SHALLOW GROUNDWATER FLOW IN UNMINED REGIONS OF THE NORTHERN APPALACHIAN PLATEAU: PART 2. GEOCHEMICAL CHARACTERISTICS[1]

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ABSTRACT. Surface mines in Pennsylvania occur in the shallow (< 60 m depth) groundwater flow system and typically are located in groundwater recharge areas. Two shallow flow systems are usually present in unmined areas: an upper weathered-rock zone and a deeper unweathered-rock zone. The weathered-rock zone, although variable, is commonly 6 to 12 m thick. Groundwater in the weathered-rock flow system, as evidenced by shallow wells and cropline springs, has low dissolved solids (specific conductance < 50 µS/cm). The deeper unweathered-rock flow system, as evidenced by water from wells deeper than 10 m, has higher concentrations of dissolved constituents. The differences in water quality are due to previous intensive leaching of minerals within the weathered-rock zone and to much higher flow rates in the more porous and fractured weathered zone. In particular, calcareous minerals are absent or negligible in the weathered-rock zone, but can be appreciable in the unweathered-rock zone. This distribution of calcareous minerals, groundwater contact time with rock, and flow path influence the groundwater composition and concentrations of dissolved ions. A positive relationship exists between the presence and abundance of calcareous minerals and associated groundwater alkalinity.

Our observations are probably applicable to much of the Appalachian Plateau. Groundwater alkalinity can help determine the presence and distribution of calcareous minerals within coal overburden. Coal-cropline springs should not be depended upon for showing groundwater quality associated with the coal seam; they typically only reflect shallow flow through weathered rock. Deeper wells are required to determine the chemical characteristics of water in the unweathered rock zone.

Additional Key Words: groundwater chemistry, acid-base accounting, weathering, groundwater flow

Introduction

The companion paper (Hawkins et al., 1996, this proceedings) provides a review of groundwater hydrology studies on the plateau. This paper addresses chemical evidence in support of that model. Our model defines two separate shallow groundwater flow systems in unmined areas within the unglaciated portions of the Appalachian Plateau of western Pennsylvania. Numerous studies throughout the plateau, from Kentucky to New York have examined shallow groundwater hydrologic characteristics, but few have related water chemistry to the groundwater hydrology.

The three areas discussed in this paper lie within the Allegheny Mountain section of the Appalachian Plateau physiographic province. This portion of the plateau has moderate to high relief (90 to 300 m), marked by deep, V-shaped valleys (Berg et al., 1989). Stratigraphically the sites occur within the Pennsylvanian Period middle Allegheny Group (Sites A and B) and upper Allegheny Group/lower Glenshaw Formation (Site C). Structurally the rocks are horizontal to gently dipping (generally < 6°).

Natural water quality in shallow groundwater flow systems of the Appalachian Plateau results primarily from the influence of three factors: (1) the chemistry/mineralogy of the rock that the water contacts, (2) flow path, and (3) water and rock contact time. Although many solutes are present, we concentrate on bicarbonate alkalinity, because it can be compared to overburden neutralization potential (NP) (an estimation of calcareous mineral content) and because it can be used as a mine drainage quality prediction tool. Other water quality parameters will be addressed where appropriate.

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Shallow groundwater is associated with two distinct flow-systems. The one system, represented by coal-cropline springs, is recharged from the near-surface zone of weathered rock up slope from the spring. This zone consists of soil, colluvium (in some areas), and weathered and highly fractured rock. This weathering is both chemical and physical. The weathering is enhanced by stress-relief fracturing on the hill slopes and by bedding plane separations, which promote intensified chemical weathering and resulting porosity increases (Hawkins et al., 1996). The weathered zone, as seen in strip mines and drill logs, is typically 6 to 12 m thick, but can extend deeper along fractures. The weathered zone is typically devoid of calcareous minerals and pyrite (Singh et al., 1982; Brady et al., 1988). It is characterized by a yellow-red-brown color resulting from iron oxidation. The lower boundary of the weathered zone is an irregular surface. The irregularity is caused by variations in fractures, topography and lithology.

The other flow-system is below the weathered rock within the zone of largely unweathered bedrock. The unweathered bedrock zone is much less fractured, having fewer bedding plane separations and stress-relief fractures. The bedrock zone retains calcareous minerals and pyrite (if originally present) and the rocks are typically gray, with iron oxidation restricted to some fractures and bedding plane separations.

Most water flowing through the weathered zone has a relatively short residence time (days to weeks) because of the shallow nature of this material and higher permeability which is induced by the factors cited above. Some storage is present, however, because the springs continue to flow during dry periods. The absence of readily leachable or oxidizable minerals and the short residence time results in spring-water quality which typically has low concentrations of dissolved ions.

The water flowing through the unweathered-rock zone has longer residence time (months to years) because of lower permeabilities (Hawkins et al., 1996) and the slower flow rate allows longer contact with soluble minerals. Groundwater in unweathered rock typically has greater concentrations of dissolved solids than water emanating from weathered regolith. Water chemistry from unmined areas can provide information concerning the groundwater flow system.

Methods

The three study areas discussed in this paper were selected because they had: (1) water chemistry data from coal-cropline springs, (2) water quality from wells completed down to the same coal seam as the cropline springs, and (3) acid-base accounting (ABA) data.

ABA is defined by two parameters, neutralization potential (NP), which is an approximation of calcareous mineral content (reported in terms of parts per thousand $CaCO_3$; traditionally reported as tons $CaCO_3$/1000 tons of material), and maximum potential acidity (MPA), which is an approximation of pyrite content. MPA is converted to the same units as NP by multiplication of the weight percent total sulfur by the stoichiometric equivalence factor of 31.25 (Cravotta et al., 1990). Average NP's and MPA's were determined for each overburden drill-hole by using thickness weighting and assuming each hole represented a column of constant diameter, following the methods described in Smith and Brady (1990).

All water quality sample locations were represented by multiple samples. Medians were determined for pH. Other water quality parameters discussed in this paper, unless specified otherwise, are mean concentrations.

Mine Sites

To illustrate the relationship between rock chemistry and water chemistry, several specific examples will be given. All sites discussed are isolated hill tops where the only recharge is from direct precipitation. In all cases the coal outcrops along the sides of the hill, and cropline-springs and bedrock monitoring wells are present.

MINE A: Boggs Township, Clearfield County

Mine A is the Kauffman mine where various research studies have been and are being conducted (see Abate, 1993; Evans, 1994; Rose et al., 1995; Hawkins et al., 1996, this volume). Mine-site topography, locations of drill holes and water-sample points for this mine are shown on Figure 1. This map also shows alkalinity and specific conductivity of wells and springs associated with the lower Kittanning (LK) coal seam, plus a few springs flowing from the Clarion #2 cropline. All the wells are completed as 10-cm-diameter piezometers that are open for 1.5 m at the interval of the LK coal. Figure 1 also

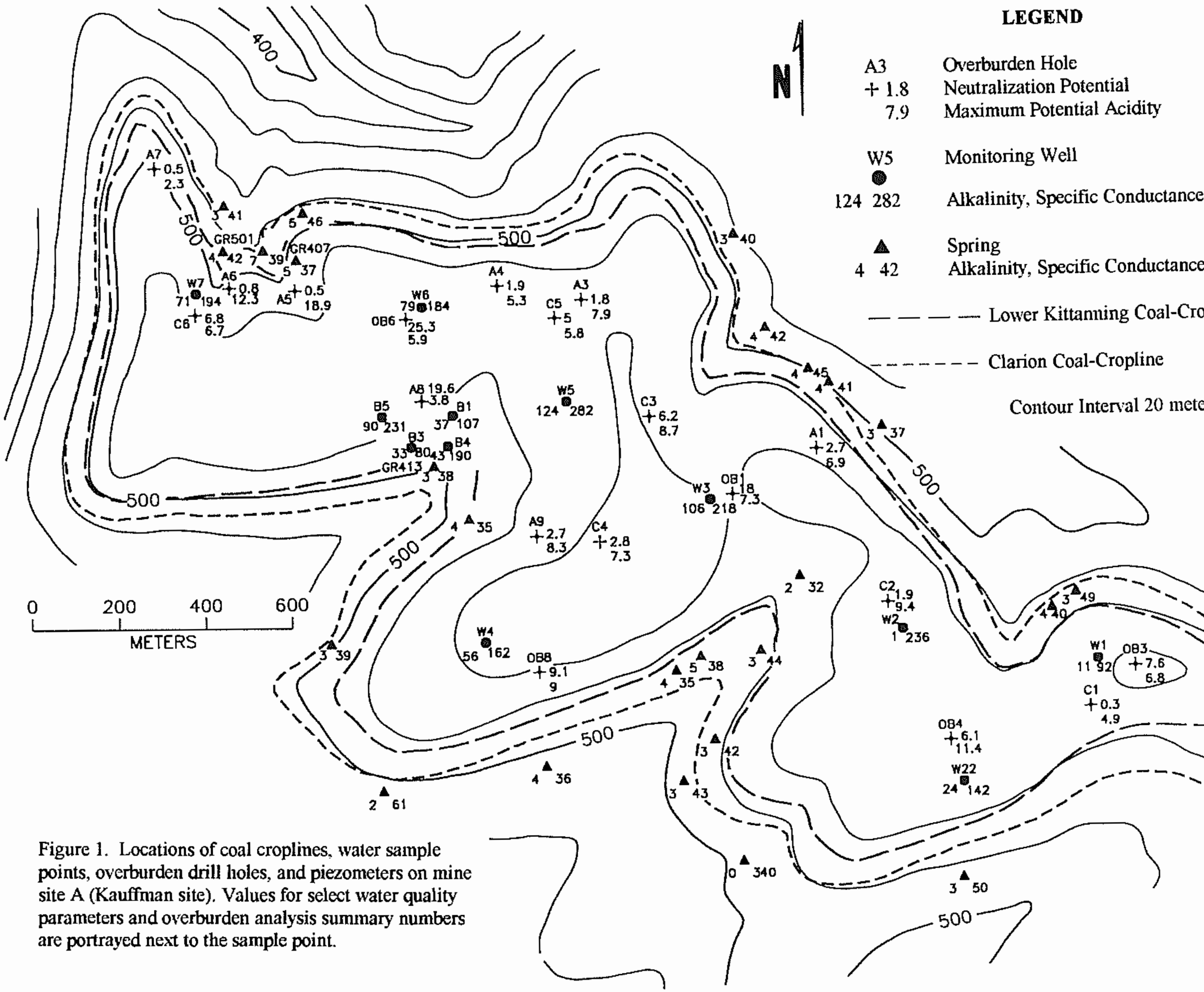

Figure 1. Locations of coal croplines, water sample points, overburden drill holes, and piezometers on mine site A (Kauffman site). Values for select water quality parameters and overburden analysis summary numbers are portrayed next to the sample point.

shows summaries of acid-base accounting data for overburden drill holes.

Figure 1 clearly indicates that spring-water quality is significantly lower in alkalinity and specific conductance than well water. Alkalinity of springs is typically less than 5 mg/L and conductivity less than 50 µS/cm. In contrast, wells typically have much higher alkalinity (typically >70 mg/L) and specific conductivity (~200 µS/cm). Piezometers completed within the hill of the Kauffman site indicate a steep downward flow gradient at the horizon of the LK coal. Between the lower permeability of the unweathered-rock zone and the downward component of much of the flow, little water from the unweathered-rock zone is contributed to the springs. It is also apparent that there is a regional distribution of well water alkalinity. Wells on the eastern portion of the area have lower alkalinity than those on the western portion. This pattern is consistent with the higher NP's reflected in the overburden data on the western portion of the site (Fig. 1).

The geologic controls on distribution of calcareous units are complex on this site. Observations of highwalls show that the calcareous material occurs as calcite and minor siderite as cement between sandstone grains in trough bottoms of some channel sandstone (Skema, 1995, personal communication). These calcareous trough deposits are laterally discontinuous and only occur in the basal portion (bottom 3 to 5 m) of a thick (18 to 24 m) channel-sandstone unit. Observations of drill core also suggest that some of the calcareous cement in sandstone is associated with vertical fractures and bedding plane separations. However, calcareous minerals are not found in most fractures.

Overburden holes were paired with wells or springs within 140 m for comparisons of alkalinity of groundwater with overburden NP. NP and alkalinity show a strong positive relationship (Figure 2), with alkalinity (mg/L) being four times the NP value (tons/1000 tons). A similar relationship is seen between specific conductance and NP (correlation coefficient, $r = 0.82$). As would be expected, specific conductance and alkalinity show a strong positive relationship ($r = 0.94$). These relationships imply that dissolution of calcareous minerals, where present, has a significant impact on groundwater chemistry.

Sulfate, a conservative aqueous ion, is a weathering product of pyrite. Therefore, a comparison was made between maximum potential acidity (MPA) and sulfate. MPA shows no relation to sulfate in nearby groundwater and has, if anything, an inverse relation to specific conductance. Sulfate concentrations were generally less than 35 mg/L.

Detailed Study of Water Quality at the GR-413 Spring. Zhradnik (1994) investigated the flow patterns in a small area at the Kauffman mine. Five air rotary drill holes (B1 through B-5, Fig. 1) were drilled within the area that apparently feeds groundwater to the GR-413 spring. The drill holes were completed with 2.5-cm-diameter piezometers in the LK coal horizon. The piezometric surface as measured in these five holes is just above the coal elevation, and indicates that water in the coal has a component of flow toward the cropline. Figure 3 is a cross-section showing the stratigraphic and hydrologic relationships up gradient from spring GR 413. The flow of the spring in conjunction with estimated evapotranspiration values indicates that the spring must drain an area of about 140,000 m^2, including the area of holes B-1 through B-5 (Abate, 1993).

Based on four years of quarterly sampling, plus Zahradnik's data, the average specific conductivity of the spring water is 42.9 µS/cm, with a standard deviation of 10.8 (Fig. 4). In contrast, water from the B-series wells ranges from 74 to 270, averaging 171 µS/cm (s.d. 72), or about four times as high. Comparison of Ca, Mg, K, and SO_4 values indicates similar ratios, as indicated in Table 1. During periods of high flow and during many periods of low flow, SO_4 is 7-12 mg/L, but during some periods of low flow, SO_4 increases to 15-25 mg/L, or even higher (Fig. 5). Most of these high SO_4 values are during late winter and early spring. This pattern indicates that most of the year, the spring is fed mainly by dilute water that does not penetrate as deeply as the LK coal horizon. Instead, the spring flow must pass through shallower horizons, very likely in the zone of highly fractured rock described by Hawkins et al. (1996). Hydrographs of this spring (Fig. 6) indicate that rainfall is accompanied almost immediately by a sharp peak in flow resulting from surface runoff (observed at the site), then a few days later by a broader peak that is interpreted to result from flow through the shallow weathered zone. Appreciable storage must exist in this shallow zone to account for the year-round flow of this spring.

MINE B: Wharton Township, Fayette County

The principal coal seam mined at site B is the upper Kittanning (UK). Field pH and specific conductance were measured prior to mining in several uncased drill holes which were completed down to the UK seam. Additionally, numerous UK cropline springs

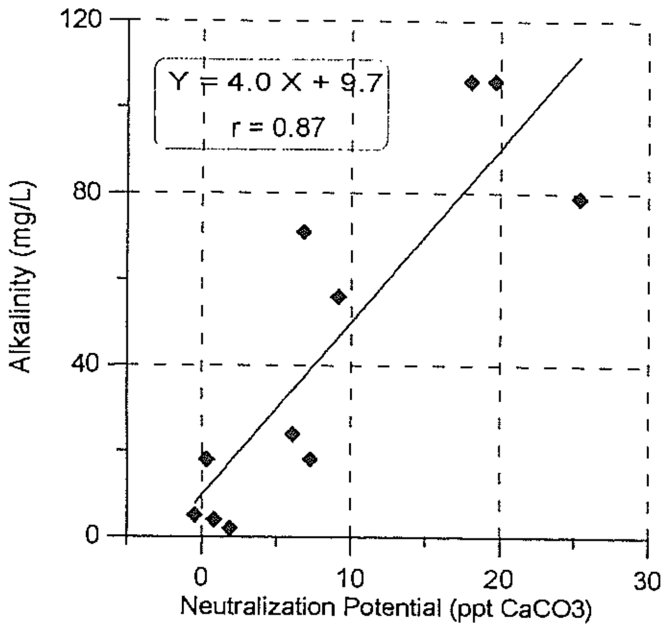

Figure 2. Alkalinity of groundwater associated with the lower Kittanning coal seam as a function of NP at mine site A.

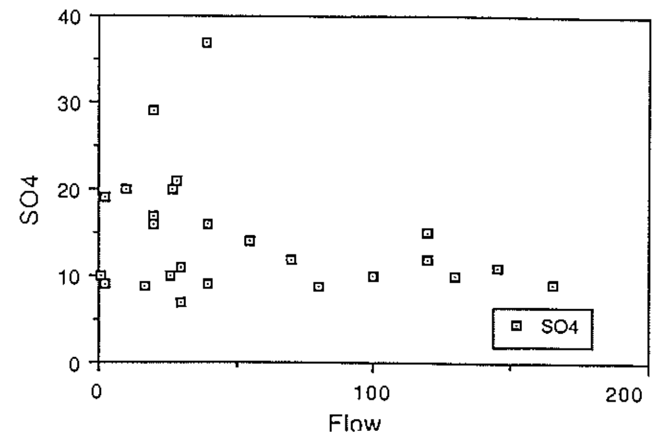

Figure 5. Sulfate as a function of flow. Note higher sulfate values during low flows.

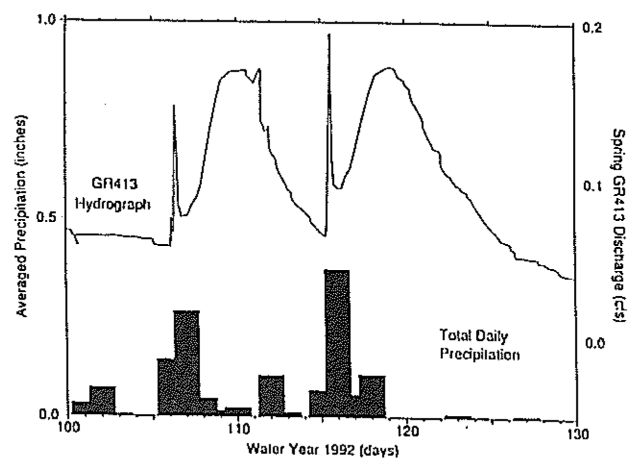

Figure 6. Spring GR-413 response to individual storm events. The initial spikes are from surface runoff (from Abate, 1993).

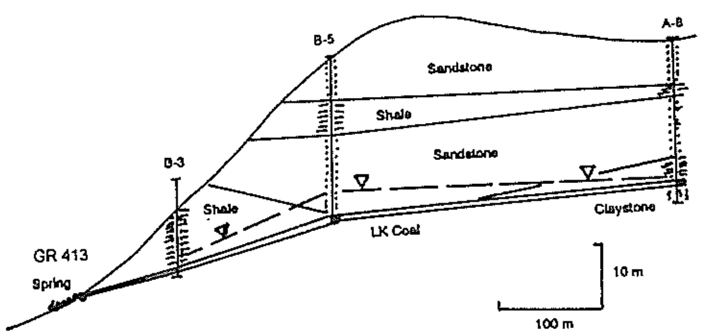

Figure 3. Cross-section through the area of GR-413.

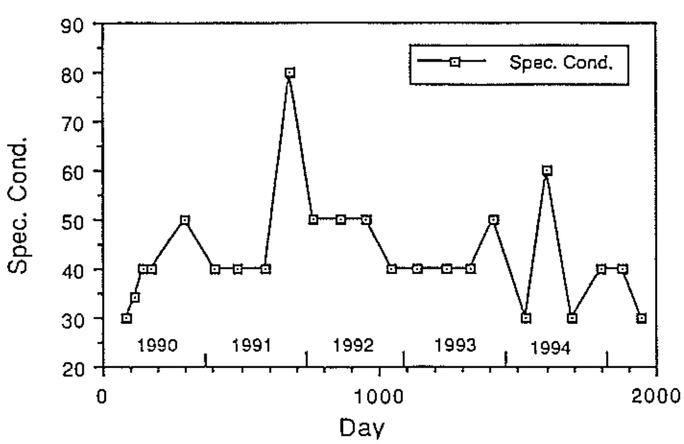

Figure 4. Specific conductivity as a function of time for spring GR-413.

Table 1. Representative chemical data for the GR-413 spring area (Zahradnik, 1994).

Constituent	B-1	B-2	B-3	B-5	GR-413
SiO_2 (mg/L)	4.7	6.3	4.9	4.2	2.2
Ca (mg/L)	7.9	11.5	4.5	26.7	1.7
Mg (mg/L)	5.2	8.9	3.4	4.8	1.9
Na (mg/L)	4.5	4.5	2.8	1.3	.3
K (mg/L)	3.2	3.1	3.6	3.3	1.2
HCO_3 (mg/L)	6.1	0.0	4.9	14.6	2.4
Cl (mg/L)	3.1	2.3	2.2	2.2	0.7
SO_4 (mg/L)	28.1	97	15.7	14.1	8.9
pH	6.5	3.9	6.5	6.9	5.6
Sp. Cond. (μS/cm)	120	240	80	180	40
Temp. (°C)	11	10	11	9	14

Date of Sampling: Dec. 5, 1993. Oct. 28, 1995 data shows similar relations.

were sampled during collection of background data. Figure 7 is a map showing the Upper Kittanning coal cropline and water sample points.

The specific conductivity of the crop springs and shallow (near crop) wells have lower values (38-62 μS/cm) than the drill holes located toward the middle of the hill where depth to the coal is the greatest (158-221 μS/cm). The pH of the springs is also lower than the wells. NP is negligible in areas with less than 9-12 m of cover, evidently because of weathering (Fig. 8). The higher pH and conductance increase are both coincident with an increase in NP (Fig. 8 and 9). The water in deeper drill holes exhibits higher dissolved solids than in cropline springs and holes with shallow cover, due to the increasing abundance of calcareous minerals with increasing overburden thickness. The spring water is very similar in quality to that of the shallowest drill holes. The high NP strata are freshwater limestones and calcareous shales. The geology of this area is addressed in Brady et al. (1988), where the mine site is refered to as area "C".

Cropline springs have alkalinity between 1 and 9 mg/l. Unfortunately, alkalinity was not sampled in the drill holes, but it is a near certainty that the alkalinities were higher, judging from elevated pH and conductance. This hilltop has been mined and reclaimed and is producing drainage with an average alkalinity of 380 mg/L.

MINE SITE C: Lower Turkeyfoot Township, Somerset County

Mine Site C (Fig. 10) is an example of a site lacking significant calcareous overburden rock within the proposed mine area. This deficiency is shown by the low NP's of the two overburden holes (OB-A and OB-C), and by the low alkalinity of cropline springs, small country bank mines, and water collected from the two overburden holes, which were uncased down to the coal. Near the actual area mined, the highest alkalinity is 11 mg/L from cropline spring SP-14. Two of the springs below the coal cropline have alkalinity as high as 31 mg/L. Apparently calcareous strata exists below the coal.

The two overburden holes encountered predominately sandstone, with coal at 16.4 m and 22.4 m for OB-A and OB-C respectively. The highest neutralization potential in OB-A is 19 tons/1000 tons, the highest in OB-C is 15 tons/1000 tons. The highest percent sulfur (excluding the coal) in OB-A was a 0.3 m binder within the coal bed that had 2.0 percent sulfur (% S). A 1.2 m-thick shale overlying the coal contained 0.5 % S. The highest percent sulfur in OB-C was the shale below the coal, which had 1.7 % S. The next highest sulfur in the overburden is only 0.2 %. The overburden shows the presence of acid-producing strata, but lacks alkalinity producing strata.

Table 3 compares rock chemistry and water chemistry in the two overburden drill holes. The water quality is consistent with the overburden data in indicating a lack of calcareous rocks. Because of the lack of naturally occurring calcareous rocks, an average of 45 tons $CaCO_3$/acre was brought to the site. Additionally, the material with percent sulfur greater than 0.5 % was selectively placed in "pods" that were located such that they would be above the postmining water table. Twenty tons/acre of the alkaline material was placed on the pit floor, with most of the remainder mixed into the high-sulfur spoil pods. Analyses of water from sample point SP-14, within a year after backfilling was completed, show degradation due to mining (Table 3). Evidently the amount of alkaline material added was inadequate to prevent acidic drainage.

Figure 10 includes water quality for some springs, up slope and to the north of the mine site, that have higher alkalinity (35 to 52 mg/L) than cropline springs. The recharge of these springs is stratigraphically and topographically higher than the upper Freeport coal. The Glenshaw Formation, which is the unit from which these springs arise, is known to contain several calcareous marine zones (Flint, 1973). These higher alkalinities may indicate that there is some calcareous material preserved within the shallow groundwater flow system and/or the springs may be receiving some water from a deeper source. Although no deeper well data exists for the Glenshaw Fm. in the immediate area of the mine site, a 40 m deep well 3 km north-northeast of the site, which penetrates the lower portion of the Glenshaw Formation, has alkalinity of 106 mg/L, conductance of 260 μmhos/cm, and sulfate of 9 mg/L (Tom McElroy, 1995, personal communication). Although these data are limited, it appears that wells within the Glenshaw Formation also have higher alkalinity than springs associated with the same strata.

Comparison with Other Parts of the Appalachian Basin

Climate in the Appalachian Basin from Pennsylvania to Alabama is fairly similar. Average annual temperature in the north is ~10° C and in the south >15° C. Precipitation also increases from north to

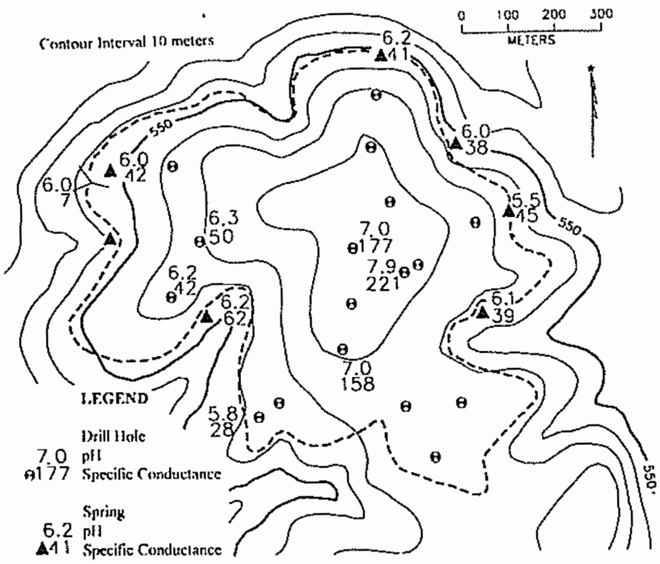

Figure 7. Location of cropline, drill holes and water sample points, and water quality data at mine site B.

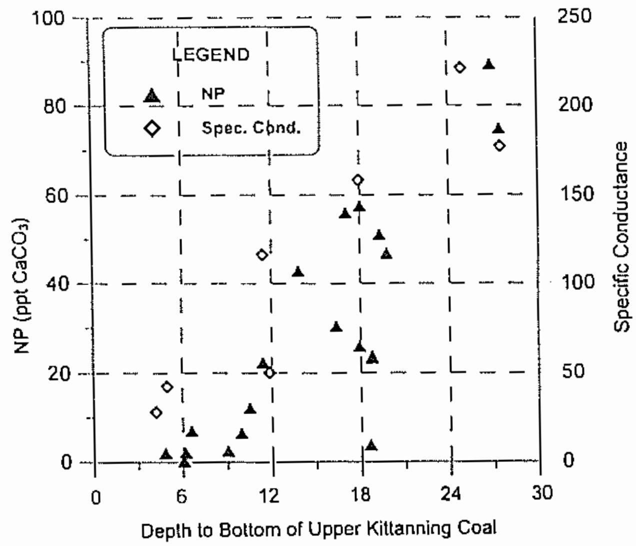

Figure 9. NP and specific conductance (µS/cm) as a function of depth (meters) from the surface to the bottom of the upper Kittanning coal seam for overburden holes (NP), and drill holes and springs (alkalinity).

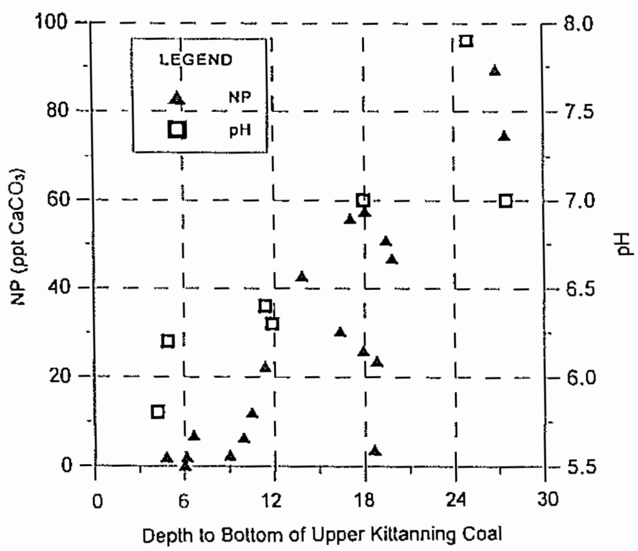

Figure 8. NP and pH as a function of depth (meters) from the surface to the bottom of the upper Kittanning coal seam for overburden holes (NP), and drill holes and springs (alkalinity).

Table 2. Overburden and water quality comparisons for drill holes OBA and OB B on Mine Site C.

Drill Hole	Parameter	NP (ppt)	Alkal. (mg/L)	MPA (ppt)	SO_4 (mg/L)
OB A	ABA (1)	3.5		4.4	
	ABA (2)	0.0		2.4	
	water		5.5		34
OB B	ABA (1)	4.5		2.8	
	ABA (2)	0.0		1.0	
	water		6.5		10

Notes: NP, neutralization potential; MPA, maximum potential acidity. ABA (1) is the traditional method of ABA computation, which includes all determined NP and MPA values. ABA (2) computations were made such that all NP's < 30 and % S's < 0.5 are assigned a value of zero. Methods of computation from Smith and Brady (1990).

Table 3. Postmining water quality at SP-14.

Date	pH	Acidity (mg/L)	Mn (mg/L)	Al (mg/L)	SO_4 (mg/L)
1/12/94	3.7	22	33	35	930
4/21/94	3.8	434	54	54	434

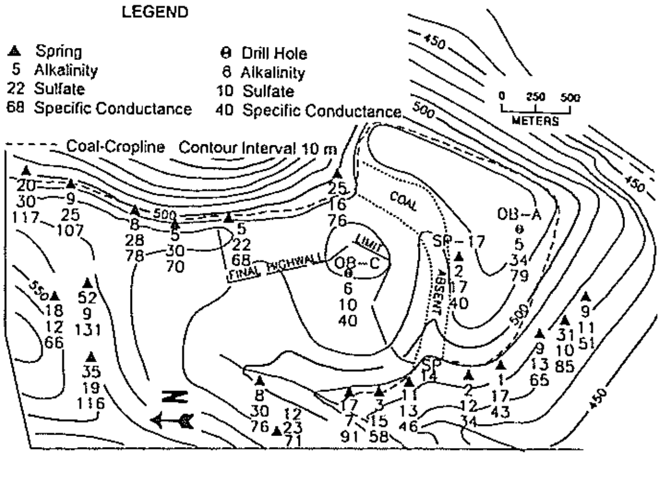

Figure 10. Locations of coal cropline, water sample points, select water quality parameters and overburden holes for mine site C.

south, with rainfall averaging 90 cm in northern Pennsylvania to more than 140 cm in Alabama (Weeks et al., 1968). Annually the infiltration rate of water is sufficient that groundwater is continually flushed through the rock strata from recharge to discharge points. This flow tends to leach out the more soluble minerals. Therefore, shallow groundwater on the Appalachian Plateau has low dissolved solids compared with arid regions.

Geology throughout the Appalachian Plateau is also similar in many respects. The rocks are predominately flat-lying, consisting of sandstone, conglomerate, siltstone, shale, claystone, limestone and coal (Miller et al., 1968). Hills have been subjected to stress-relief forces which have intensified fracturing and subsequently weathering of the slopes, and resulted in higher permeabilities within the weathered zone (Hawkins, et al., 1996). These geologic and climatologic factors result in similar groundwater hydrologic characteristics throughout the plateau.

Numerous studies have investigated the groundwater hydrologic characteristics on the Appalachian Plateau, but very few studies have related the hydrology, groundwater chemistry and rock chemistry. Powell and Larson (1985) investigated water quality in an unmined watershed in a coal-producing region of the Appalachian Plateau of southwestern Virginia. The rock strata are in the Pennsylvanian Norton Formation. The most common carbonate present was siderite, following by calcite and dolomite. Minor amounts of pyrite were generally associated with coal and adjacent strata. They observed that water from springs typically had lower concentrations of alkalinity and dissolved solids than water from dug and drilled wells (Fig. 11). The springs typically have lower alkalinity than dug wells, which have lower alkalinity than drilled wells. Sulfate concentrations are similar for springs, dug wells and drilled wells (with one exception, SO_4 was less than 40 mg/L).

Powell and Larson (1985) envisioned two groundwater flow systems in their study area. One of these "moves under and through the weathered rock or soil layer along the surface of the consolidated rock." The other system "flows through rock fractures and provides the main source of domestic supply" (most domestic supplies were drilled wells). Water in the shallow flow system flows relatively rapidly through rocks thoroughly leached of calcareous minerals. A few of the springs, and many of the deeper waters have high alkalinity (>100 mg/L) (Fig. 11). The high alkalinity springs probably issue from deeper flow systems; however these are the exception rather than the rule.

Singh et al. (1982) in a study of the Mahoning Sandstone in Preston Co. WV, found a weathered zone of about 6 m deep which was low in sulfur and "exchangeable bases" (e.g., Ca and Mg). This indicates that both pyrite and calcareous minerals were removed by weathering within this zone. Brady et al. (1988), in a study that included the area of Mine C of this study also documented the loss of calcareous minerals within ~6 m of the surface. These findings on surface rock-weathering are consistent with the current study.

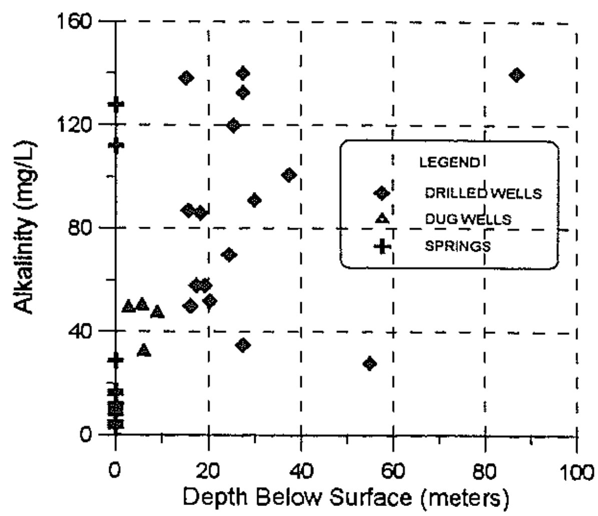

Figure 11. Sulfate as a function of depth of groundwater sample souce in Buchanan Co., VA. Springs are shown at zero depth. Data are from Powell and Larson (1985).

The combined observations of Powell and Larson (1985), Singh et al. (1982), Brady et al. (1988), and this study show evidence for a shallow chemically and physically weathered zone, and two separate shallow flow systems. Figure 5 in the companion paper (Hawkins et al., 1996) is our conceptual model of groundwater flow on the Appalachian Plateau. The literature review in Hawkins et al. (1996) demonstrates the consistency of groundwater hydrologic properties throughout the Appalachian Plateau. Although less research has been done on rock and water chemistry, that which has been done shows results similar to those in PA. It appears that the principals observed in Pennsylvania are applicable to much of the Appalachian Plateau.

Discussion

Surface mining in Pennsylvania mainly occurs within 30 m of the surface and most mines are in groundwater recharge areas (e.g., hilltops). A common misconception has been that water quality of cropline springs in unmined areas is typical of water associated with the coal seam. As illustrated at Mine Sites A and B, water associated with coal- cropline springs can be much more dilute than water from the same coal seam under deeper overburden cover. The cropline springs and shallow wells represent water flowing through the near-surface weathered-rock zone. This weathered-rock zone is quite permeable due to chemical and mechanical weathering. Typically calcareous minerals are absent or negligible within this weathered zone. The rapid flow-through time for the water along with the leached nature of the weathered-rock zone results in water that lacks alkalinity and contains low dissolved solids.

Wells penetrating deeper overburden are completed in unweathered or less weathered materials with lower permeability. Groundwater flow is primarily along fractures and bedding planes. The combination of calcareous minerals, and longer residence time for the groundwater, results in significant dissolution of calcareous minerals forming bicarbonate alkalinity. Downward flow and substantially lower hydraulic conductivities probably result in little of this water reaching the cropline springs.

Mine Site C is an example of a site that lacks significant calcareous rocks. This situation persists from shallow cover to deep cover (maximum overburden that would be disturbed by mining). The lack of calcareous rocks is confirmed by the chemistry of the two overburden test holes and water quality associated with springs, country bank mines, and the overburden drill holes.

From Mine Sites A and B there appears to be a direct relationship between the amount of calcareous material preserved in the overburden and the alkalinity, conductivity and pH of the groundwater. No such relationship exists when comparing MPA (i.e., percent sulfur) with sulfate, probably because of the very limited oxidation of pyrite under saturated conditions. Calcareous minerals are rather soluble in groundwater, whereas pyrite is not. The acid in acid mine drainage is not produced by a simple dissolution process, but by an oxidation process. Pyrite in unmined areas remains largely in an unoxidized state. Premining water quality in deeper drill holes provides a second confirmatory tool, along with acid-base accounting NP, to determine the relative presence or absence of calcareous rock and its distribution within the proposed mine area.

Conclusions and Implications

All of the Pennsylvania sites studied were isolated hilltops within groundwater recharge areas. In all cases the coal cropped out on the sides of the hill. The dominant flow systems for all mines are relatively shallow, with the deepest monitoring wells (completed to the coal seam) on the order of 35 m deep. Where conditions are similar to those given in the examples above, groundwater alkalinity reflects the presence or absence, and abundance, of calcareous rock.

Water quality is directly related to the flow path, the dissolution of material contacted by the groundwater, and the contact time of the water with the rock.

Cropline springs and shallow wells (6 to 9 m deep) that have low or no alkalinity are indicative of shallow leached/weathered overburden. No significant NP's are likely to occur within this zone. Where calcareous rocks are present, such as some deeper cover situations, the calcareous minerals will dissolve in the water and can be measured as alkalinity. Low alkalinity in well or spring water indicates the absence of calcareous strata within the groundwater flow path for that well or spring. It might be expected that sulfate would reflect the amount of pyrite that is present, but there is no relationship between the amount of pyrite (in terms of MPA) and sulfate concentration, thus indicating that pyrite oxidation prior to mining is negligible.

The findings of this study have several important implications:

(1) Coal cropline springs typically reflect very shallow flow through a weathered rock zone and do not necessarily reflect water quality under deep groundwater conditions. Wells are needed to ascertain water quality in the deeper groundwater systems.

(2) Groundwater chemistry, when used with groundwater hydrologic data, can help in better defining groundwater flow systems.

(3) There is a relationship between overburden neutralization potential and groundwater chemistry. If the site is hydrologically isolated such that the only recharge to the site is precipitation, and if alkalinity in wells is high (> 50 mg/L), calcareous minerals are within the flow system and probably near the water sampling point. Where alkalinity is low in wells or springs (< 15 mg/L), the recharge area lacks appreciable calcareous rock.

(5) Groundwater alkalinity can be used to help determine whether overburden sampling for NP has been representative. If overburden analysis does not indicate significant calcareous rocks to be present, but water from wells into the same units are alkaline, the overburden sampling may not be representative of site conditions and additional overburden drilling and testing would be warranted. The combination of groundwater and overburden chemistry can be used together to better define the extent of calcareous overburden.

(6) Overburden sampling and water sampling must represent both shallow and deep overburden cover to adequately represent the entire mine-site hydrology and overburden chemistry. Holes drilled at greater than the maximum cover to be mined may overestimate NP in the overburden that will be disturbed by mining.

(7) There is no relationship between MPA in the overburden and sulfate in the groundwater, or for that matter, between MPA and any other measured parameter. Sulfate in groundwater from unmined watersheds is typically less than 40 mg/L, regardless of flow system.

(8) The above conclusions are probably applicable to a large portion of the Appalachian Plateau. However, the applicability to areas with different climate, physiography and/or geology is unknown.

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