable to and overlap with both Group 2 and 3 springs. Group 1 springs have distinctly lower pHs and SCs than the other springs (Figure 4). 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 2. Locations of sampling sites and bedrock geology type. (a) Monroe County WV with the Peters Mountain area boxed; (b) Preston County WV springs; (c) Huntingdon County PA springs.

Group 2 springs have generally lower SCs than do Group 3 springs. It is possible that the Group 2 springs associated with the Martinsburg Formation likely also collect and discharge surface water from colluvium deposits upslope thereby diluting the carbonate signature. Group 3 springs generally have higher average SCs than the other groups. The sample with the highest SC (ZEN, 750 $\mu\text{S}/\text{cm}$, not

shown on Figure 4) discharges from dolomitic water. Additional evidence for this is seen in low Ca/Mg ratios and consistent water temperature (discussed later). As expected, the stream water chemistry is highly variable and overlaps with both Groups 2 and 3.

The Ca concentrations in Group 1 are much lower than detected in the other waters (Figure 5); however the Group 2 and Group 3 Ca concentrations are generally within the same range of values (Figure 5, Table 2). With the exception of OLDU, there is a trend within the Group 2 springs where the lower elevation springs contain higher concentrations of Ca (Figure 6).

The Ca/Mg molar ratio is a better indicator of the spring water source than the individual concentrations (Figure 5). Group 2 springs had higher Ca/Mg ratios (5.66–14.9, mean 11.5) than the Group 3 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. Olson Spring (OLSON, Group 2) has a Ca/Mg molar ratio closer to that of Group 3 springs, potentially due to a greater input

Figure 3. Piper diagram for water samples collected.

Group & ID		n	Temp (C)	pH	SC (μS/ cm)	Alk (mg/L CaCO ₃)	Ca (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Cl (mg/L)	SO4 (mg/L)
Group 1	APPL	1	15.60	5.04	55	0.94	2.04	0.66	1.08	0.82	1.28	7.05
	HCOLD	1	10.60	4.83	40	6.95	2.73	<1	1.22	0.64	2.20	8.63
	HDUBB	1	9.96	4.14	28	5.48	1.44	<1	0.78	0.09	0.77	7.40
	RBSH	1	11.20	6.02	24	9.89	1.60	<1	1.11	0.28	0.82	5.41
	RBWG	1	9.00	5.60	34	9.52	3.81	<1	1.01	0.43	0.58	8.17
Group 2	BROY	3	10.59	7.25	237	124	49.7	0.48	1.92	1.26	1.82	8.66
	ECH	2	9.60	7.56	131	67.3	25.9	0.36	1.26	0.90	1.29	4.07
	GMILL	3	9.26	7.30	116	52.3	20.9	0.46	1.17	1.11	1.05	5.87
	HANCK	2	9.97	7.51	182	101	42.7	0.44	2.31	1.47	1.88	7.26
	LUGER	2	8.95	7.72	109	45.3	18.8	0.40	1.03	1.03	0.94	6.91
	OLDU	2	10.29	7.60	243	124	48.0	0.55	1.99	2.75	11.5	5.27
	OLSON	3	9.23	7.06	100	46.5	18.7	0.64	2.02	1.45	1.02	8.96
Group 3	CBRN	1	11.00	6.75	166	96.9	38.7	0.73	5.40	1.03	1.53	6.91
	CRABT	5	11.32	6.85	272	135	40.7	1.01	10.3	1.30	1.68	7.85
	DROPL	3	10.44	7.49	226	116	28.5	0.77	11.4	0.86	2.00	6.34
	HATCH	2	10.55	7.38	165	95.7	35.1	0.68	3.76	0.98	2.02	7.19
	MEFF	2	9.87	7.61	185	95.2	31.8	0.62	4.40	1.21	2.39	5.41
	ZEN	4	11.14	7.23	498	217	50.5	1.14	27.4	0.60	1.16	9.01
Stream	QHAN	4	11.90	7.46	189	91.8	29.4	2.40	6.33	4.10	6.58	10.6
	QIND	2	9.20	8.07	183	102	33.4	0.96	6.58	2.71	3.50	8.82
	QRCH	3	10.47	7.59	194	99.1	35.0	1.83	6.85	3.71	5.85	12.0
	QSEC	4	11.13	7.94	193	105	35.9	1.44	6.57	2.02	3.52	4.39
	QSWT	4	11.28	7.15	297	146	47.2	1.78	8.92	2.65	4.20	11.9

Table 2. Average values for field data and major ion chemistry.

Notes: Groups as defined in text; n=number of samples for the average values. SC=Specific Conductivity; Alk=Alkalinity. Only complete datasets with charge balance errors <10% are included.

from carbonate sources. Additional data will be collected to clarify this difference.

Temperature Fluctuations

Temperature variations at the springs are highly influenced by the nature of the recharge and its transmission through the system (Luhmann et al., 2011). The balance between advective and conductive heat transport is a function of the amount of water and heat in the system and depends on porosity, thermal characteristic of the rock, flow rate, and the extent of conduits and fractures (Benderitter and Roy, 1993; Manga, 2001). Thus, the variability in spring water temperature is an indicator of how rapidly the spring is recharged from rainwater. Consistent temperatures indicate longer residence times and “flashy” temperature responses indicate shorter residence times.

Based on the available data from 2017, all three groups of springs included members that were highly consistent and members that varied significantly with storms and/or seasons, similar to the thermal patterns identified by Luhmann et al. (2011); (Figure 7, Table 3).

Of the Group 1 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 location for the logger at

Figure 4. Average field screening parameters measured in springs and stream samples. The high value for ZEN (750 $\mu\text{S}/\text{cm}$) is not included on the graph.

HCOLD, it is possible that the temperature spike may be due to overland flow from a storm.

Group 2 and Group 3 springs include locations with very consistent and more variable temperatures. For the Group 2 springs, there is a general trend between elevation and the temperature variability in 2017. This may be because the

Figure 5. Average Ca vs Ca/Mg ratios for springs and comparison streams.

Figure 6. Average Ca concentrations and elevations for the Group 2 springs.

higher elevation corresponds to the less calcareous layers of the Martinsburg Fm. This interpretation is supported by the fact that the higher elevation Group 2 springs contain lower concentrations of Ca (Figure 6); however, it is also possible that there is sufficient change in the Martinsburg lithology from northeast to southwest to account for these variations. The Group 2 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 3 and 7, Table 3).

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 springs located on the ridge tops and flanks also play a critical role as headwater sources and for ecosystem support. The smaller springs studied in this project had 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. The springs flowing from sandstone units (Group 1) are generally low in pH, SC and dissolved ions; the (Group 2) springs flowing from the Martinsburg Fm on the valley flanks may be similar to the carbonate springs or discharge a more dilute chemistry. The range of behaviors and chemistries of the Group 2 springs may be tied to changes in the formation either vertically or spatially.

Additional data are needed to better understand spring chemistries and storm responses. Better geologic

Figure 7. Temperature data for locations with dataloggers. All data plotted using the same scale. Within each group, the plots are organized by elevation with the highest elevation spring at the top and the lowest elevation spring at the bottom.

mapping is critical; if springs are used to map geologic contacts then the resulting geologic maps may not 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

Location	Site ID	Elevation, m above MSL	Average Temp, C	RSD Temp, %
Group 2	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
Group 3	OLSON	847	9.94	8.9
	CRABT	645	12.0	19.5
	CBRN	583	11.5	5.4
	DROPL	741	10.9	3.5
	HATCH	636	11.3	5.1
Group 1 (Preston County, WV)	ZEN	667	12.0	0.4
	RBSH	548	13.5	14
Group 1 (Huntingdon County, PA)	RBWG	524	10.9	6.6
	HCOLD	221	10.9	1.2
Group 1 (Huntingdon County, PA)	HDUBB	221	11.7	8.9

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

Table 3. Elevation and temperature data for locations with data illustrated in Figure 7.

Initiative (funded by the National Science Foundation under Award Number 1458952). Additional field support provided by members of the Indian Creek Watershed Association.

References

- Bausher, E. In progress. Qualitative and Quantitative Analysis of Carbonate Waters in the Peter’s Mountain Region of Monroe County, WV. West Virginia University. MS Thesis.
- Benderitter Y, Roy B. 1993. Flow Characterization Through Heat Transfer Evidence in a Carbonate Fractured Medium: First Approach. *Water Resources Research* 29: 3741–3747.
- Dean SL, Kulander BR. 1992. Geological investigation of Gap Mills spring area, Monroe County, West Virginia.
- Dicken CL, Nicholson SW, Horton JD, Kinney SA, Gunther G, Foote MP, Mueller JA. 2008. Preliminary integrated geologic map databases for the United States: Delaware, Maryland, New York, Pennsylvania, and Virginia. Version 1.1. Open-File Report 2005–1325.
- Glazier DS. 1991. The fauna of North America temperate cold springs: patterns and hypotheses. *Freshwater Biology* 26: 527–542.

- Glazier DS, Gooch JL. 1987. Macroinvertebrate assemblages in Pennsylvania (USA) springs. *Hydrobiologia* 150: 33–43.
- Herman EK, Toran L, White WB. 2009. Quantifying the place of karst aquifers in the ground water to surface water continuum: A time series analysis of storm behavior in Pennsylvania water resources. *Journal of Hydrology* 376: 307–317.
- Hobba WAJ, Fisher DW, Pearson FJJ, Chemerys JC. 1979. *Hydrology and Geochemistry of Thermal Springs of the Appalachians*.
- Indian Creek Watershed Association (ICWA) 2017 Unpublished data.
- Jacobson RL, Langmuir D. 1974. Controls on the quality variations of some carbonate spring waters. *Journal of Hydrology* 23: 247–265.
- Luhmann AJ, Covington MD, Peters AJ, Alexander SC, Anger CT, Green JA, Runkel AC, Alexander EC. 2011. Classification of Thermal Patterns at Karst Springs and Cave Streams. *Groundwater* 49: 324–335.
- Manga M. 2001. Using Springs to Study Groundwater Flow and Active Geologic Processes. *Annual Review of Earth and Planetary Sciences* 29: 201–228.
- McColloch JS 1986. *Springs of West Virginia*, vol V-6A, 50th Anniversary Revised Edition edn. Charleston, WV: West Virginia Geological and Economic Survey.
- McDowell RC, Schultz AP. (1990) Structural and stratigraphic framework of the Giles County area, a part of the Appalachian Basin of Virginia and West Virginia. In: Schultz AP, Rice CL, Schwietering JF, Pohn HA, Purdy TL, Orndorff RC (eds) *Evolution of Sedimentary Basins - Appalachian Basin*. US Geological Survey Bulletin 1839-E, Washington DC, p. 24.
- Nicholson SW, Dicken CL, Horton JD, Labay KA, Foote MP, Mueller JA. 2007. Preliminary integrated geologic map databases for the United States: Kentucky, Ohio, Tennessee, and West Virginia. Version 1.1. Open-File Report 2005–1324.
- Richards BG. 2006. Aqueous geochemistry of springs along Peters Mountain in Monroe County, WV. West Virginia University MS Thesis. 73 p.
- Shuster ET, White WB. 1971. Seasonal fluctuations in the chemistry of limestone springs: a possible means for characterizing carbonate aquifers. *Journal of Hydrology* 14: 93–128.
- Toran L, Reisch CE. 2012. Using stormwater hysteresis to characterize karst spring discharge. *Groundwater* 51: 575–587.