GEOCHEMISTRY, HYDROGEOLOGY, AND EFFECTS FROM THE PLUGGING OF ARTESIAN FLOWS OF ACID MINE DRAINAGE: CLARION RIVER WATERSHED, NORTHWESTERN PENNSYLVANIA [1]

Sherry L. Stafford, Theodore J. Weaver, and Robert S. Hedin[2]

Abstract. Numerous abandoned gas wells drilled during the late 1800's through the mid 1900's in the Clarion River watershed are acting as conduits for the artesian flow of iron-polluted waters to the surface. These shallow wells are located near surface mines, which were mined during the 1940's through the 1970's and had little if any surface reclamation. The geochemistry of the artesian well discharges suggests that they are originating in the open pit mine spoils located at the headwaters of tributaries to the Clarion River. Surface water filters through exposed mine spoils and weathers pyrite (FeS_2) producing water with low pH and elevated sulfate, acidity, and Al. The polluted water flows down through the fractured pit pavement into lower stratigraphic units and then flows laterally and down the synclinal structures through moderate to high productivity aquifers. The contaminated groundwater artesians to the surface through natural fissures or abandoned gas wells. Samples collected from twenty artesian discharges had pH values of 4.7 to 6.1, alkalinity concentrations of 26 to 110 mg/L as $CaCO_3$, sulfate concentrations of 33 to 1254 mg/L, and iron concentrations of 10 to 215 mg/L. Aluminum concentrations were less than 1 mg/L. Eighteen of the twenty samples were strongly acidic due to the presence of high concentrations of Fe. The change in chemistry between the surface mines and the artesian discharges is attributed to reaction with iron carbonate minerals such as siderite. The effect of plugging efforts on eight artesian flowing gas wells was monitored. Four wells were successfully plugged. Flow shifted rapidly from plugged wells to unplugged wells. The rapid response suggests that the wells drain a shallow contaminated aquifer. Because of the flow transfer, the plugging program had minimal remedial effect on the targeted watershed.

Additional Key Words: gas wells

---

[1]Paper was presented at the 2004 National Meeting of the American Society of Mining and Reclamation and The 25th West Virginia Surface Mine Drainage Task Force, April 18-24, 2004. Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.

[2]Sherry L. Stafford is a Graduate Student in Geology, Univ. of Pittsburgh, Pittsburgh PA 15112. Theodore J. Weaver is a Project Manager for Hedin Environmental, Pittsburgh PA 15228. Robert S. Hedin is the President of Hedin Environmental, Pittsburgh PA 15228.

Proceedings America Society of Mining and Reclamation, 2004 pp 1792-1818
DOI: 10.21000/JASMR04011792

https://doi.org/10.21000/JASMR04011792

Introduction

Abandoned coal mine drainage (AMD) is the most extensive and important water quality problem in the Appalachian region (Kleinmann, 1988, 1989) and it is also one of the oldest and most persistent pollution problems in the region. As early as 1698, Gabriel Thomas said of North America, "…and I have reason to believe that there are good coals, also, for I observed the runs of water which have the same color as that which proceeds from the mines in Wales…(Earle and Callaghan, 1999)." As mining operations and technology developed, especially over the last century, polluted discharges developed in surface mines, underground mines, and on coal refuse piles. In 1995, the US EPA and US DOI estimated that Pennsylvania had 3,239 miles of streams with reduced or no aquatic life, degraded water, damaged structures, and little or no aesthetic and recreational value (US EPA and US DOI, 1995).

Clarion County, Pennsylvania is scarred by many years of coal mining and oil/gas development. In the late 1800's and early 1900's, thousands of oil/gas wells were drilled in this region. Most of the wells tapped the Devonian Bradford Sands, which are typically 800 – 1,000 feet below the surface. These wells extended far below the coal beds (0-100 feet below the land surface). While there were some spatial overlaps between oil/gas wells and mining areas, a large majority of the oil and gas wells were located downstream from the hilltop mining operations at the headwaters of the watersheds. Over the years, production of oil/gas declined in the region, and most of the wells were abandoned. Some of these wells have become conduits for the discharge of groundwater. In Pennsylvania's coalfields, many artesian discharges from abandoned oil/gas wells are visibly contaminated with iron and are major causes of stream degradation. The chemical characteristics and geochemical origins of these artesian discharges have not been described in detail.

The plugging of abandoned oil/gas wells has become a remediation tool in northwestern PA. Well plugging was a major component of the successful restoration of Toms Run in Cook Forest State Park (Merritt and Emrich, 1970). Hydrologic conditions are rarely considered in well plugging efforts, in part because of assumptions that the discharges result from deep aquifers and that well-plugging will permanently and completely eliminate flow paths to the surface. The transfer of flow from plugged wells to unplugged wells, springs or fractures is rarely considered.

During the course of our investigation of the geochemistry of artesian groundwater discharges, one of our study areas became the focus of well plugging activities. Background flow and chemistry data were already available for nine artesian flows within the effected watershed. Flow measurements were subsequently made for the wells as plugging progressed. The results provide an indication of the interconnectedness of the wells and the general hydrology of the contaminated aquifer.

In this paper we describe the geochemistry and hydrogeology of artesian Fe-contaminated groundwater flows in Clarion County, PA. The geochemical objective was accomplished by sampling twenty artesian discharges and analyzing their chemical constituents. The hydrogeologic objective was accomplished by studying local hydrogeology and observing the short-term hydrologic consequences of a well plugging effort.

Background

Setting of the Study Area

Most of the investigation occurred in Clarion County, Pennsylvania (Figure 1). The study area is located in the Pittsburgh High Plateau Section of the Appalachian Plateau Physiographic Province. The maximum relief is approximately 1000 feet with the topographic extremes at opposite ends of the county (Leggette, 1936). The hills are capped mostly with the Clarion coal, a productive coal measure that has been extensively mined (Lesley, 1885). There are a few hills capped with the Mahoning sandstone to the south, and the Pottsville conglomerate is exposed in the north. The river valleys are partially filled with glacial outwash from the last glaciation. Several anticlinal folds and the complementary basins (Leggette, 1936) trend northeastward paralleling the Appalachian structure that is prominent in the region to the southeast (Newport 1973). The anticlinal plunge is approximately 1% to the southwest. The structure of the area creates opportunities for artesian flows in synclinal areas (Leggette, 1936). The synclinal/anticlinal axes are shown in Fig. 1.

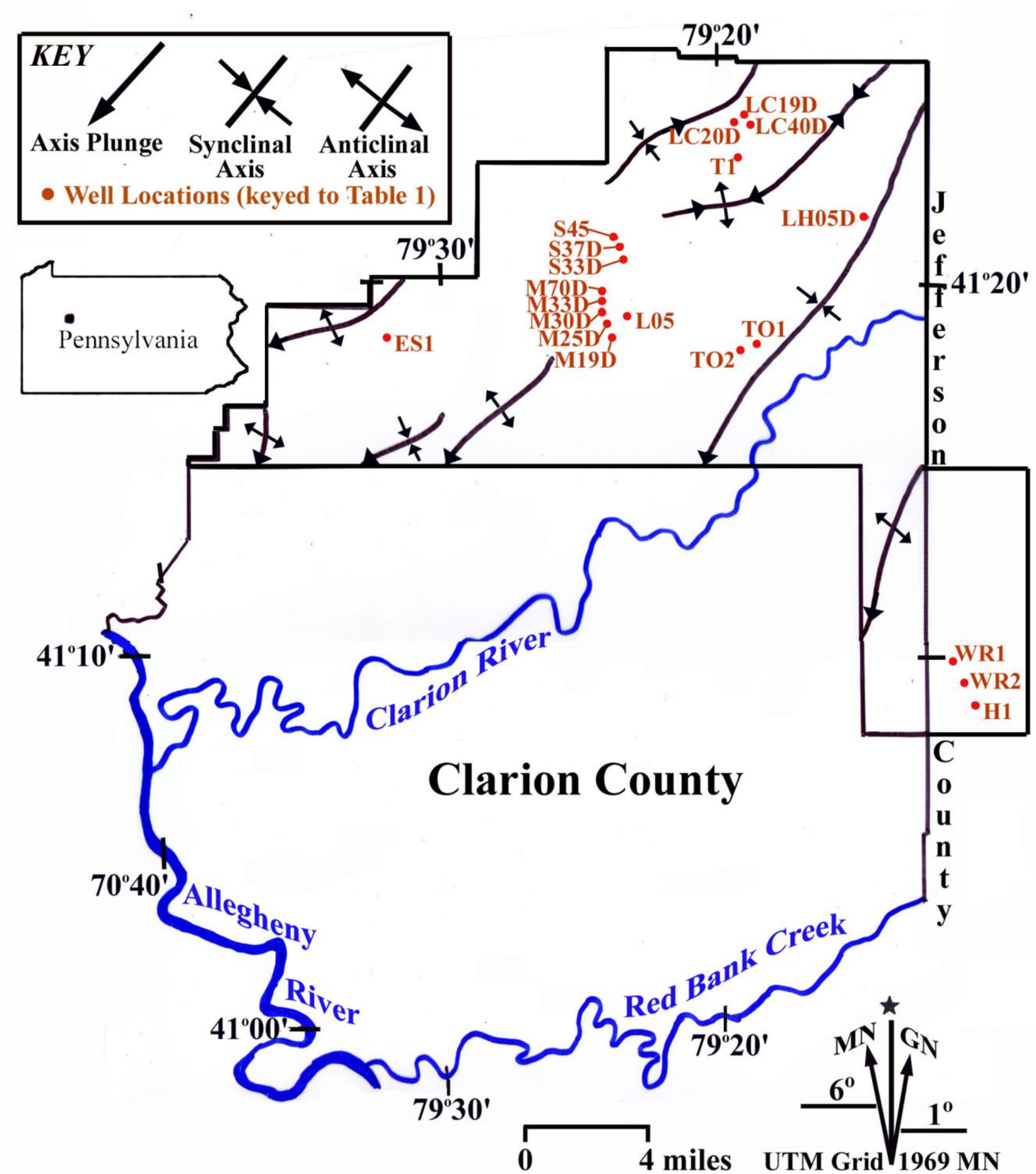

Figure 1. Anticlinal/synclinal axes and gas well sample locations in Clarion and Jefferson Counties (modified from Glover, 1987 and Newport, 1973).

Stratigraphy of Clarion County

More than 1000 feet of rock are exposed in the Clarion County. Most of the exposed rocks are Pennsylvanian in age and part of the Allegheny Group, which ranges between 345 feet and 370 feet in thickness. The group as a whole does not vary much in thickness, however individual beds may vary greatly. The dark gray and fossiliferous, Vanport limestone is a common marker bed in the area. The bed averages 7 feet in thickness, and is 110-130 feet above the bottom of the Allegheny Group. The Clarion coal is below the limestone (see Fig. 2). The coal splits into two benches, which are between 2 and 25 feet apart. The lower coal is anywhere from 20 to 50 feet below the Vanport. The Brookville coal is 40 to 70 feet below the Lower Clarion coal (Leggette, 1936). The Brookville coal is not as regular in thickness or quality as the Clarion coal. Sandstone units are typically massive in the Allegheny Group and yield moderate amounts of water that is relatively high in Fe (Newport, 1973). At the top of the Pottsville, the Homewood sandstone is massive and cross-bedded. It has an average thickness of 40 feet (Leggette, 1936). It supplies moderate amounts of water. The Mercer shale is below the sandstone. It contains thin coal in some places and is quite variable in thickness. The Connoquenessing is the lowest Formation in the Pottsville Group. It is loosely cemented and is capable of supplying moderate amounts of water. The Burgoon sandstone, directly below the Pottsville Group, is the primary water producer in the area. As long ago as 1936, Leggette reported that the aquifer was sometimes heavily mineralized (Leggette, 1936). Alternating layers of sandstone and shale are common in Clarion County. Impermeable shale layers, such as the Mercer shale, affect groundwater flow by acting as confining layers (see Fig. 2). Typical groundwater flows laterally at confining layers creating local water tables and springs.

Mining Practices

The mining practices in Clarion County have greatly affected water quality and normal drainage conditions. Problems associated with AMD in the Clarion County watersheds can be attributed to pre-SMCRA (Surface Mining Control and Reclamation Act of 1977, Public Law 95-87) mining activity. Most of the surface mines, which are located on the ridge tops at the headwaters of streams, were mined from crop to crop (i.e. hilltop removal). Most, if not all of the coal has been removed from these mines. In some cases, refuse and waste coal was brought

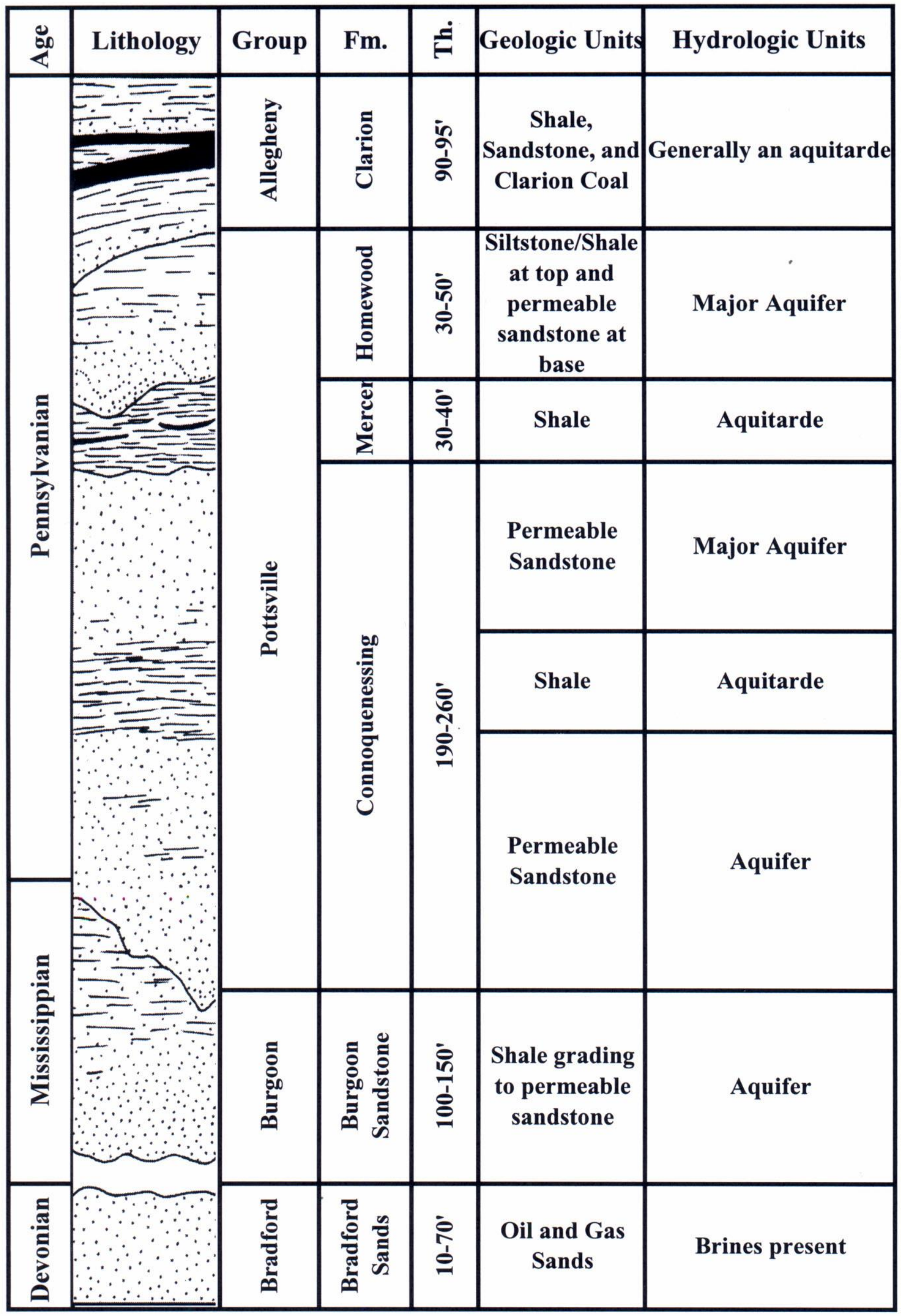

Figure 2. Generalized stratigraphic section for Clarion County (modified from Merritt and Emrich, 1970).

back into the pits and buried. There was no reclamation performed on these sites other than the planting of coniferous trees. The abandoned surface mines contain ungraded spoil piles, highwalls, and final cut pits. The weathered spoils that developed on these mines tend to have highly acidic soils (pH < 4) and little vegetative cover.

Before the sites were mined, the natural flow of shallow groundwater was likely controlled by the presence of the permeable coal bed, underlain by an impermeable clay or claystone. Seeps off the coal seams were likely common. A generalization of this situation is shown in Figure 3A. During mining, excavation proceeded to the underclay. Because of poor drainage, water often accumulated in the pits and became a problem. A common method for lessening water problems was to fracture the pit floor and drain the water to the underlying aquifer. One consequence of this practice was the permanent loss of water from the surface mine sites. A thorough assessment of AMD flow and chemistry in the Little Coon Run watershed found that flows from headwater surface mines were much less than was expected from precipitation and infiltration (Hedin Environmental, 2003). The assessment suggested that most precipitation to hilltop surface mines infiltrated through the acidic spoils and fractured underclays into the underlying strata. Artesian discharges located lower in the watershed were hypothesized to be a consequence of this infiltration. Most of the artesian discharges were from abandoned non-producing oil/gas wells, which were acting as efficient conduits for the release of infiltrating mine water. Figure 3B shows this situation.

<u>Oil Drilling Practices</u>

The drilling of oils wells in this area began in the mid to late 1800's, soon after the discovery of oil in nearby Titusville, PA. The abandoned wells considered in this study were largely drilled in the 1800's and early 1900's. The wells were drilled into the Devonian Bradford Sands, which are located 800 – 1000 feet below the surface and hundreds of feet below the coal producing strata. Many of the wells were located adjacent to streams, because the early gas/oil development relied on water access for the drilling process, because the Devonian rocks were closer to the surface in stream valleys, and because stress relief fractures are common in stream valleys of the Appalachian Plateau (Wyrick and Borchers, 1981). Current well drilling practices include the placement of casing (solid pipe and a concrete sleeve) through coal measures and aquifers. The

A

B

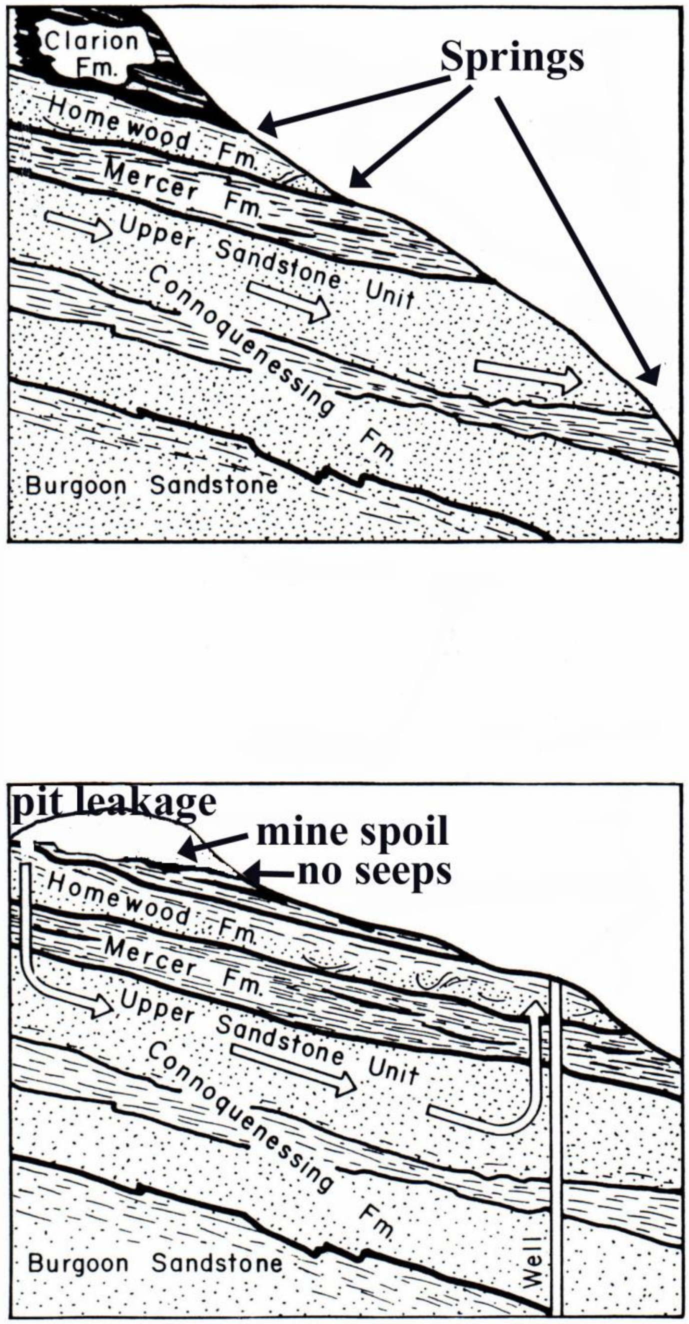

Figure 3. Typical cross section of the pre and post-mining water drainage. 3A illustrates drainage through undisturbed rock (pre-mining). 3B shows

drainage from abandoned surface mines (post-mining) (modified from Merritt and Emrich, 1970).

presence of casing in the abandoned wells is variable, and even where casing is present, it is sometimes corroded and ineffective at excluding groundwater inflows.

Well Plugging Watershed

Abandoned oil/gas wells are commonly plugged because of safety concerns associated with oil and gas leakage. Recently, many wells that produce polluted water have been plugged as part of stream restoration programs. The effectiveness of well plugging was assessed in the Mahle Run watershed. The stream is located within the boundaries of northern Clarion County in west-central Pennsylvania. It originates near the town of Fryburg and flows south into Huefner. Mahle Run is a headwater tributary stream to the Deer Creek Watershed that drains into the Clarion River near the town of Clarion, Pa. The stream's total drainage area is approximately 4 square miles. The headwater areas are a combination of farmland and woodlot, while the middle and lower stretches of the stream are located in heavily forested areas.

The headwaters of Mahle Run originate 10,000 feet southwest off of the crest of the northeast to southwest trending Leeper Anticline, and flows down dip to the south towards the northeast to southwest trending Clarion Junction Syncline, or to the southeast towards the northeast to southwest trending Kane Syncline. The synclinal basins of each of these synclines are located within five miles of one another. The rock strata in the region slope at approximately 1% to the southwest.

Mining in the Mahle Run watershed was limited to surface mines in the Clarion coal which is limited to hilltops and ridges. The surface mines are all unreclaimed and contain poorly vegetated, acidic spoil piles. No mining occurred in the middle and lower portions of the watershed. Mahle Run is also polluted by artesian flows from abandoned wells. The wells are located in the middle and lower portions of the watershed. In the Mahle Run watershed, nine polluted artesian flows were located along a 7500 ft stretch of the stream. Eight of the wells were targeted for plugging, and flows from all nine were monitored during the plugging process.

Methods

Water samples were collected from twenty artesian flows that were known to contain elevated Fe concentrations due to previous analyses or by visual observations. Chemical parameters were measured using standard field and laboratory techniques. Specific conductivity, alkalinity, and pH were measured at each field site. Water was collected in acid cleaned polyethylene bottles for anion analysis (500 ml) and trace metal analysis (125 ml). Samples for trace metal analysis were filtered with a 0.45 micron filter and acidified with 2% HNO_3. Aluminum (Al), calcium (Ca), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), sodium (Na), sulfur (S), silica (Si), and strontium (Sr) concentrations were determined by Spectro-Flame Modula, End-on-Plasma, Inductively-Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) at the University of Pittsburgh using EPA QA/QC protocol SW846. Sample concentrations below detection limits were reported as less than the detection limit (i.e. <0.1). Total blanks were analyzed to measure contamination from sampling and preservation techniques. Sulfate was estimated from sulfur concentrations. Chloride and acidity (hot peroxide method) were analyzed by G & C Laboratories (Pennsylvania Department of Protection certification #33-325). Acidity and alkalinity were expressed as mg/L $CaCO_3$, while all other parameters were expressed as mg/L.

Flow rates were measured by directing all of the discharge flow into a pipe and then timing the collection of a known volume (bucket and stopwatch method). Flows were expressed as gallons per minute (gpm).

Results and Discussion

Geochemistry of Artesian Groundwater Discharges

Water chemistry results for samples of artesian flows are shown in Table 1. All of the discharges had near-neutral pH, elevated concentrations of Fe and very low concentrations of Al. Iron concentrations averaged 97 mg/L (range 10 – 215 mg/L). All of the samples contained bicarbonate alkalinity, but only two were net alkaline. The other eighteen samples were net acidic due to the acidic characteristics of the elevated iron concentrations. The alkaline and

Table 1. Water data for artesian flows from gas wells in Clarion and Jefferson Counties.

			Field Measurements			**Cations**									**Anions**			**Charge**
Site Name	**Sample Date**	**Watershed**	**Cond. µS**	**Alk ppm**	**pH S.U.**	**Acid ppm**	**Ca^{2+} ppm**	**Mg^{2+} ppm**	**Na^{+} ppm**	**Fe^{2+} ppm**	**Mn^{2+} ppm**	**Al^{3+} ppm**	**K^{+} ppm**	**Si^{0} ppm**	**$HCO3^{-}$ ppm**	**Cl^{-} ppm**	**$SO4^{2+}$ ppm**	**Balance %**
M70D	05/29/99	Mahle	1258	50	6.0	111	115.2	69.8	7.1	87.0	14.4	<0.05	5.6	5.4	61	6	657	5.0
T1	05/29/99	Licking	1518	26	5.9	358	104.6	89.2	4.3	215.0	13.8	<0.05	6.3	5.2	31	5	977	0.7
LH05D	05/29/99	L. Hefren	716	41	6.1	82	47.9	28.3	7.2	66.8	4.8	<0.05	4.6	4.5	50	1	322	2.2
LC40D	05/29/99	Little Coon	1624	36	5.5	322	119.0	94.9	5.5	196.2	13.4	<0.05	6.8	4.7	44	5	1012	-1.1
ES1	05/29/99	East Sandy	790	56	5.6	27	57.0	23.1	38.9	40.3	3.1	0.1	4.8	4.4	68	70	283	-9.4
TO1	06/17/99	Toby Creek	1389	30	5.8	286	87.7	82.6	7.7	161.6	13.4	<0.05	5.3	3.9	36	3	809	2.4
TO2	06/17/99	Toby Creek	1360	49	5.4	123	164.4	84.2	20.7	84.5	9.6	<0.05	5.4	4.2	60	13	827	5.4
S33D	06/17/99	Step Run	480	94	5.9	-77	12.4	4.9	64.2	10.1	0.6	<0.05	3.3	3.4	114	63	33	-1.6
S37D	06/17/99	Step Run	1139	36	5.6	234	59.3	57.1	6.9	145.6	9.3	0.1	5.3	4.6	43	4	595	3.5
S45	06/17/99	Step Run	933	43	5.7	133	64.9	43.4	7.9	88.7	6.1	<0.05	4.8	4.1	52	2	455	2.8
M25D	06/16/99	Mahle	525	110	6.1	-84	15.9	5.3	66.0	12.8	0.4	0.1	3.6	3.8	134	63	45	-4.9
M30D	06/16/99	Mahle	876	69	5.5	36	71.9	27.5	30.0	46.6	4.0	<0.05	4.9	3.9	84	15	360	-1.9
M33D	06/16/99	Mahle	971	68	5.4	46	81.0	33.2	32.7	51.9	4.8	<0.05	5.1	4.0	83	25	385	3.0
L05	06/16/99	Licking	1483	78	5.5	117	157.6	44.2	33.0	97.7	5.6	<0.05	6.3	5.3	95	19	707	0.0
M19D	06/16/99	Mahle	629	33	5.6	125	86.6	35.9	13.0	83.1	4.7	<0.05	4.5	5.0	40	4	481	3.3
H1	08/01/99	Welsh Run	1459	44	5.9	241	185.4	148.8	10.8	131.2	20.8	<0.05	8.0	6.3	54	2	1254	2.3
WR1	08/01/99	Welsh Run	382	78	5.8	128	191.0	85.2	36.2	81.0	17.4	<0.05	7.5	6.9	95	10	928	3.3
WR2	08/18/99	Welsh Run	1747	37	4.7	244	196.8	102.4	23.7	115.4	29.2	1.0	7.9	7.5	45	11	1139	0.3
LC19	09/02/99	Little Coon	1011	38	5.5	176	76.3	59.3	9.4	113.2	12.9	0.1	6.3	4.0	46	3	601	3.2
LC20	09/02/99	Little Coon	1197	56	5.2	197	75.6	61.0	9.5	109.2	12.7	0.1	6.3	4.2	68	3	587	2.5

acidic samples differed in their chemical compositions. The dominant cations for the net acidic samples were calcium and magnesium. Sodium was the dominant cation for the net alkaline samples. Manganese was less than 1 mg/L in the net alkaline samples and ranged between 3 and 29 mg/L for the net acidic samples. Aluminum was < 1 mg/L for all samples and below detection (0.1 mg/L) for half of the samples. Minor but detectable elements included Si (3-8 mg/L), K (3-7 mg/L), and Sr (0.1 – 1.0 mg/L).

Sulfate (SO_4) was the dominant anion for net acidic samples, while bicarbonate and chloride were dominant anions for the net alkaline samples. Sulfate concentrations for the net acidic samples ranged between 300 and 1,300 mg/L.

The accuracy and completeness of the analyses was evaluated by comparing anion and cation totals, and by comparing measured acidity and calculated acidity values. In both analyses, all Fe was assumed present as ferrous. Cation totals averaged 14.7 meq/L compared to an average anion total of 14.5 mg/L. On an individual sample basis, the cation/anion ratios ranged from 0.91 to 1.05. This good correspondence of cation and anion totals indicates that all major chemical constituents were accurately accounted for. Acidity values were estimated from the measured concentrations of the acidic and alkaline parameters as described by Hedin (2004). The average calculated acidity was 138 mg/L $CaCO_3$, while the average measured acidity was 141 mg/L $CaCO_3$. This good correspondence reinforces the accuracy of the measurements of acidity, alkalinity, Fe, and Mn.

Water samples were grouped based on knowledge of end member groups for water chemistry plotted on a trilinear diagram (see Fig. 4) (Piper, 1944). Four types of waters are distinguished by Piper diagrams:

(1) Ca-HCO_3 waters, which are typical of shallow, fresh groundwater. Local uncontaminated groundwater springs, which would be in this group, have sulfate concentrations less than 50 mg/L and low Na concentrations.

(2) Na-HCO_3 waters, which are typical of deep fresh groundwater that is influenced by ion exchange. During exchange reactions, Ca is removed from water and Na is added to the water (Rose and Cravotta, 1998).

(3) Na-Cl waters, which are typical of marine and very deep, ancient groundwater. Local brines (pumped from active oil/gas wells) have Na, K, and Cl concentrations greater than 10,000 mg/L (Merritt and Emrich, 1970).

(4) Ca/Mg-SO_4 waters are typical of mine drainage (Capo et al., 2001). The chemistry of these waters is produced when mining activities promote the oxidation of pyrite (FeS_2) to an acidic sulfate-rich solution that is partially or whole neutralized by carbonate minerals, producing high concentrations of Ca and Mg.

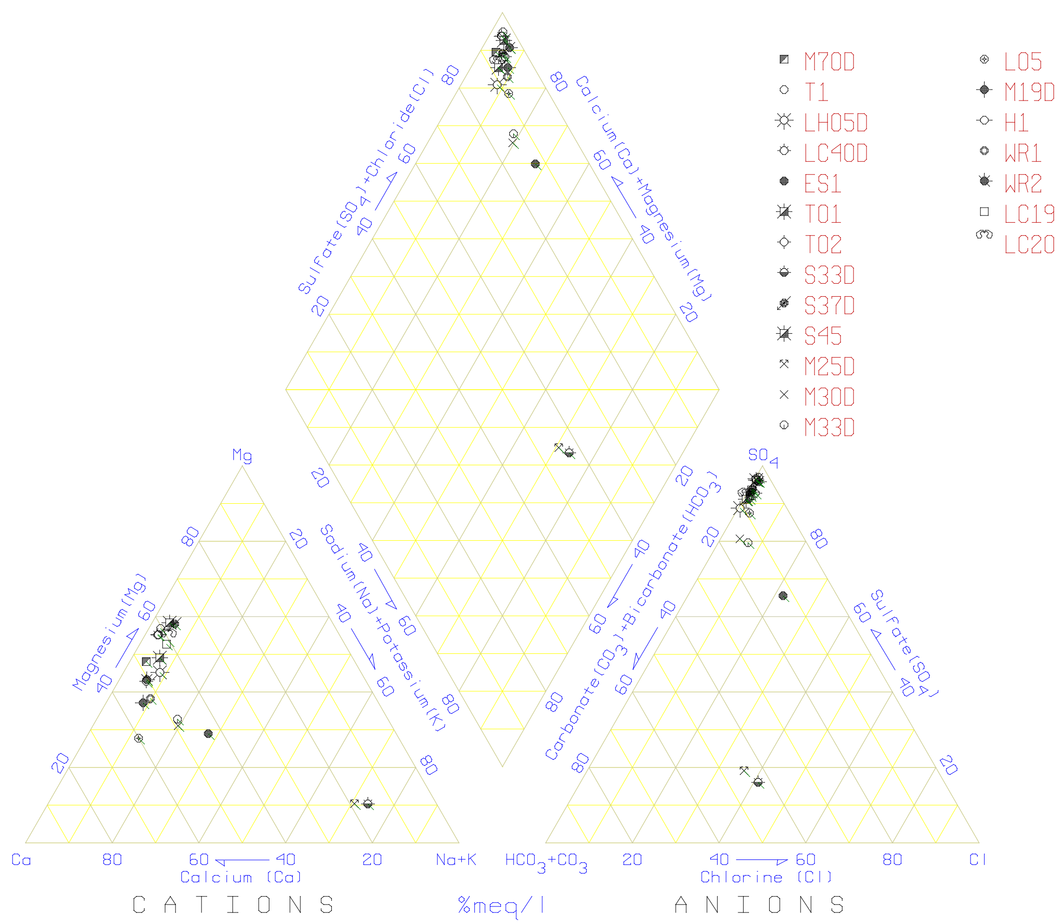

Figure 4. Piper plot showing the major water classifications and water chemistry for artesian gas well samples in Clarion and Jefferson Counties.

Two water samples were distinguished by the Piper plots. Discharges S33D and M25D differed from the other 18 samples by their low total dissolved solids, their net alkaline conditions, and their low sulfate concentrations. The anions chemistry of these two samples was dominated by bicarbonate and chloride. These discharges most likely represent uncontaminated ground water that penetrated the wells and mixed, to a small degree, with deeper brines before discharging. The low sulfate concentrations infer that the iron content of these samples is not a consequence of local coal mining activities.

The remaining eighteen samples clustered in the mine drainage region of the Piper plot. These samples had high concentrations of SO_4, Ca, and Mg, were net acidic, and were contaminated with iron. Moderate concentrations of sodium and chloride (up to 70 mg/L) suggested some influence from deep brines. However, the primary geochemical influence on these eighteen samples was pyrite oxidation associated with near-surface coal mining.

The geochemistry of the artesian discharges differs from seeps collected directly from surface mine spoils in the study area. Table 2 shows the chemistry of several toe-of-spoil discharges from hilltop surface mines in Clarion County. The discharges are net acidic with low pH, no alkalinity, and elevated concentrations of Al. Concentrations of Fe are variable, but generally low. This condition is attributed to the precipitation of ferric iron minerals within the spoils and the dissolution of aluminum-containing clays by the low-pH acidic solution.

Table 2. Chemical characteristics of several spoil discharges from unreclaimed hilltop surface mines in Clarion County, PA.

Site name*	**pH S.U.**	**conductivity umhos**	**Acidity ppm**	**Fe ppm**	**Mn ppm**	**Al ppm**	**SO4 ppm**
HR25D	3.5	670	82	0.5	5.5	9.2	332
HR27D	3.2	1875	358	0.5	5.5	9.2	1269
HR40D	3.1	1228	365	34.2	10.7	38.8	774
LC60D	3.3	1258	268	21.2	12.6	28.6	792
LC57D	3.3	1956	396	1.4	26.7	55.8	1285
LC47D	3.4	1653	600	4.6	13.8	98.1	1125
LC46D	3.6	1554	398	2.9	14.3	57.5	1005
LC45D	3.3	2143	481	2.7	24.6	70.0	1415
LC37D	3.6	2240	316	2.1	26.3	40.1	1582
R63D	3.7	780	153	0.9	5.5	21.5	423
R64D	3.8	1000	176	0.3	6.5	30.3	621

HR25D, HR27D, and HR40D are in the Henrys Run watershed; LC60D, C57D, LC47D, LC46D, LC45D, and LC37D in the Little Coon Creek watershed; R63D and R64D are in the Rattlesnake Run watershed.

As noted previously, a thorough assessment of mine drainage flows in the Little Coon Run watershed (Clarion County) found few perennial flows of AMD from hilltop surface mines, suggesting substantial infiltration to deeper aquifers (Hedin Environmental, 2003). Artesian flows from gas/oil wells likely represent the missing acidic, sulfate-rich water (Figure 3B). However, while the chemistry of most of the artesian discharges is acidic and sulfate-rich, the contaminant composition varies substantially between the spoil seeps and the artesian ground water flows. Most notably, spoil discharges have low pH, elevated Al and generally low Fe, while artesian well discharges have near-neutral pH, elevated Fe, and low Al.

The differences in the chemical composition of spoil seeps and artesian well discharges could be explained by several geochemical reactions that are known to increase the pH of acidic mine water. We assessed the probable significance of silicate weathering, ion exchange, and carbonate dissolution to explain the results.

Silicate weathering consumes H^+ ions, raising pH according to the following generalized reaction (Rose and Cravotta, 1998):

$$2\ KAlSi_3O_8\ (\text{K feldspar}) + 2H^+ + 2H_2O = 2K^+ + Al_2Si_2O_5(OH)_4 + 4SiO_2 \qquad (1)$$

This process does not account for the observed increases in alkalinity and Fe, and the loss of Al during the flow path. Also, highly elevated K and Si concentrations were not observed in the artesian flows.

Ion exchange processes can decrease acidity by exchanging Ca^{2+} ions for Na^+ ions and, under high CO_2 partial pressures, promoting calcite dissolution (Foster, 1950; Cerling et al., 1989). This process is important in the genesis of net alkaline deep mine discharges in southwestern PA (Weaver, 1998).

$$\text{Clay-2Na} + CaCO_3 + H_2CO_3 \rightarrow \text{Clay-Ca} + 2\ Na^+ + HCO_3^- \qquad (2)$$

Ion exchange cannot explain the chemistry of the net acidic artesian discharges. These flows do not contain elevated Na concentrations. Ion exchange cannot account for the observed increase in Fe.

Acidic mine waters are commonly neutralized by reaction with Ca and Mg carbonates. The reactions increase pH and alkalinity as shown below.

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^- \quad (3)$$

$$MgCO_3 + H^+ = Mg^{2+} + HCO_3^- \quad (4)$$

The increase in pH would cause the precipitation of Al hydroxide solids. These reactions, however, cannot account for the increase in Fe or the retention of acidic conditions. Reaction with the iron carbonate, siderite, can increase Fe and can account for the observed changes in pH, alkalinity, and Al.

$$FeCO_3 + H^+ = Fe^{2+} + HCO_3^- \quad (5)$$

$$Al^{3+} + H^+ + 4FeCO_3 + 3H_2O \rightarrow Al(OH)_3 + 4Fe^{2+} + 4HCO_3^- \quad (6)$$

Siderite dissolution is neutral with respect to acidity because the acidic characteristic of the solubilized ferrous iron is equal to that of the precipitated Al and neutralized H^+. Reaction of an acidic Al-contaminated solution with pure siderite should result in an alkaline Fe-contaminated solution that has the same net acidity.

In order to further investigate the origins of the dissolved iron, an acid mass balance was calculated. Total neutralization was calculated by subtracting acidity measured in meq/L from potential acidity [2*(SO4 in meq/L)] according to the amount of acidity produced with sulfate generation in pyrite oxidation. Potential acid consumption in meq/L, assuming a pH of < 6.3, would equal [(2* Mg or Ca in meq/L) + (Fe in meq/L)]. Fig. 5 shows a plot of total neutralization (meq/L) versus potential acid consumption (meq/L). A one to one relationship between total neutralization and potential acid consumption only exists when Fe is added to the balance. This result supports the hypothesis that iron carbonate, not pyrite, is the source of dissolved iron in acidic artesian groundwater flows. The hypothesis is also supported by geologic information. Siderite is present in the Clarion County stratigraphy (Leggette, 1936), and is especially abundant in the lower Allegheny Group (K. Brady, PADEP, personal communication).

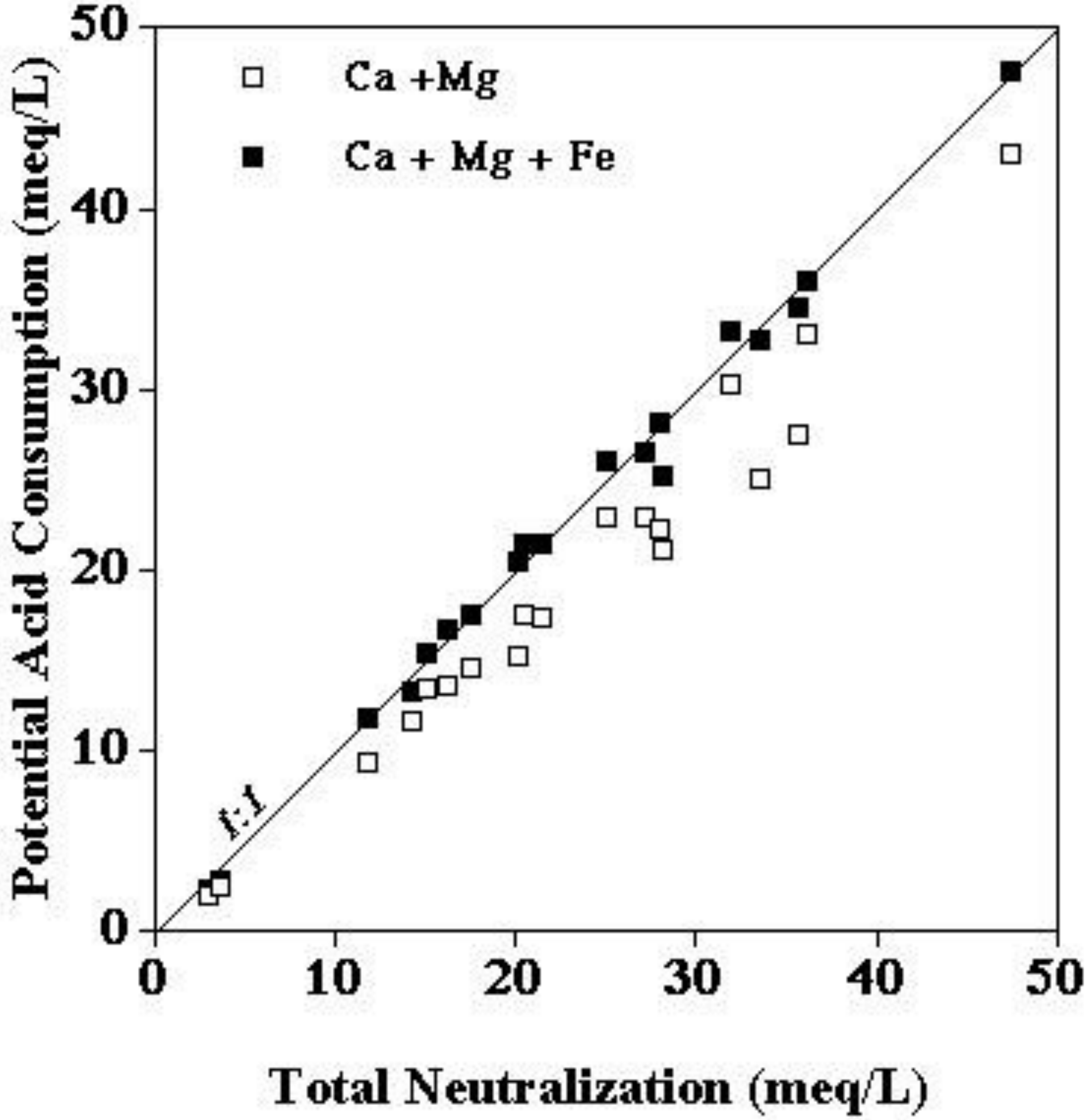

Figure 5. Total neutralization (meq/L) in polluted mine waters versus potential acid consumption (meq/L) from Ca, Mg and Fe-bearing carbonates.

Hydrologic Interconnectedness of Artesian Well Flows in the Mahle Run Watershed

In 2002, the Lucinda Antler Club and Hedin Environmental conducted a field investigation of Mahle Run that identified nine artesian discharges that polluted the stream with iron and acidity. All discharges were sampled for chemical constituents, and flow rates were measured several times in 2002. Five of the discharges were sampled as part of this study and are included in Table 1.

In the autumn of 2003, the local non-profit Alliance for Wetlands, in partnership with the US Natural Resource Conservation Service and the Clarion County Conservation District, initiated a well plugging program in the Mahle Run watershed. Eight of nine artesian flows were targeted for plugging. The ninth site was not included in the plan because an abandoned oil/gas well was not visually evident at the discharge location. Plugging was initiated in October and proceeded into January of 2004. This paper describes observations made until December 17, 2003, when a majority of the plugging efforts had been completed.

The plugging of artesian flows from gas wells is accomplished by situating a truck mounted cable tool rig over the top of a discharge to allow access to the hole from the rig. A wooden platform is installed around the hole to provide a stable safe and dry work area. The plugging effort proceeds by reaming and cleaning out the well hole with well cleaning tools attached to the cable rig. The goal is to remove all obstructions between the top and bottom of the well. Often times, cleaning the well temporarily increases the flow of water from the hole. Next, steel casing and other conduit is removed. Once the well hole has been thoroughly cleaned, the well is filled with a clay bentonite product in the oil/gas bearing zone. Then, the well is filled with aggregate to the top of the water-producing aquifer. The aggregate is periodically compacted with the rig in an attempt to plug the hole and to stop the flow of water. If the flow is successfully stopped, a concrete plug is placed on top of the aggregate seal.

Not all plugging efforts are successful. In some cases the artesian flow of water is not stopped through the compaction of aggregate in the water-producing zone, and placement of the concrete plug does not stop the flow. In these cases, water continues to discharge from the plugged well. It is possible that these wells could be plugged using alternative techniques. Such efforts were not attempted in Mahle Run.

The location of wells in the Mahle Run watershed are shown in Fig. 6. The nine wells were divided into two clusters. An upper cluster of six wells was the first target for plugging. These wells are located in the upper reaches of the watershed in close proximity to the junction point of four small tributaries. A lower cluster of three wells was the secondary target of plugging activities. These wells are located in the Middle section of Mahle Run and are within 400 feet of each other.

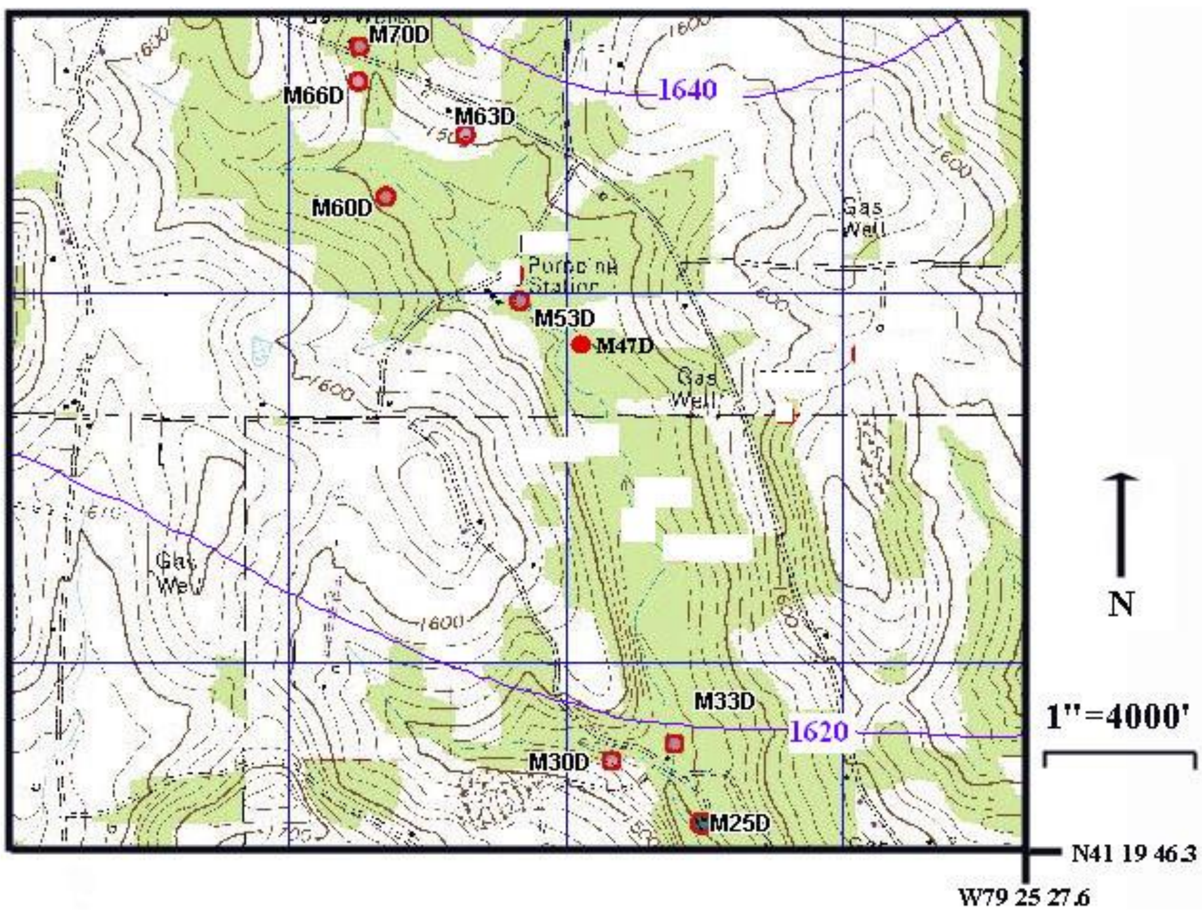

Figure 6. Location of artesian discharges in the Mahle Run watershed. The upper cluster of six wells and the lower cluster of three wells are apparent.

Flow rates for the wells before, during, and after the plugging activities were completed are shown in Table 3. Plots of the data are shown in Fig. 7. Seven measurements of flow from the wells were made between June and December 2002. One measurement was made of the well

Table 3. Fow rates before (2002 average and 9/7/03) and during plugging of artesian wells in the Mahle Run watershed, Clarion County, PA.

Date **Well**	**2002** **Average**	**09/06/99** **Pre-plug**	**10/04/99**	**10/12/99**	**10/20/99**	**10/26/99**	**10/31/99**	**11/10/99**	**11/17/99**	**11/29/99**	**12/16/99**
M70D	28	28	*Plugged*	0	0	0	0	0	0	0	0
M66D	25	28	78	48	42	37	41	39	41	41	44
M63D	12	10	10	28	30	34	32	34	35	30	47
M60D	49	54	*Plugged*	0	0	0	0	0	0	0	0
M54D	3	3	5	8	13	12	17	21	41	11	3
M47D	7	9	13	15	35	46	15	20	30	19	26
Total Upper	***124***	***132***	***106***	***99***	***120***	***129***	***105***	***114***	***147***	***101***	***120***
M33D	14	9	17	14	22	25	28	21	16	16	22
M30D	22	23	24	12	*Plugged*	0	0	0	0	0	0
M25D	2	5	3	4	*Plugged*	0	0	0	0	0	0
Total Lower	***39***	***37***	***44***	***30***	***22***	***25***	***28***	***21***	***16***	***16***	***22***
Total All	***162***	***169***	***150***	***129***	***142***	***154***	***133***	***135***	***163***	***117***	***142***

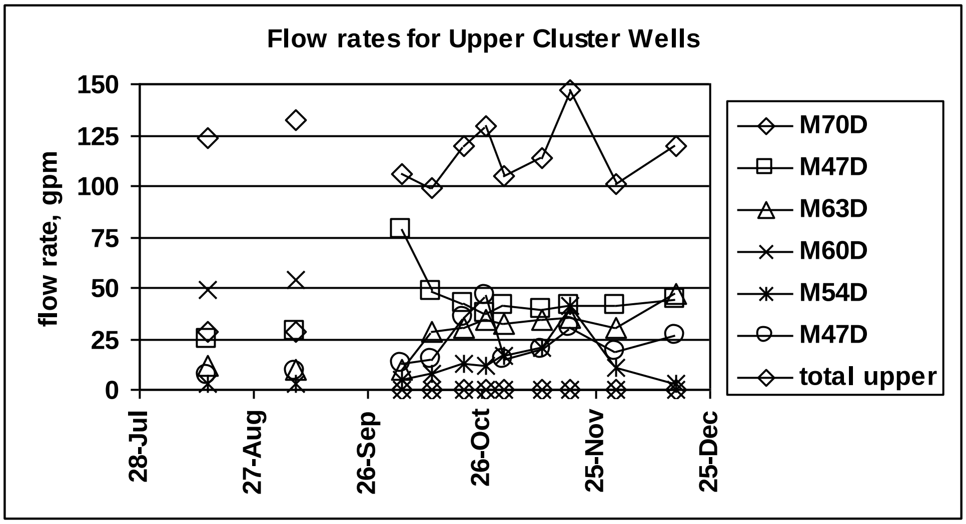

Figure 7a. Flow rates for the upper cluster of wells. The first column of symbols represents 2002 averages. The second column is pre-plugging measurements made in September 2003. Symbols connected with lines are flow rates measured during plugging activities.

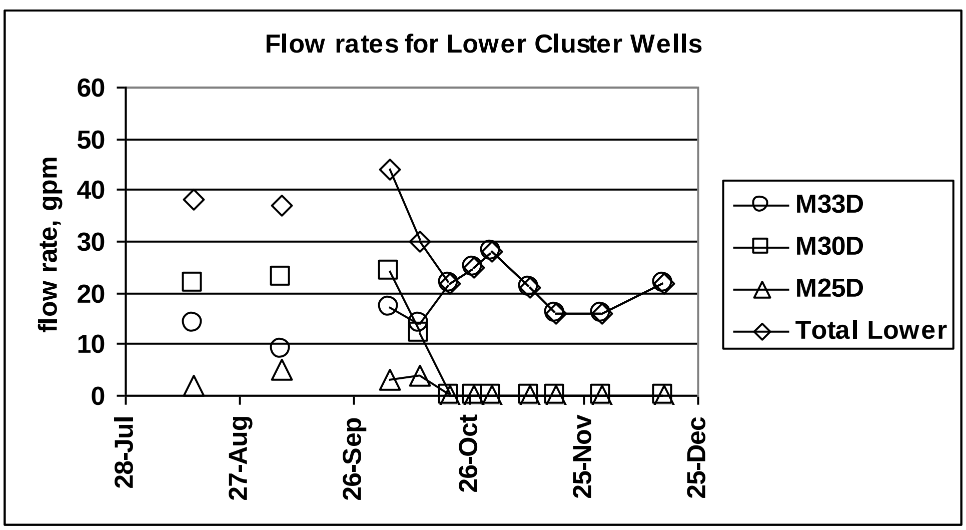

Figure 7b. Flow rates for the lower cluster of wells. The first column of symbols represents 2002 averages. The second column is pre-plugging measurements made in September 2003. Symbols connected with lines are flow rates measured during plugging activities.

flows in September 2003, before plugging activities began. The 2002 and September 2003 flow rates were similar. Well plugging began in October 2003 and proceeded through December 2003. Flow rates for all nine wells were monitored every 1-2 weeks while plugging occurred (Table 3).

The sealing of the wells occurred in an upstream to downstream progression. There was approximately 100 feet of surface elevation difference between the highest and lowest wells (M70D and M25D, respectively), but no more than twenty feet difference in structural contour elevations existed.

The first well plugged was M70D, which was the highest surface elevation discharge and was the highest discharge situated on the synclinal limb. The successful plugging of M70D was followed quickly by the plugging of M60D, eliminating 28 gpm and 54 gpm of flow, respectively. The contractor reported that the well was cleaned to a depth of approximately 300 feet and the water source was sealed off at a depth of approximately 60 feet.

Wells M66D and M63D are located less than 600 feet across the stream from M60D. Within hours of sealing M60D, increased flow rates were noted at M66D. Three days after sealing of M60D, the flow rate at M66D had increased from 28 gpm to 78 gpm. Subsequent attempts to seal M66D reduced the flow from 78 gpm to 40 gpm, but the contractor was unable to stop the flow. Flow increased at M47D from 9 gpm to as high as 46 gpm. The contractor was unable to completely seal this well. When the plugging attempts were abandoned, the flow at M47D was 26 gpm. Flow at M54D increased from 3 gpm to as high as 41 gpm. The contractor was able to lower the flow to 3 gpm before abandoning the effort. Flow also increased at M63D, rising from 10 gpm to 47 gpm. Because this discharge did not have identified well casing, no attempts were made to plug it.

The increased flow of water at unplugged wells was contaminated. A sample of the M66D discharge was collected in October when the flow rate was twice the pre-plugging flow. The sample was acidic with 75 mg/L Fe. The contaminant concentrations were similar to samples collected in 2002, before the plugging began. Contaminant loadings to the stream from M66D, however, were twice the pre-plugging measurements.

Plugging difficulties were also encountered in the lower cluster. M25D and M30D were successfully plugged, but attempts to plug M33 were unsuccessful. Flow at M33D increased from 9 gpm to 22 gpm.

The well plugging activities only decreased the measured flow of contaminated groundwater to Mahle Run from 169 gpm (September 7, 2003) to 142 gpm (December 17, 2003). The lack of success was attributable to the relocation of groundwater from plugged wells to unplugged wells. The transfer was especially apparent in the upper cluster where two wells that originally accounted for 62% of the total flow were successfully plugged, but the total flow from the cluster only decreased by 9%. Efforts in the lower cluster were better, but still only decreased flow by 41%.

The unplugged wells demonstrated rapid hydrologic response to the plugging of nearby wells. Increases in flow were observed within hours of plugging activities. This rapid response indicates that the wells are connected to a common aquifer. The contractor reported that the flowing water was regularly encountered in the wells within 60 feet of the surface. These observations indicate that the source of polluted water is a shallow local aquifer, not a deep aquifer associated with the original oil/gas drilling.

Our measurements only accounted for identified point sources of contaminated water. Contaminated groundwater is known to discharge in this region from springs and from stream bottom fractures. It is possible that the water eliminated from point sources by successful plugging activities will eventually discharge from non-point sources. The control and remediation of these non-point discharges can be difficult – much more difficult than the original point sources eliminated by the plugging.

The transfer of contaminated groundwater between wells documented in this study is not limited by watershed boundaries. In this part of Pennsylvania, it is common for several small watersheds to share the same synclinal basin. Subsurface watershed boundaries are structurally controlled and do not share the same boundaries as surface flow. Well plugging activities that affect shallow contaminated aquifers will almost certainly transfer water from targeted watersheds to untargeted watersheds in the same structural basin.

It is worth noting that the inter-well transfer of contaminated water documented in this study could be used advantageously in restoration activity. The chemistry of the well discharges

(Table 1) is well suited for reliable passive treatment with anoxic limestone drains, settling ponds and wetlands. It may be feasible to use plugging to eliminate artesian flows in problematic areas (on steep slopes or adjacent to a stream) and to transfer the water to areas where passive treatment is possible. In this context, this study is not a general indictment of well plugging activities, but a warning that the activities must occur within a hydrogeologic context. Indeed, well plugging could be a valuable tool used appropriately in comprehensive stream restoration activities.

Conclusions

Artesian flows discharging from abandoned oil/gas wells are an important source of water pollution in parts of northwestern PA. Contaminated flows from the wells are characterized by near-neutral pH and high concentrations of acidity, Fe, and SO_4. The origin of these discharges appears to be unreclaimed surface mines in headwater areas that leak highly acidic, Al-contaminated water into the underlying sandstone aquifers. As the acidic water flows through these aquifers, its chemistry is modified. The observed increases in pH, alkalinity, and Fe suggest interaction with an iron carbonate mineral such as siderite.

Abandoned oil/gas wells act as discharge conduits for the contaminated groundwater aquifers. The aquifer in Mahle Run appears to be shallow in nature – occurring within 60 feet of the surface. The aquifer has a high level of transmissivity. The plugging of wells resulted in rapid increases in flow at nearby unplugged wells. Unless the plugging operations are completely successful, this transfer of water between conduits will compromise the remediation goals. Several months of plugging efforts in the Mahle Run watershed only decreased the cumulative measured discharges by 16%.

The limited success of the Mahle Run plugging program justifies a cautious approach to well plugging efforts. Before undertaking plugging activities, an investigation of the local hydrogeology is warranted. This information will identify other watersheds that might be impacted by the plugging activities (and that should be investigated for artesian well flows) and should provide a basis to prioritize the plugging activities. Contaminated springs and streambed upwellings, that are unsuitable for plugging, should be identified and considered as probable recipients of increased flow as plugging proceeds. Wells in locations not suitable for treatment should be plugged first. Wells in areas suitable for passive treatment might be left unplugged so that the contaminated aquifer has a controlled discharge that can be treated.

The chemistry of the artesian flows is ideally suited for reliable passive treatment with buried beds of limestone followed by settling ponds and aerobic wetlands. It is possible that the most cost-effective restoration plan for streams polluted by these artesian flows may involve the use of plugging to eliminate problematic discharges and to redirect the polluted flow to one or two sites where passive treatment is implemented.

Acknowledgements

We thank Christopher London for providing assistance with water collection and field measurements. Rosemary C. Capo and Brian W. Stewart at the University of Pittsburgh provided ICP-AES analyses of water samples. Brian Games, also at the University of Pittsburgh, was instrumental in helping us run the major element analysis. Additional thanks go to C. G. Walton, P.G. and the anonymous reviewer.

Literature Cited

Brady, K. B. C. 2004. Pennsylvania Department of Environmental Protection, personal communication.

Capo, R. C., S. L. Stafford, C. L. Kairies, B. W. Stewart, and R. S. Hedin. 2001. Strontium and neodymium isotopic composition of coal mine drainage as a tracer of subsurface geochemistry, Applied Isotope Geochemistry Conf. IV: Pacific Grove, CA.

Cerling, T. E., B. L. Penderson, and K. L. Damm. 1989. Sodium-calcium ion exchange in the weathering of shales: Implications for global weathering budgets: Geology, v. 17, p. 552-554. http://dx.doi.org/10.1130/0091-7613(1989)017<0552:SCIEIT>2.3.CO;2.

Earle, J., and T. Callaghan. 1998. Impacts of mine drainage on aquatic life, water uses, and man-made structures, *In* Brady, K. B. C., M. W. Smith, and J. Schueck (Co-Eds.). Coal Mine

Drainage Prediction and Pollution Prevention in Pennsylvania: Harrisburg, Department of Environmental Protection, p. 4-1 to 4-10.

Foster, M. D. 1950. The origin of high sodium bicarbonate waters in the Atlantic and gulf coastal plains: Geochimica et Cosmochimica Acta, v. 1, p. 33-48. http://dx.doi.org/10.1016/0016-7037(50)90007-X.

Glover, A. D. 1987. Coal Resources of Clarion County, Pennsylvania: Part 1. Coal Crop Lines, Mined-out Areas, and Structure Contours, PA Topographic and Geologic Survey, Mineral Resource Report 92, Part 1, 119 p.

Hedin, R. S. 2004. The use of measured and calculated acidity values to improve the quality of mine drainage data sets. paper in these proceedings.
https://doi.org/10.21000/JASMR04010879
Hedin Environmental. 2003. Little Coon Run and Walley Run Mine Drainage Assessment and Restoration Plan, prepared for the Farmington Township Supervisors.

Kleinmann, R. L. P. 1989. Acid mine drainage: U. S. Bureau of Mines researches and develops control methods for both coal and metal mines: Eng. Min. J., v. 190, p. 161-167.

Kleinmann, R. L. P., J. R. Jones, and P. M. Erickson. 1988. An assessment of the coal mine drainage problem, Proceedings of the 10th Annual Conference of the Association of Abandoned Mine Land programs, PA Bureau of Abandoned Mine Land Reclamation, p. 1-9.

Leggette, R. M. 1936. Ground Water in Northwestern Pennsylvania: Harrisburg, Topographic and Geologic Survey, 215 p.

Lesley, J. P. 1885. A Geological Hand Atlas of the Sixty-seven Counties of Pennsylvania: Harrisburg, Board of Commissioners for the Second Geological Survey.

Merritt, G. L., and G. H. Emrich. 1970. The need for a hydrologic evaluation in a mine drainage abatement program: a case study: Toms Run, Clarion County, Pennsylvania, *In* C.T. Holland (ed.). 3rd Symposium on Coal Mine Drainage Research: Pittsburgh, Pennsylvania, Mellon Institute.

Newport, T. G. 1973. Summary Ground-Water Resources of Clarion County, Pennsylvania: Harrisburg, Pennsylvania Geological Survey, Fourth Series, 42 p.

Piper, A. M. 1944. A graphic procedure in the geochemical interpretation of water analyses: American Geophysical Union Transactions, v. 25, p. 914-923. http://dx.doi.org/10.1029/TR025i006p00914.

Rose, A. W., and C. A. Cravotta, III. 1998. Geochemistry of coal mine drainage, *In* Brady, K. B. C., M. W. Smith, and J. Schueck (Co-Eds.). Coal Mine Drainage Prediction and Pollution Prevention in Pennsylvania: Harrisburg, Department of Environmental Protection, p. 1-1 to 1-22.

USEPA and US DOI. 1995. Progress Report Statement of Mutual Intent Strategic Plan for the Restoration and Protection of Streams and Watersheds Polluted by Acid mine Drainage from Abandoned Coal Mines, Department of the Interior, 33 p.

Weaver, T. J. 1998. Occurrence and Significance of Alkaline Mine Drainage in Northern Appalachia: Pittsburgh, University of Pittsburgh, 48 p.

Wyrick, G. G., and J. W. Borchers. 1981. Hydrologic Effects of Stress-Relief Fracturing in an Appalachian Valley. Geologic Survey Water-Supply Paper 2177: Washington, United States Government Printing Office, 51 p.