Bedrock Lithologic and Stratigraphic Influences on the Water Quality of Springs in Cameron and McKean Counties, Pennsylvania

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ABSTRACT

Recent research conducted on springs during a routine mapping project led to interesting correlative relationships between the characteristic groundwater of springs and the bedrock formations they flow through. This spring study is to gain a better understanding of bedrock influence on groundwater chemistry in northwest Cameron County and southeast McKean County, Pennsylvania. During geologic mapping of the Norwich and Rich Valley 7.5-minute quadrangles, over 90 springs within the Pottsville Formation (Pp), Waverly Group (MDw), Catskill Formation (Dck), and Lock Haven Formation (Dlh) were inventoried and analyzed for yield, pH, specific conductance, and temperature. Twelve springs had additional laboratory analyses including alkalinity, hardness, sulfate, sulfide, chloride, bromide, mercury, and metals (arsenic, barium, calcium, iron, lead, potassium, magnesium, manganese, sodium, strontium, and vanadium). Water quality results were compared to bulk rock geochemistry and XRD mineralogy to identify unique lithologic properties in each formation and how they affect the water chemistry. General trends observed include acidic waters in the coal-bearing Pottsville Formation transitioning to slightly acidic to slightly alkaline waters by the time the groundwater has percolated to the Waverly Group/Catskill Formation contact; seasonal increases in specific conductance and pH during base-flow conditions in late summer/early autumn; and a groundwater temperature range of 4.5° C (late winter) to 15.5° C (late summer/early autumn). These studies provide groundwater characteristics by geologic formation in a dominantly rural community that depends on groundwater as a drinking water supply. The data from this study provide the private homeowner, well driller, land manager, and land developer information that can inform water-well design/siting, use of springs as a water source, and strategic placement of future infrastructure in the study area.

INTRODUCTION

During routine mapping of the Norwich and Rich Valley 7.5-minute quadrangles' bedrock geology, the author encountered numerous springs which were inventoried and were analyzed on site for water temperature, pH, and specific conductance. A general trend of increasing pH and specific conductance was observed as the water moves from the recharge sites on the top of the mountains to discharge sites on the hillside and valley bottom springs. This is correlated to the bulk rock geochemistry/mineralogy in these formations is changing the groundwater's chemistry. Twelve sites were additionally sampled for lab-quality analysis to determine if other geochemical trends could be observed and to highlight possible naturally occurring contaminants that could be consumed from drinking spring water. Bedrock composition was analyzed by use of core and field samples for mineralogy and geochemical analysis. These results were then compared to the water quality data to identify lithologies and their stratigraphic position that were critical in changing variable water chemistry in the springs. All spring data were entered into the Pennsylvania Groundwater Information System which can be accessed online.

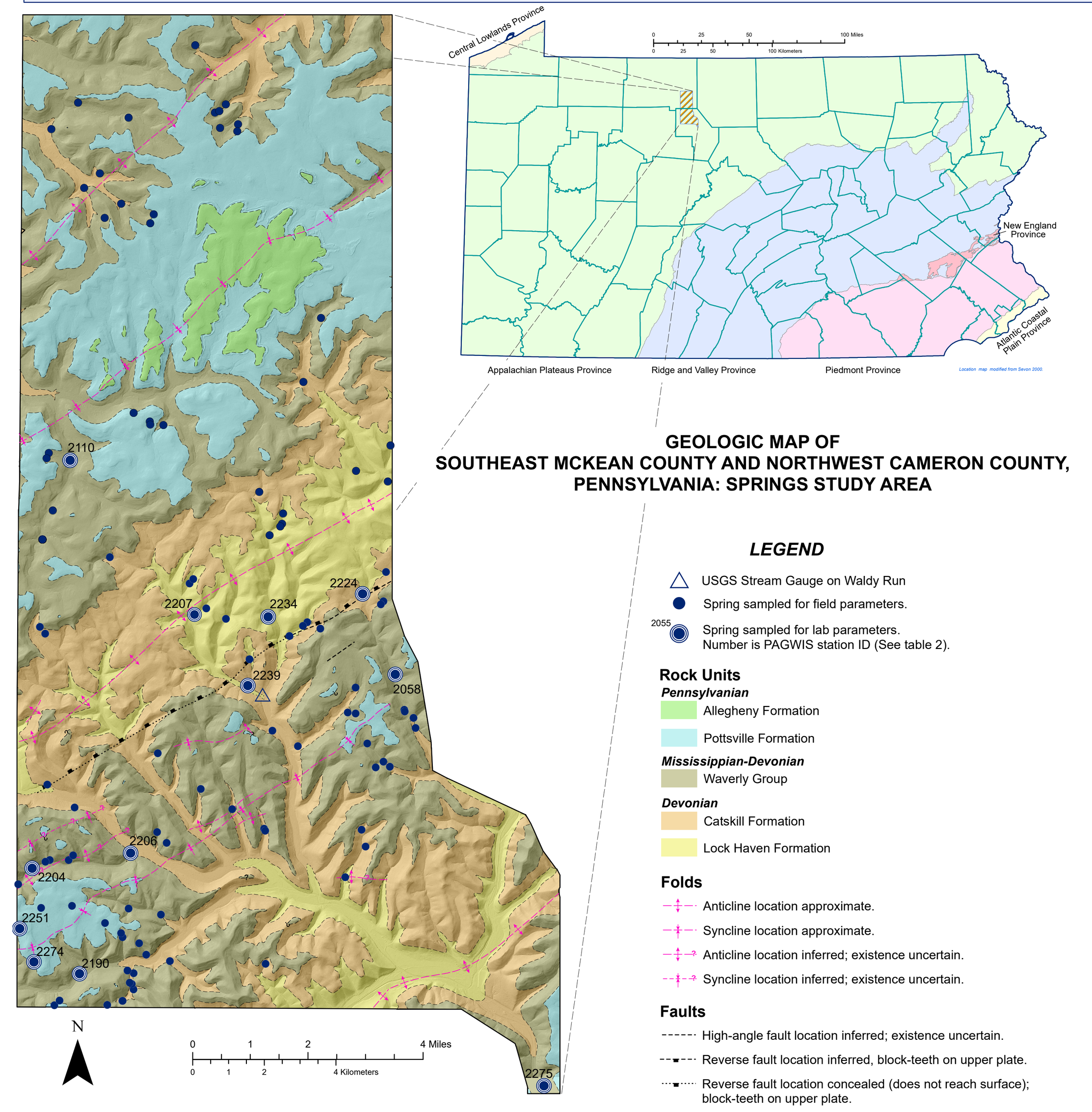
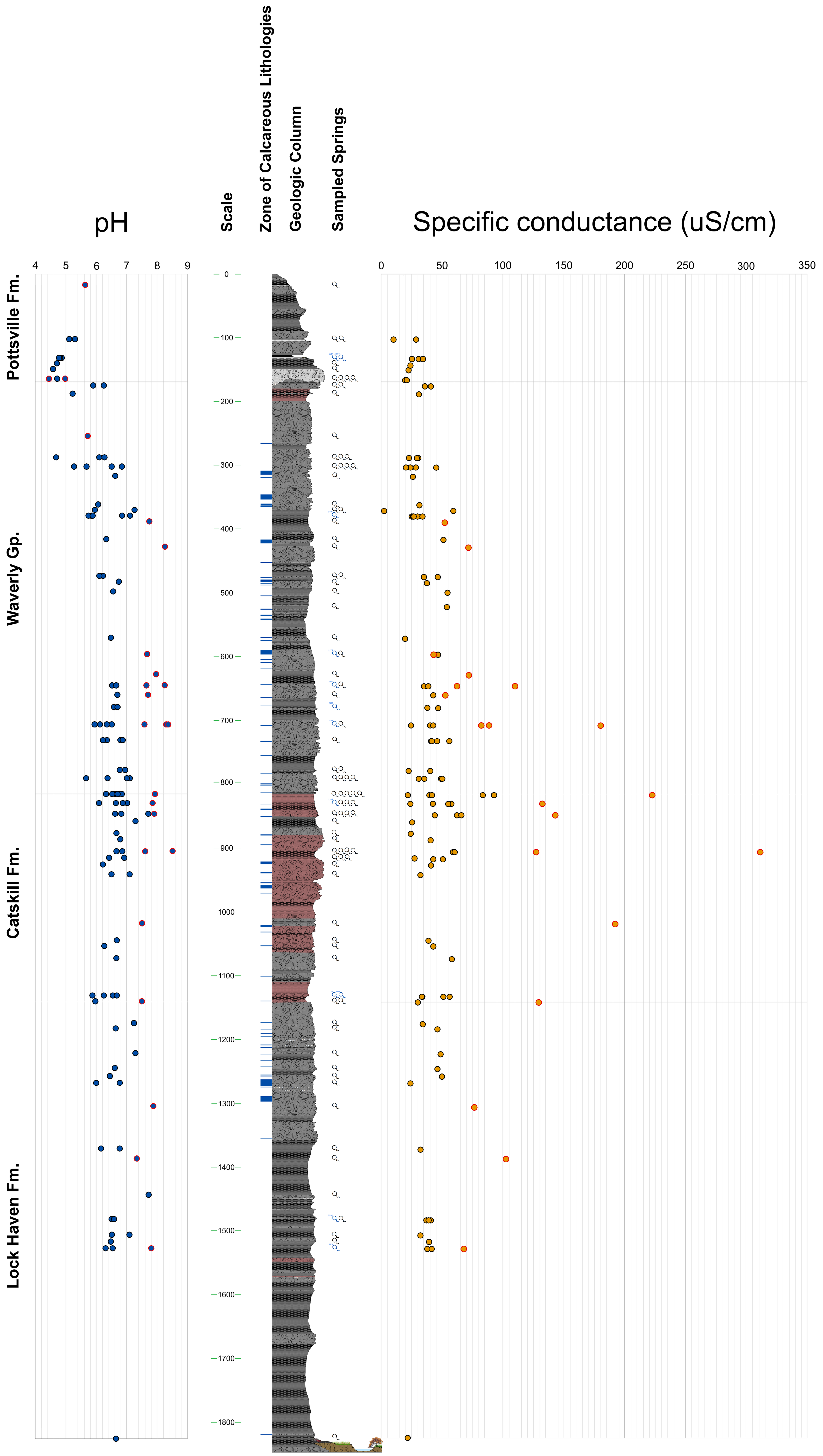


Photo: Spring 2206 located in the upper Catskill Formation during the December 2018 water sampling for lab-quality parameters (See table 2).



MINERALOGY/BULK ROCK GEOCHEMISTRY

The more acidic nature of the Pottsville Formation in the study area is correlated to the sulfur-bearing coal seams of the Quakertown complex. The overlying upper Mercer coal was not analyzed, but pH level in springs discharging from the coal suggest it contains less sulfur in the study area than the Quakertown complex. The combination of sulfur-bearing coals, lack of carbonate lithologies, and the coal's underclays acting as aquitards (therefore increasing the groundwater's exposure time to the coals) results in the acidic waters with pH values in the mid 4's and low 5's. Interestingly, sulfate concentrations are lower in the more acidic waters of the Pottsville Formation and upper Waverly Group and hydrogen sulfide was not detected. Also noteworthy, the intraformational conglomerates in the Waverly Group and Catskill Formation have elevated sulfur content (both organic material and pyrite have been observed) but any sulfur introduced in the groundwater from these rocks is buffered from the calcite content also found in these litholgies.

Carbonate minerals, calcite and dolomite, were identifed by thin section and x-ray diffraction in varying amounts throughout the Waverly Group, Catskill Formation, and Lock Haven Formation. Carbonate minerals were found dominantly as intergranular cement in sandstones and intraformational conglomerate but invertebrate skeletal material and pedigenic nodules were observed. These calcareous sandstones, intraformational conglomerates, and biosparite limestones provide the alkaline buffer to offset acidic water coming from the stratigraphically higher Pottsville Formation and to a lesser extent from the acidic nature of rain water recharging these aquifers.

Analysis of a core drilled on State Game Lands 293 (GPS: 41.50019°, -78.40765°) reveals that carbonate-bearing rocks make up approximately 8.9 percent of the Waverly Group, 5.7 percent of the Catskill Formation, and 10.6 percent of the upper 220 feet of the Lock Haven Formation. It should be noted that only the Waverly Group has true limestones of which it composes less than 2.2 percent of the Group's total lithology.

CHANGES IN SEASONAL GROUNDWATER

During seasonal droughts, such as observed during the late summer of 2017, groundwater discharging from the Waverly Group and Catskill Formation increases in both pH and specific conductance (See figure to left). This seasonal drought was captured by USGS stream gauge 01542810 at Waldy Run. Temperatures at springs increased during this same drought (See figure below). Increase in groundwater temperatures would speed-up chemical rections between carbonate minerals and the groundwater. Likewise, decreased groundwater flow would increase the time of exposure the water has with the bedrock and dissolved ions would be more concentrated providing a correlation explaining the increase in specific conductance and more alkaline conditons observed in summer base-flow conditions.

Comparision of Water Temperature Fluctuation of Local Springs to Seasonal Base-flow Conditions of Waldy Run, Cameron County, Pennsylvania

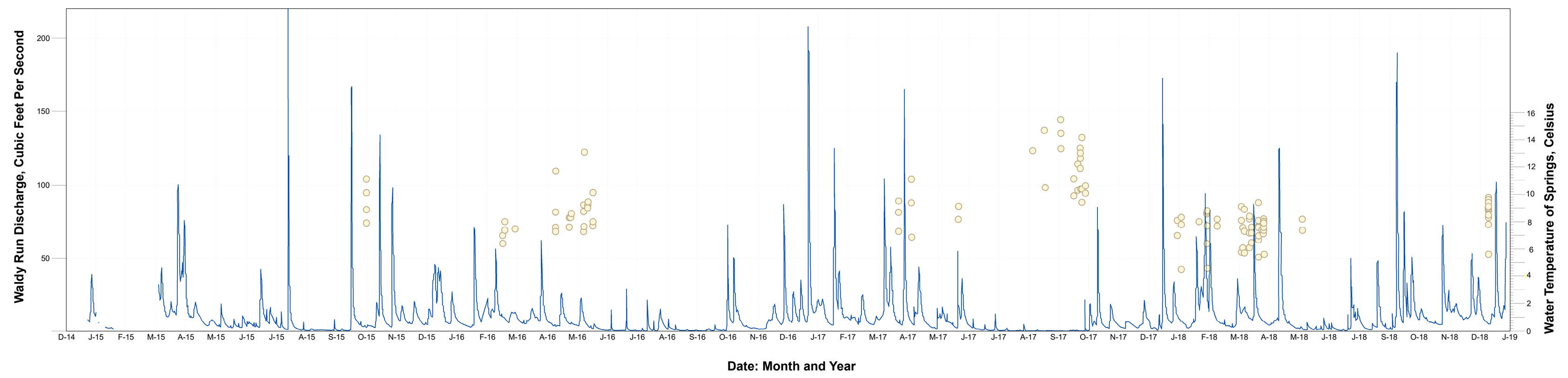
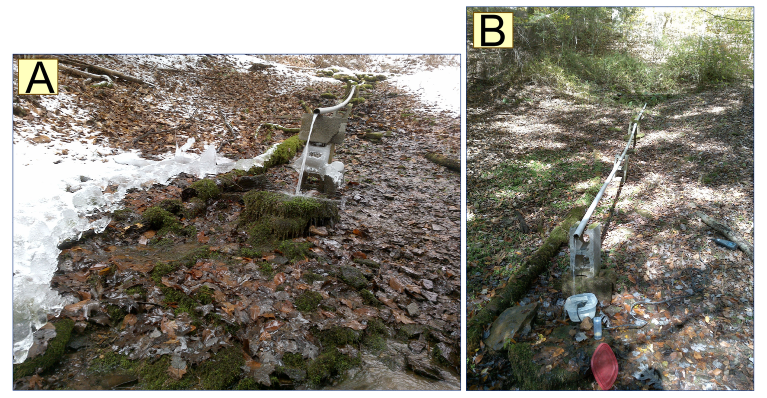
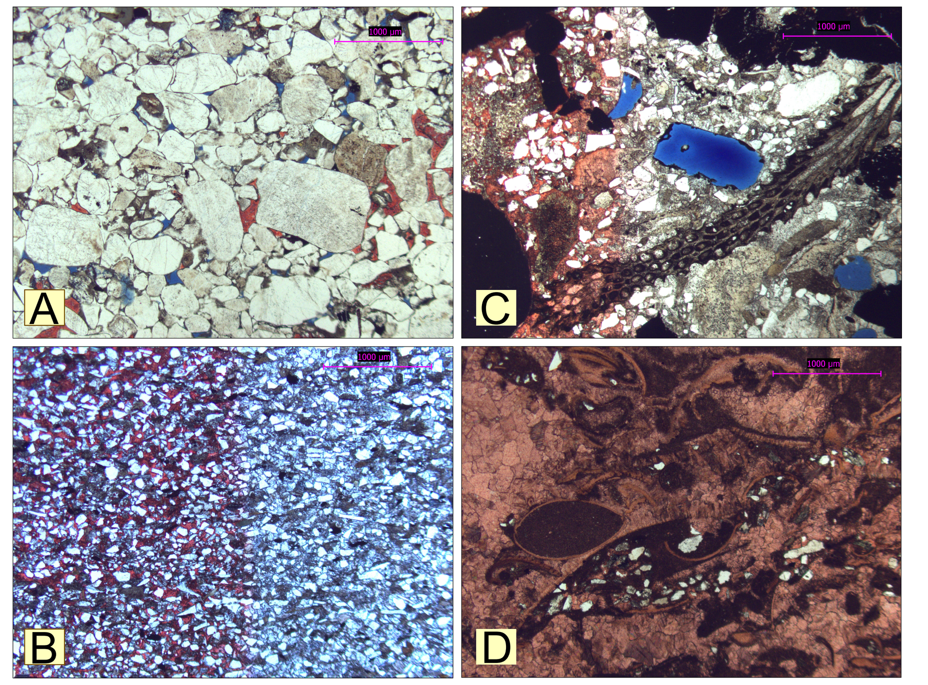


Figure Above: Chart displaying water temperature of springs sampled in the field (tan dots) and comparing this data with the discharge values recorded from the USGS stream Gauge on Waldy Run. This stream guage captures a small watershed of 5.22 square miles (StreamStats 2019) within the study area.

Figure Left: Dot diagram showing the stratigraphic position of springs sampled in the field with the spring's specific conductance (orange dots) and pH values (blue dots) plotted. Values plotted with red rings were taken during the months of August to mid-October which tend to obtain the lowest base flow conditions. Also displayed, is the extent of calcareous lithologies with data largely coming from detailed core analysis supplemented by observations in the field.

Photos Right: Two photos of Spring 2207 located within the Lock Haven Formation. Photo A taken during base-flow conditions in December 2018 bearing a yield of 7.99 gallons/minute, specific conductance: 41.2 μS/cm, and a pH: 6.32. Photo B taken during base-flow conditions in October 2017 bearing a yield of 0.4 gallons/minute, specific conductance of 67.0 μS/cm and a pH: 7.8.





Photos Above: Four petrographic thinsection photos from the Waverly Group with calcite stained with alizarin red and open pore space being filled with blue epoxy. All four slides were campled from core drilled on State Game Lands 293 in western Cameron County, Pennsylvania. Image A: Slightly calcareous sandstone displaying intergranular calcite-cement; entire slide was stained. Image B: Calcareous sandstone displaying intergranular calcite cement; left half of slide was stained. image C: Sandy intraformational conglomerate bearing a fossil bryozoan; left half of slide was stained. Image D: Slightly sandy biosparitic limestone; entire slide stained. Fossils are brachiopods.

Table 1: Bulk Rock Geochemistry

Rock Unit	Lithology	As ppm	Ba ppm	CaO %	Fe2O3 %	Hg ppb	K2O %	MgO %	MnO %	Na2O %	Pb ppm	Total S %	Sr ppm	V ppm
Pottsville Formation	Coal	8	141	0.04	1.03	NA	0.25	0.06	0.003	0.02	14	0.72	30	50
Pottsville Formation	Coal	3	316	0.03	0.90	NA	0.55	0.09	0.003	0.04	26	0.43	64	82
Pottsville Formation	Coal	11	358	0.05	1.10	NA	0.46	0.06	0.005	0.02	22	0.65	62	89
Pottsville Formation	Coal	14	185	0.03	1.00	NA	0.46	0.07	0.001	0.04	24	0.69	48	95
Pottsville Formation	Claystone (Coal Underclay)	50	598	0.07	5.25	239	3.40	0.71	0.019	0.23	26	0.04	153	171
Pottsville Formation	Claystone (Coal Underclay)	7	573	0.14	2.36	110	3.64	0.67	0.015	0.21	27	0.02	75	133
Pottsville Formation	Sandstone	6	30	0.10	0.69	< 5	0.22	0.05	0.017	0.02	< 5	< 0.01	8	7
Pottsville Formation	Sandstone	4	46	0.02	1.01	< 5	0.10	0.02	0.059	0.01	17	< 0.01	11	9
Waverly Group	Sandstone	2	217	0.05	3.67	< 5	1.39	0.40	0.018	0.07	5	< 0.01	28	48
Waverly Group	Shale	6	401	0.18	6.02	7	2.72	1.10	0.041	0.26	15	< 0.01	64	106
Waverly Group	Claystone (Red Bed)	6	528	0.11	9.39	< 5	3.97	1.47	0.034	0.31	6	< 0.01	78	131
Waverly Group	Intraforamtional Conglomerate	65	121	24.85	6.83	16	0.79	0.92	0.580	0.33	32	0.38	354	37
Waverly Group	Sandstone	12	166	16.69	3.43	13	1.40	0.64	0.677	0.60	< 5	0.04	200	45
Waverly Group	Sandstone	15	337	0.20	5.24	5	1.89	1.07	0.032	0.61	< 5	< 0.01	43	68
Waverly Group	Intraforamtional Conglomerate	64	118	27.06	7.65	14	0.96	1.74	0.857	0.19	21	0.35	244	42
Catskill Formation	Sandstone	7	348	0.21	4.49	7	2.07	0.88	0.047	0.72	< 5	< 0.01	49	73
Catskill Formation	Intraformational Conglomerate	84	139	27.62	4.93	14	1.17	6.05	1.241	0.27	36	0.17	397	41
Catskill Formation	Sandstone (Red Bed)	4	384	0.25	6.08	< 5	2.50	1.13	0.031	0.79	5	< 0.01	65	80
Catskill Formation	Siltstone (Red Bed)	7	375	0.23	7.12	< 5	3.00	1.14	0.040	0.65	5	< 0.01	71	100
Lock Haven Formation	Conglomerate	8	104	0.41	2.28	6	0.29	0.14	0.154	0.10	76	< 0.01	20	15
Lock Haven Formation	Shale	24	456	0.44	6.45	< 5	4.05	1.76	0.075	0.71	9	0.17	140	131
Lock Haven Formation	Conglomerate	18	155	4.05	10.08	18	0.79	0.46	0.040	0.55	11	0.02	143	69
Lock Haven Formation	Shale	6	663	0.24	9.70	7	4.49	1.93	0.052	0.51	6	< 0.01	118	152

Table 1 (Left): Bulk rock geochemistry of rock hand samples collected within the Rich Valley and Norwich 7.5-minute quadrangles of Cameron and McKean counties, Pennsylvania. Chart is organized stratigraphically. Coals are from the Quakertown complex.

Table 2 (Below): Water quality analysis of 12 springs within the study area. All springs except for the two springs in the Pottsville Formation are used as water sources for local residents or seasonal camps. Additional water parameters including arsenic, bromide, chloride, hydrogen sulfide, lead, mercury, and vanadium were sampled but not detected. Metals were analyzed using EPA methods 200.7, 200.8, and 245.1. Chart is organized stratigraphically. Sampling occured from December 12, 2018 to December 13, 2018.

Table 2: Spring Water Quality Analysis

Station	Rock Unit	Alkalinity mg/L	pH (lab) pH_Units	pH (field) pH_Units	Specific Conductance (Lab) umho/cm	Sulfate mg/L	Total Dissolved Solids (Lab) mg/L	Hardness mg/L	Barium, Total mg/L	Calcium, Total mg/L	Calcium Hardness mg/L	Iron, Total mg/L	Magnesium, Total mg/L	Manganese, Total mg/L	Potassium, Total mg/L	Sodium, Total mg/L	Strontium mg/L
2274	Pottsville	ND	5.71	4.79	23	6.3	28	6.8	0.0390	1.3	3.2	0.15	0.88	0.0580	1.20	0.32	0.0130
2251	Pottsville	ND	5.87	4.84	30	7.4	38	9.8	0.0210	1.8	4.6	0.23	1.30	0.0140	1.50	0.33	0.0110
2110	Waverly	ND	6.14	NA	25	5.5	59	8.1	0.0300	1.4	3.6	ND	1.10	ND	0.68	0.53	0.0086
2275	Waverly	ND	6.68	6.43	31	9.1	39	11.3	0.0078	2.6	6.6	ND	1.20	0.0058	0.69	ND	0.0160
2204	Waverly	8	6.88	6.54	34	8.1	35	13.0	0.0120	3.8	9.4	ND	0.89	ND	0.68	0.53	0.0110
2058	Waverly	13	7.01	6.69	41	8.1	46	15.7	0.0063	4.5	11.3	ND	1.10	ND	0.78	0.83	0.0540
2190	Waverly	14	7.05	6.52	39	8.6	52	15.0	0.0069	4.2	10.6	ND	1.10	ND	0.82	0.57	0.0220
2206	Catskill	12	7.00	6.63	50	9.3	27	19.3	ND	5.8	14.5	ND	1.20	ND	0.73	0.93	0.0220
2224	Catskill	6	6.62	6.23	31	7.4	63	10.6	0.0091	2.3	5.8	ND	1.20	ND	0.82	0.78	0.0089
2239	Catskill	12	7.05	6.57	50	9.5	59	18.4	0.0130	4.6	11.6	ND	1.60	ND	0.81	1.40	0.0140
2234	Lock Haven	6	6.79	6.51	36	8.2	43	12.6	ND	2.8	7.0	ND	1.40	ND	0.91	0.85	0.0083
2207	Lock Haven	7	7.00	6.32	38	8.1	45	13.0	ND	2.9	7.2	ND	1.40	ND	0.79	0.84	0.0100

Recommended Future Research

Though this study highlights general trends in the groundwater, a more thorough study would include establishing several springs from each formation for daily sampling which would establish a better correlation of the amount of flucuation in the groundwater's chemical and physical characteristics. A chemical study of the precipitation landing in the recharge areas is useful to highlight the chemistry of the water before entering the bedrock and would give insight on the severity (or lack) of chemical reactions with the bedrock minerals. Also critical would be determining the rate in which water passes through the groundwater system from recharge site to discharge at the springs which will give insight on how long the groundwater has exposure to the bedrock.

Conclusions

Once groundwater percolates through the Pottsville Formation, the water begins to interact with calcite-bearing sandstones, intraformational conglomerates, and sandy biospartic limestones. These lithologies buffer the acidic waters from meteoric waters and/or sulfur-bearing coals to near neutral pH. During seasonal droughts, the buffering becomes more pronounced as waters become is further alkaline sometimes reaching pH in the mid 8's. Furthermore specific conductance is elevated in seasonal droughts as dissolved ions are concentrated in the decreased discharge of perennial springs. Lab analyzed water shows elevated iron, maganese, potassium, and barium and decreased sodium in the Pottsville Formation compared to the Mississippian and upper Devonian Formations. At the time of sampling all twelve springs pass EPA drinking water standards for tested parameters except for springs in the Pottsville Formation where iron failed secondary drinking water standards in both springs and maganese in one spring. It is encouraged that water wells drilled within the Pottsville Formation are drilled and cased through the entire Pottsville Formation and the first 100 feet of Waverly Group (when overlain by Pottsvillle Formation) to ensure the best possible water quality the aquifer can provide.

Acknowledgments

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REFERENCES:

Eseme, Emmanuel, 2018, Bulk rock geochemistry-Reports A18-10718 and A18-10719: unpublished data from Activation Labratories LTD [on file at the Pennsylvania Geological Survey]

Leung, Sarah, 2019, Water analytical results- Report 3005917: unpublished data from ALS Environmental Laboratory [on file at Pennsylvania Geological Survey]

Pennsyvania Geological Survey, [2018], Pennsylvania Groundwater Information System (PAGWIS): Pennsylvania Geological Survey, 4th ser., SQL database [Janurary 1, 2019]; https://www.dcnr.pa.gov/Conservation/Water/Groundwater/PAGroundwaterInformationSystem/Pages/default.aspx.

United States Geological Survey, 2019, StreamStats, SQL database [March 5, 2019]; https://streamstats.usgs.gov/ss/

United States Geological Survey, 2019, National Water Information System: USGS 01542810 Waldy Run Near Emporium, PA, SQL database [March 5, 2019]; https://waterdata.usgs.gov/pa/nwis/uv/?site_no=01542810&PARAmeter_cd=00065,00060,00010