MODIFICATION OF ACID MINE DRAINAGE IN A FRESHWATER WETLAND *

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ABSTRACT

Tub 'Run Bog, a freshwater wetland in the Appalachian Mountains of West Virginia, is bounded along its eastern edge by an abandoned surface mine. Through the weathering of the exposed pyrite-bearing overburden rocks, acid mine drainage is formed and flows into the wetland irk overland and subsurface flow. lie present three lines of evidence to suggest that Tub Run Bog is effectively ameliorating the quality of the acid mine drainage as it percolates through the wetland. First, interstitial water from-tube lysimeters across-70 m long transects from the surface mine edge into the wetland shows a general decline in the, concentrations of hydrogen and sulfate ions with increasing distance from the surface mine. Second, hydrogen sulfide determinations in interstitial water indicate that biological sulfate reduction is occurring at Tub Run Bog. Third, the chemistry of stream water draining; Tub Run Bog is similar to the chemistry of stream water draining other nearby watersheds and shows little influence of acid mine drainage. We suggest that biological sulfate reduction and the subsequent precipitation of insoluble iron sulfides and/or the evolution of reduced sulfur gases from the wetland soil may be the important processes in modifying the acid mine drainage.

INTRODUCTION

The reduction of stream water quality by acid mine drainage is a serious problem throughout Appalachia and is especially widespread in Pennsylvania,, eastern Ohio, and West Virginia (Appalachian Regional Commission 1969). Iron sulfide minerals (e.g., pyrite and marcasite) exposed during coal mining 'activities are oxidized by autotrophic bacteria such as Thiobacillus spp. This oxidation contributes the abundant hydrogen, sulfate, and iron ions that characterize acid mine drainage.

Of the numerous procedures that have been developed to improve the water quality of acid mine drainage, biological treatment using sulfate-reducing bacteria has received relatively little attention. Sulfate-reducing bacteria utilize sulfate rather than oxygen as a terminal electron acceptor in anaerobic respiration. In reducing sulfate to sulfide.. insoluble iron sulfide precipitates (FeS and FeS_2) are formed, and hydrogen ions are removed from solution in the formation of hydrogen sulfide. Tuttle et al. (1969a) reported that upon percolation through a sawdust pile, acid mine water exhibited a decline in acidity and in the concentrations of sulfate and dissolved iron. These chemical changes were attributed to the activity of sulfate-reducing bacteria. Subsequent laboratory studies (Tuttle et al. 1969b, Hsu and Rice 1970) provided further evidence to suggest that sulfate-reducing bacteria could be effective in treating acid mine drainage. Rice and Rabolini (1974) described an industrial biological treatment process using sulfate-reducers but noted that a large scale facility may be economically unfeasible and would produce a high biological oxygen demand effluent which in itself would be undesirable.

In a reconnaissance of freshwater wetlands we noted a situation where a wetland (Tub Run Bog) was situated adjacent to an abandoned surface mine from which the Upper Freeport Coal had been removed. The acid mine drainage into the wetland bad a pH of 3.4 and-a specific conductance of 222 uS/cm.

In the wetland there was a noticeable odor of hydrogen sulfide. The water draining Tub Run Bog had a pH of 4.5 and a specific conductance of 38 uS/cm which was similar to that found in stream water draining a nearby wetland (pH 4.2, 30 us/cm) not influenced by acid. mine drainage (Big Run Bog). Based on these preliminary observations we formulated a working *hypothesis that* acid mine drainage is chemically modified as it percolates through the wetland from the activity of naturally occurring populations of sulfate-reducing bacteria Three 'independent lines of investigation were used to examine this hypothesis. These included: 1) quantification of the changes in the chemistry of. subsurface water as it flows from the surface mine through the wetland, 2) measurement of hydrogen sulfide concentrations in the interstitial waters of Tub Run Bog, and 3) comparison of stream water chemistry between Tub Run and two other streams draining nearby watersheds. The results of these investigations are presented in this paper.

SITE DESCRIPTIONS

Tub Run Bog (39007' N x 79033' W) is a 23 ha wetland situated in a 275 ha watershed. The wetland is located at the headwaters of Tub Run at 950 m above sea level. The vegetation of Tub Run Bog is typical of high elevation-wetlands in central West Virginia, consisting of communities dominated by both Sphagnum and Polytrichum mosses, with numerous associated sedges and rushes, including Carex folliculata C scoparia, Dulichium arundinaceum, Eriophorum virginicum, Scirpus cyperinus Juncus brevicaudatus,, and J. effusus, and several shrub species, including Pyrus arbutifolia Hypericum densiflorum., and Viburnum cassinoides (Walbridge 1982). Trees are a relatively unimportant component of the wetland vegetation. Most of the substrate in the wetland is a water-saturated organic peat, generally less than 1 m in depth. Although most of the watershed surrounding Tub Run Bog supports a mixed hardwood -hemlock forest, the entire eastern edge of the wetland is bounded by an abandoned surface mine. Tub Run Bog is receiving considerable inputs of acidity, iron, and sulfate in surface and subsurface runoff from the adjacent mine.

Big Run Bog ($39^{o}07'$ N x $79^{o}34'$ W) is a 15 ha wetland within a 280 ha watershed. The wetland is located about 2.5 km west of Tub Run Bog at 980 m above sea level. The vegetation has been well characterized (Wieder et al. 1981, Walbridge 1982) and is similar to the vegetation at Tub Run Bog.

Unlike Tub Run Bog, however, Big Run Bog is entirely surrounded by mixed hardwood-hemlock forest and is not influenced by acid mine drainage.

The East Fork of Big Run (39007' N x 79'341 W) is situated about midway between Tub Run Bog and Big Run Bog and drains a 332 ha watershed which is entirely covered by a mixed hardwood-hemlock forest. No wetland is present within the watershed and no. portion of 'the watershed has been mined for coal.

The streams draining each of these three watersheds are first-order headwater streams, which eventually enter the Blackwater River. All three watersheds are situated on sandstones of the Pottsville Group (Diehl 1981), and because of their close geographic proximity to one another, presumably receive comparable precipitation and dry deposition inputs on an area basis.

METHODS

In the spring of 1981P two transects, each 70 m long and originating -from the surface mine-wetland boundary and extending into the wetland, were established in Tub Run Bog. A slight but discernable break in slope was noted at about 35 and 25 m from the mine-wetland boundary in transects 1 and 2, respectively. Above this break in slope, shrubs including Viburnum cassinoides, Pyrus arbutifolia-; and Nemopanthus mucronata dominated the vegetation, with a corresponding low cover of bryophytes and sedges. Beyond the break in slope, shrub cover progressively declined while Sphagnum Polytrichum, and sedge cover progressively increased. over the entire 70 m, the average slopes of transects I and 2 were 5.2 and 2.9 percent, respectively.

.At 10 m intervals along each transects a porous cup tube lysimeter was installed to a depth of 20-30 cm. In both transects, the lysimeter at the surface-mine wetland boundary was installed in barren soil. On three dates,,(2 July 1981, 24 August 1981, and 24 October 1981) interstitial soil water was collected by applying approximately 60 centibars suction to each lysimeter. After about 24 h, water in each lysimeter was evacuated and partitioned into two separate bottles. Water in one bottle was analyzed for pH upon return to. the-'laboratory. Water in the other, bottle was retained for iron and sulfate analyses- To minimize any possible oxidation of hydrogen sulfide to sulfate, 5 drops of 2M zinc acetate was added to this bottle. The water in these bottles was retained for about 12 h in the laboratory, before decanting into plastic bottles and freezing.

Between 9 July and 16 July 1981, a 30 cm, deep soil core was collected within I m of each lysimeter and was divided into depth intervals on the basis of color. Soil subcores were oven-dried for 48 h at 70^{o}C and then ground it with a mortar and pestle.. One ' g aliquots were combusted at 600'C for 6 h. Organic matter content was determined from loss on ignition. After combustion, the remaining ash was extracted with 6N HCl to determine total iron content. To convert organic matter and iron values on a per gram dry mass basis to a volumetric basis, bulk density values were estimated using an empirical relationship between soil organic matter content and bulk density that had been previously derived for Big Run Bog soils. This relationship is:

$\log_e$(bulk density, g dry soil/cm^3) = -0.0297(% organic matter) -0.3135.

where n = 63, r2 = 0.95, F< 0.0001. .

Hydrogen sulfide concentrations in interstitial water were determined at Tub Run Bog. Two wells were installed in a Sphagnum-Polytrichum dominated area at the edge of the wetland near the strip mine and two wells in a Dulichium arundinaceum dominated area in the center of-the wetland less than 5 m from the min stream channel. Each well was constructed by drilling numerous 0.5 cm holes in a 50 cm long, 10 cm diameter plastic pipe. The pipe was wrapped with two layers of fiberglass mesh screening and was capped at the bottom, thereby providing a water column within each well which was relatively free of particulate matter. Using a hand vacuum pump, water was evacuated from a particular depth below the water table through a glass tube directly into a 125 ml capacity glass bottle containing 5 drops of 2M zinc acetate. Hydrogen sulfide concentrations of the water samples were determined by iodometric, titration (APHA 1976).

Stream water samples were collected at the reference points defining the watersheds of Tub Run, Big Run, and the East Fork of Big Run at approximately two-week intervals from 8 October 1980 through 31 December 1981. pH values for stream water were determined immediately upon return to the laboratory; the remaining water was frozen for subsequent sulfate and iron determinations.

Iron concentrations of the water samples and the soil extractions were determined with a Varian Model AA6 Atomic Absorption Spectrophotometer using standard techniques. Sulfate concentrations in water samples were determined turbidimetrically, using a Technicon AutoAnalyzer and the manifold configuration of Cronan (1979). Precipitation and stream discharge data were obtained from the U.S. Geological Survey (Rauch, unpublished data).

RESULTS AND DISCUSSION

Changes in pH and in concentrations of sulfate and total iron in interstitial water as a function of distance from the edge of the surface mine are shown in Figure 1. In general, the respective behaviors of hydrogen and sulfate ions in the interstitial water along the two transects were qualitatively similar, although the magnitudes of the concentrations differed. A progressive increase in pH and a concomitant decline in sulfate concentration occurred with increasing distance from-the surface mine. For example, in transect 1 the pH generally increased over the first 5gm, with pH values ranging from 3.05-3.55 at the surface mine edge to 5.45-6.05 at 50 m. Between 50 and 70 m, pH changed only slightly. Sulfate concentration in the interstitial water declined sharply within the first 20 m, dropping from 210-275 mg/l at the surface *mine* edge to 5-15 mg/l at ~O m. From 20 to 70 m, the sulfate concentration remained relatively constant and below 20 mg/l. Total iron concentration in interstitial water along transect. 1 was consistently the highest At the edge of the surface mine, with values ranging between 26 and 73 mg/l, and then dropped sharply within the first 10 m. Between 10 and 70 m there was no clear trend in iron concentration with increasing distance. Total iron concentrations at the edge of the surface mine in transect 2 are considerably lower than those obtained for transect 1, and no trend *in* iron concentration as a function of distance was evident. The unusually high iron concentrations at 50 m along transect 2 my be due in part to the location of that particular lysimeter in a small, shallow pool of standing water. yellowish precipitates, presumably iron hydroxides, were occasionally observed at the bottom of this small pool.

Concomitant with the previously noted breaks in slope along each transect line and the associated shift in vegetation, the organic matter content of the top 30 cm of soil abruptly increases (Figure 2). The areas above the breaks in slope, were relatively more subject to fluctuations in water table level than the areas below the breaks, where the relatively constant soil saturation and the consequent maintenance of anaerobic *conditions and* retardation of decomposition represented conditions conducive to the development and potential accumulation of peat. The conditions for sulfate-reducing bacteria should have been optimal below the breaks in slope along each transect. Thus,-we expected to see only slight changes in interstitial water chemistry above the breaks in slope, with more pronounced increases in pH and decreases in sulfate and iron ion *concentrations below* the breaks in slope. The data for pH and sulfate along transect 2 are qualitatively in agreement with our expected results, although we were surprised to see that in transect 1, most of the decline in sulfate concentration and increase in pH occurred within the first 20 m of the transect. Organic matter contents of the soil in the upper portions of transect 1 are considerably higher than in the upper portions of transect 2 (Figure 2), and it appears that there may have been a sufficient supply of organic electron donors and a sufficiently low redox potential above the break in slope along transect I to allow for sulfate-reducing bacteria to be active.

The interpretation of the change in iron concentration in interstitial water along the two transects (Figure 1) is confounded by the fact that we measured total iron, which includes ferric and ferrous ions, as well as any suspended oxidized precipitates. The relatively high concentrations of iron at the edge of the surface mine almost certainly result from the production of acid mine drainage by autotrophic iron sulfide-oxidizing bacteria. The decrease in iron concentrations concomitant with the decrease in sulfate in the first 30 m of the two transects suggests that iron is being removed from solution by the activity of sulfate-reducing bacteria and the subsequent precipitation of insoluble iron sulfides. We also observed however, a slight increase in iron concentrations in some instances between 40 and 70 m. These slight increases my represent the -accumulation of oxidized iron precipitates such as limonite or goethite. The iron content of the soil shows a gradual decline along each transect, probably reflecting a decrease in the iron sulfide minerals associated with the surface mine (Figure 2).

For sulfate-reducing bacteria to be responsible for chemically modifying the acid mine drainage as it percolates through the wetland, certain environmental conditions must prevail. Sulfate-reducing bacteria require an anaerobic environment, and a sufficient supply of both sulfate and organic electron donors (Postgate 1965, Peck 1975). Although it is generally thought that sulfate reducers also require a pH of greater than 4.5, Tuttle et al. (1969b) showed that in laboratory mixed cultures sulfate reducers were active in solutions with pH as low as 3.5.

All of these conditions are met within the wetland at Tub Run Bog and the presence of hydrogen sulfide in interstitial water of the peats (Table 1) *indicates that* sulfate reduction is occurring. Hydrogen sulfide concentration generally increases with depth below the water table, reflecting the anaerobic requirement for sulfate-reducers. It is likely that the hydrogen sulfide in the upper portions of the water column was a result of upward diffusion from the anaerobic zone. Much of this hydrogen sulfide will eventually 'be evolved into the atmosphere. It is also evident from Table I that hydrogen sulfide concentrations were, in general, greater in the wells located relatively near to the surface mine than in the wells located in the center of the wetland near the main stream channel, reflecting the relatively greater availability of sulfate near the surface mine.

The quality of stream water leaving a watershed, with or without a wetland, is indicative of the biological, chemical, and physical transformations that have occurred within the system and provides an overall synthesis of the system's chemical dynamics. Logistically, collecting stream water is relatively easy and thus the frequency of sampling events is often high.

The pH values aver a .15 month period for Big Run and the East Fork indicate that first order streams in this region, either associated with a wetland or not,, are relatively acidic (Figure 3).' The acidity of these streams is attributable to the thin, poorly buffered soils situated over resistant Pottsville sandstones (cf. McFee 1980). Surprisingly, the pH of Tub Run stream water is consistently higher than the pH of the two other streams, which is contrary to what would be expected if Tub Run were influenced by acid mine drainage.

All three streams had low total iron concentrations less than I mg/l (Figure 3). Except for the unexplained slight increase in iron concentration in Big Run during the late summer and early fall of 1981, iron concentrations were similar among the three streams and exhibited no seasonal variation. In terms of iron oncentration, Tub Run appears to be unaffected by acid mine drainage.

Sulfate concentrations in the three streams were comparable over most of the sampling period (Figure 3). Furthermore, seasonal variation in stream water sulfate concentration was qualitatively similar in the three streams with a small decrease observed during the growing season followed by distinct peaks. in late summer-early autumn, especially in Tub Run. The appearance of autumn peaks in sulfate concentration has been reported for small streams draining entirely forested watersheds, including the Hubbard Brook Experimental Forest, New Hampshire (Likens et al. 1977), the Coweeta Hydrologic Laboratory, North Carolina (Swank and Douglass 1977), the Walker Branch Watershed, Tennessee (Shriner and Henderson 1978, Johnson and Henderson 1979) and the Birkenes watershed, southern Norway (Christophersen and Wright 1981), as well as for the stream draining the Storage watershed which contains about 20% peatland in southern Norway (Braekke 1981). There is general agreement that these autumn peaks in stream water sulfate concentration are associated with regional hydrologic conditions. In Particular, during periods of relatively low precipitation and moderate evapotranspiration typical of late summer-early autumn, water solute sulfates accumulate in shallow forest soil horizons. In Sphagnum. dominated wetlands, if the surface peats dry out sufficiently to become aerobic, reduced sulfur compounds can be oxidized to sulfates (Odelien et al. 1975, Rippon et al. 1976). When dry periods are broken by rain events, sulfates are flushed from forest soils and/or aerobic peat layers in wetlands resulting in peaks in stream water sulfate concentrations. Despite the widespread geographic documentation of autumn peaks in stream water sulfate concentration, Braekke (1981) notes that after wet or normal summers these sulfate peaks were less prominent or completely missing in the Birkenes (Christophersen and Wright 1981) and Storgama watersheds, further illustrating the ultimate control by regional hydrology.

Figure 4 illustrates the water balance between precipitation and potential evapotranspiration, calculated by the Thornthwaite method (Oliver 1973), for both Canaan Valley and Tub Run Bog. Canaan Valley is about 15 km east of Tub Run Bog and is the location of a 2,900 ha wetland complex at an elevation of about 970 m (Fortney 1975). Because the water balance calculations for Canaan Valley are based on 16 year average mean monthly temperature and precipitation data, the annual pattern should be generally characteristic of high elevation sites in West Virginia. Specifically, water surplus is high during the winter months because of low evapotranspiration, progressively declines from spring through late summer as evapotranspiration increases, and then begins to increase in early autumn as evapotranspiration decreases. Particularly relevant to the present discussion is that during July, August, and September the water surplus is very close to, zero.-- This general pattern. is reflected in the data for Tub Run Bog over the course of the study period, where the water surplus was actually negative during July and August because of relatively low precipitation (Figure 4). We do not mean to imply that Tub Run Bog (or nearby Big Run Bog) itself completely dried out in July and August of 1981. The calculation of water surplus is based on regional climatological data (i.e., mean monthly temperature and precipitation) and does not take into consideration differences in hydrologic parameters between wetland and upland areas of a watershed. At a finer level of resolution, the water regime of a wetland, because of its low-lying topographic location, is much less susceptible to changes in the region al water balance than the water regime of the surrounding upland area.

The importance of regional hydrology on stream water sulfate concentration is particularly evident for Tub Run, where the late summer-early autumn peaks are much more pronounced than for the other two streams. During protracted dry periods, sulfates and other solutes accumulate in unreclaimed mined areas and can be flushed into stream channels when these dry periods are broken by heavy rainfall and/or a sharp drop in evapotranspiration (Appalachian Regional Commission, Appendix C 1969). This phenomenon is illustrated in Figure 5 where sulfate concentration in Tub Run from July through early October is related to mean daily discharge and daily precipitation. Each of the three sulfate peaks is preceded by a protracted dry period of low precipitation and low discharge that was broken by a relatively large rain event. For the 2 September and 5 October sulfate peaks, the large rain events also resulted in sharp increases in stream discharge such that on these two dates the total fluxes of sulfate from the watershed were especially-large.

Although hydrogen and iron-ions were probably flushed from the surface mine concomitant with the sulfate ions'. sharp changes in pH and iron concentrations in Tub Run stream water were not evident (Figure 3). Considering the low pH of Tub Run, considerable inputs of hydrogen ions would be required to effect even a small change in stream water pH. Iron ions could be removed from the flushed mine drainage by various physio-chemical processes within the wetland including the precipitation of iron hydroxides and cation exchange on peats (cf. Coupal and Lalancette 1976, Lapakko and Eger 1981). Sulfate, however, is relatively unaffected by these physicochemical processes. Although it is likely that the activity of sulfate-reducing bacteria in the wetland increases in response to the pulsed input of sulfate., the unusually high sulfate loading coupled with a relatively low residence time of -the flushed mine drainage within the wetland precludes as complete a removal of sulfate as is observed prior to the flushing event.

The stream chemistry data in Figure 3 and the 16 year average water balance data for Canaan Valley in Figure 4 suggest that increases in sulfate-concentration in Tub Run stream water in late summer or early autumn may be-a recurring pattern, and that the ability of Tub Run Bog to modify acid mine drainage may be strongly influenced by regional hydrologic factors. Nonetheless, on only one sampling date did the sulfate concentration in Tub Run exceed the 20 mg/l limit used by Biesecker and George (1966) to identify streams influenced by acid mine drainage. For the most part, the chemistry of Tub Run stream water is comparable to the chemistry of Big Run and East Fork stream water. -Johnson et al. (1972) calculated average concentrations of sulfate and iron ions of 6.9 and 0.2 mg/l, respectively, in-66 tributary streams in hew England. Although the three streams examined here are relatively acidic, they exhibit typical concentrations of sulfate and iron. In general, Tub Run Bog shows little influence of acid mine drainage.

CONCLUSIONS

Each of the three lines of 'evidence presented in this pa-per is consistent with our initial-contention that freshwater wetlands largely through the activity of naturally occurring populations of sulfate -reducing bacteria, may be very effective in removing acidity, sulfate, and iron from acid mine drainage. In addition, our data indicate that in this particular setting, seasonal. variation in the regional water balance can affect the capacity of the wetland . to ameliorate acid mine drainage. We caution, however, that all of our data are indirect, in that at no time have we specifically quantified rates of sulfate reduction or the fates of reduced sulfur compounds. Further studies are planned to investigate more closely the process of sulfate reduction in freshwater wetlands and the effects of variable iron and sulfate loadings on the process. If the results of these studies are also favorably then the use of either previously existing I or artificial freshwater wetlands could provide a low. post, low maintenance method for treating acid mine. Drainage.

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Table 1. Concentrations (mg/1) of hydrogen sulfide in the interstitial waters of Tub Run Bog peats during summer-autumn 1981. See text for further information regarding the location of the sampling wells. Each value represents either a single observation or the mean of two observations. The fixed length of the water sampling wells and the variation of the water table within each well dictated the maximum sampling depth.

	24 July		6 August		28 August		9 September		25 September	
Depth below water table (cm)	Bryophyte dominated area	Sedge dominated area	Bryophyte dominated area	Sedge dominated area	Bryophyte dominated area	Sedge dominated area	Bryophyte dominated area	Sedge dominated area	Bryophyte dominated area	Sedge dominated area
5	0.55	0.45	0.35	0.3	0.55	0.25	0.3	0.2	1.35	0.4
10		0.7		0.7	0.85	0.5				0.65
15	0.7	0.9	1.2	0.6	1.8	0.8	0.45	0.4	1.6	0.3
20		1.3		0.9						
25	1.65		2.55	1.0			0.5	0.4	1.6	
30				1.2					2.5	
35	2.4		3.65				1.5			

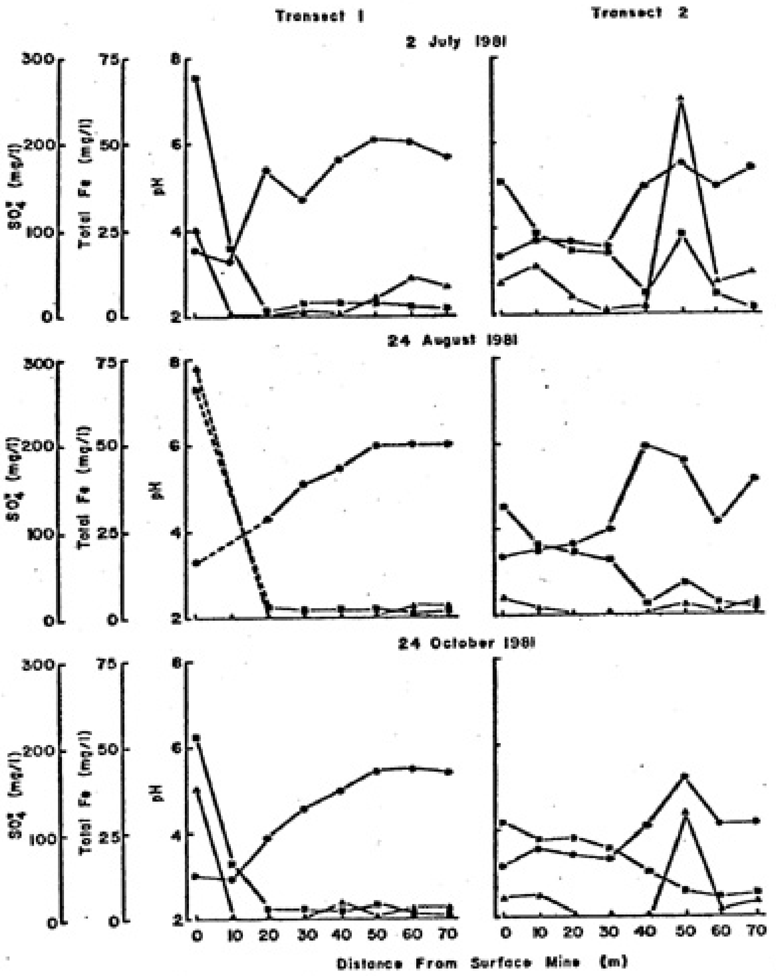

Figure 1. Changes in pH (●) and sulfate (■) and iron (▲) concentrations in interstitial water collected from a depth of 20-30 cm below the soil surface. The transects extend from the surface mine edge at 0 m into Tub Run Bog for a distance of 70 m.

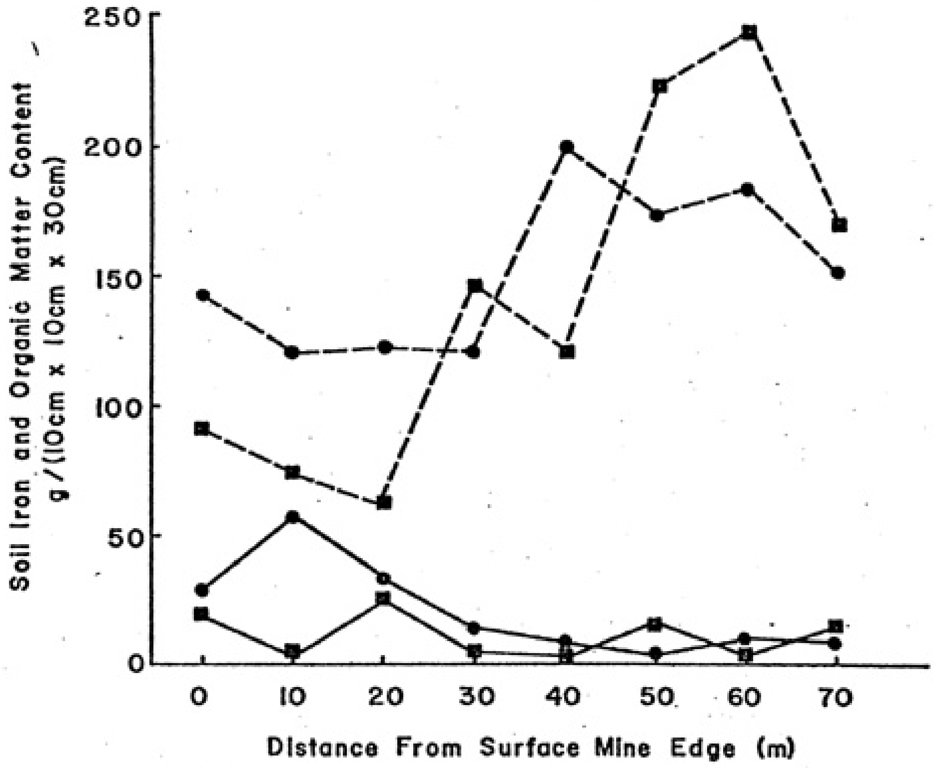

Figure 2. Changes in organic matter (----) and total iron (——) content of a 1 dm^2 block of soil 30 cm deep along transects 1 (•) and 2 (■) at Tub Run Bog.

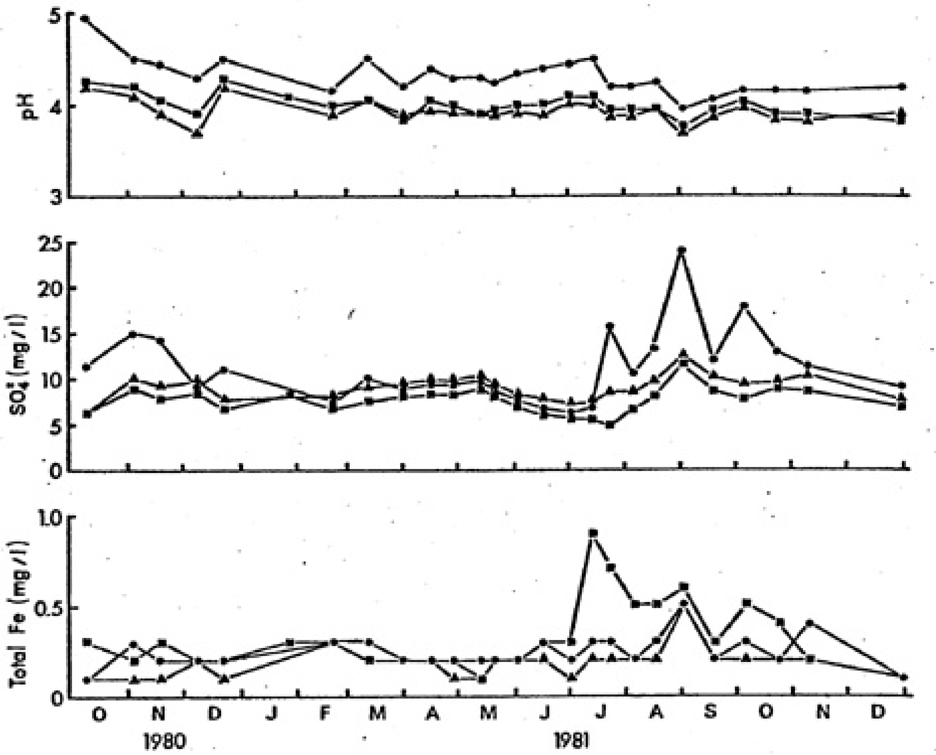

Figure 3. Comparison of pH and concentrations of sulfate and iron in the stream waters of Big Run (■), Tub Run (●), and East Fork of Big Run (▲) between 8 October 1980 and 31 December 1981.

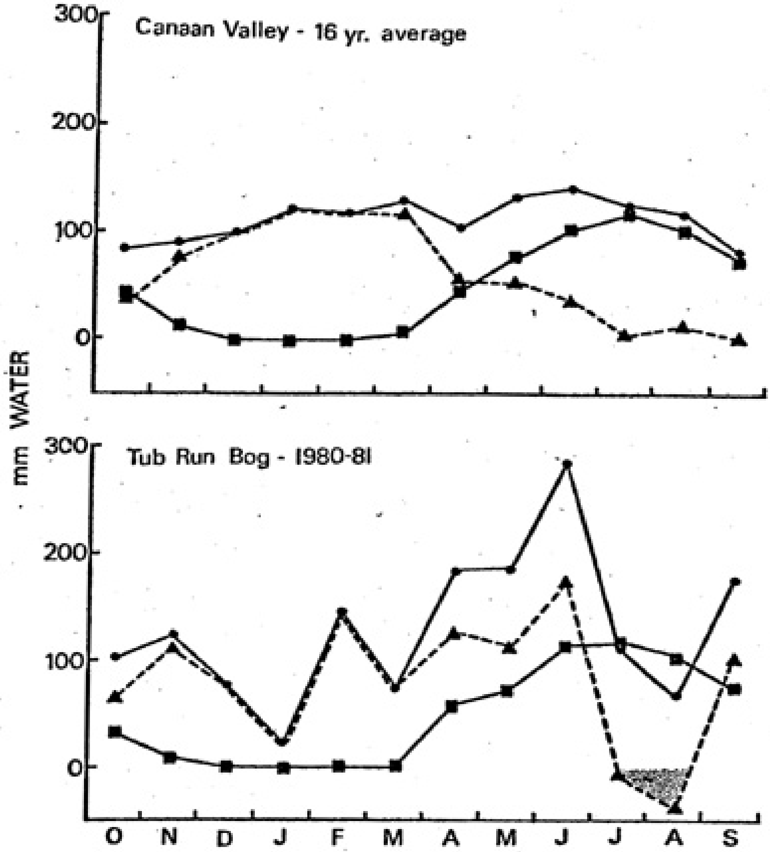

Figure 4. Seasonal variation in the water balance, surplus or deficit (▲----▲), calculated by subtracting potential evapotranspiration (■——■) from precipitation (●——●). Evapotranspiration was calculated by the Thornthwaite method (Oliver 1973). For the upper panel, the plots are based on 16 year average mean monthly precipitation and temperature data recorded at Canaan Valley, West Virginia (NOAA 1965). The lower panel covers the water year from 1 October 1980 to 30 September 1981; precipitation was measured at Tub Run Bog, and potential evapotranspiration was calculated using mean monthly temperatures recorded at Canaan Valley (NOAA 1980,1981).

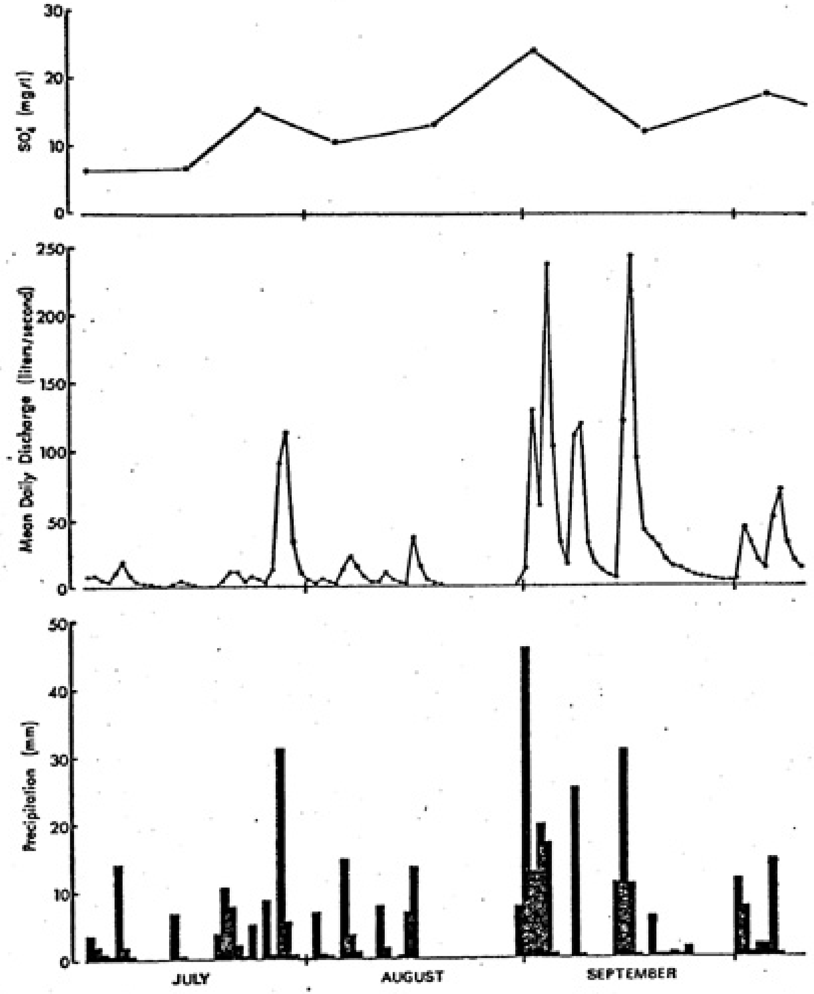

Figure 5. Sulfate concentration in stream water and mean daily discharge for Tub Run, and daily precipitation at Tub Run Bog from 1 July 1981 through October 1981.