INFLUENCE OF WETLANDS AND COAL MINING ON STREAM WATER CHEMISTRY

R. KELMAN WIEDER and GERALD E. LANG

Department of Biology, West Virginia University, Morgantown, WV 26506-6057 U.S.A.

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Abstract. Comparisons of stream water chemistry over a 2 yr period in East Fork, which drains an entirely forested watershed, and Big Run, which drains a forested watershed 8% of which is occupied by Big Run Bog, indicated that Big Run Bog had no effect on stream water H^+ or Cl^- concentrations, but with increasing stream discharge the wetland was a source of Ca^{++}, Mg^{++}, K^+, Na^+, NO_3^-, and $SO_4^=$, and a sink for Fe^{++}. Further comparisons with Tub Run, which drains a forested watershed, 13 and 12% of which is occupied by Tub Run Bog and an abandoned, unreclaimed coal surface mine, respectively, suggested that Tub Run Bog removes H^+, Ca^{++}, Mg^{++}, Fe^{++}, and $SO_4^=$ from inputs of acid mine drainage. Wetland areas on the landscape contribute to the regulation of stream water chemistry in ways that are different from upland areas, and wetlands may have considerable applied potential for minimizing the impact of the mine drainage on stream water quality.

1. Introduction

Export of cations and anions in streamflow provides a major pathway for element loss from watersheds. In comparison with the many studies that have examined stream water chemistry and ion loss in entirely forested watersheds (see Likens *et al.*, 1977; Feller and Kimmins, 1979), relatively few studies have been conducted in watersheds containing wetlands (Crisp, 1966; Verry, 1975; Braekke, 1981; Christophersen and Wright, 1981; Verry and Timmons, 1982). Thus, our understanding of the biogeochemical role of wetlands on the landscape, particularly with regard to potential impact on stream water chemistry, is deficient (Valiela and Teal, 1978; van der Valk *et al.*, 1979; Whigham and Bayley, 1979). In this paper, we compare the chemistry of three streams draining contrasting watersheds in the Appalachian Mountains of West Virginia: East Fork drains an entirely forested watershed; Big Run drains a watershed that is mostly forested but also contains Big Run Bog, a *Sphagnum*-dominated wetland; and Tub Run drains a mostly forested watershed which contains both a wetland, Tub Run Bog, and an abandoned, unreclaimed coal surface mine. Acid mine drainage, characterized by low pH and high concentrations of metals and $SO_4^=$, flows from the surface mine through Tub Run Bog before reaching the main stream channel. A test of the hypothesis that Big Run Bog influences stream water chemistry was accomplished by statistically comparing chemical data between East Fork and Big Run. Stream water chemistry in Tub Run was characterized to further explore the suggestion of Wieder and Lang (1982a), that processes within Tub Run Bog chemically modify acid mine drainage, thereby minimizing the impact of the mine drainage on stream water quality.

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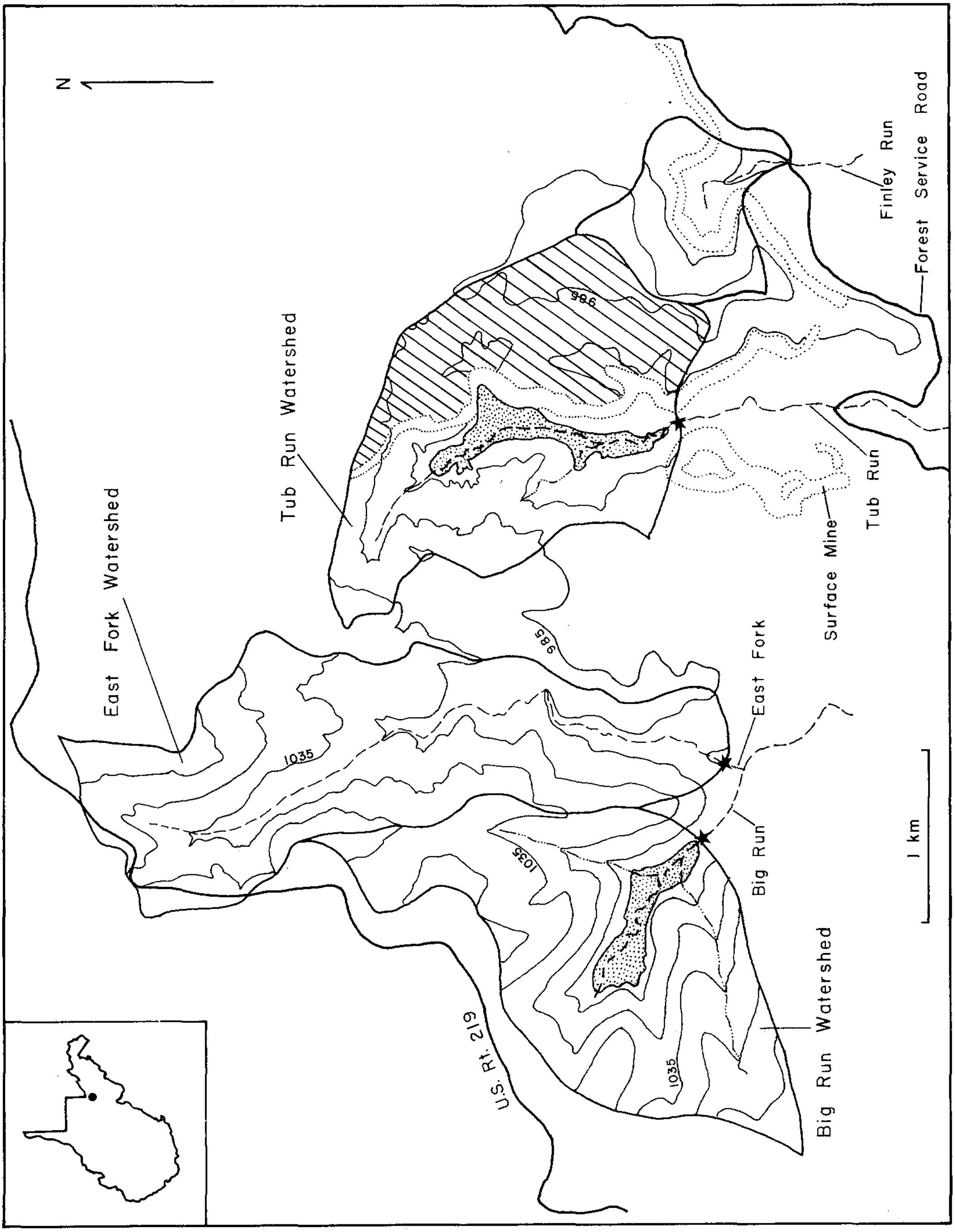

Fig. 1. Map of the general study area. Stars denote the gaging stations, wetlands are stippled, surface mines are outlined with dotted lines, and the undetermined area east of the Tub Run surface mine is hatchured. Counter interval is 25 m.

2. Study Area

The three study watersheds are located at the headwaters of small streams in the Appalachian Plateaus Physiographic Province of West Virginia (Figure 1). Second growth, 60-yr old, forest covers most of the general region. Dominant species include *Acer rubrum*, *Betula allegheniensis*, *Prunus serotina*, *Quercus* spp., *Tsuga canadensis*, and *Picea rubens* (nomenclature follows Strausbaugh and Core, 1970). The three watersheds are located at approximately 39° 06′ N, 79° 34′W, at elevations ranging from 945 to 1120 m above sea level. In all three watersheds the soils on the ridge crests and midslopes are generally either Typic Dystrochrepts or Entic Normorthods. Footslopes and drainage areas generally contain either Aquic Fragiudults or Typic Fragiaqualfs (Losche and Beverage, 1967). These soils are acidic in reaction and have low nutrient status. Surface runoff is moderately rapid and water storage capacity is low. In addition, post-logging fires in the early 1900's (Allard and Leonard, 1952) and subsequent erosion have contributed to the present-day rockiness of the upland soils. Stones and boulders cover 40 to 90% of the surface (Losche and Beverage, 1967).

The East Fork and Big Run watersheds cover 333 and 291 ha, respectively, and both watersheds are underlain mostly by sandstones of the Pottsville Group (Diehl, 1981). Within the Big Run watershed is Big Run Bog, which is really a minerotrophic poor fen (Wieder, 1982). The vegetation of Big Run Bog has been described by Wieder *et al.* (1981) and by Walbridge (1982), and peat and water chemical data for the Bog are given in Wieder (1982). Peat depth averages about 40 cm, and reaches a maximum depth of 225 cm.

The Tub Run watershed contains a 23 ha wetland, Tub Run Bog, that is vegetationally quite similar to Big Run Bog (Walbridge, 1982). In contrast to the other two watersheds, the Tub Run watershed is situated mainly on rocks of the Allegheny Formation (Diehl, 1981). Although the watershed is underlain mostly by sandstones, the Upper Freeport coal and a relatively thin layer of Upper Freeport limestone also crop out (Reger, 1923). Along the eastern edge of Tub Run Bog is a 21 ha abandoned, unreclaimed coal surface mine where the Upper Freeport coal has been removed (Figure 1). Acid mine drainage, with pH as low as 2.2, and Ca^{++}, Mg^{++}, $SO_4^{=}$, and Fe^{++} concentrations as high as 20, 7, 276, and 73 mg L^{-1}, respectively (Wieder and Lang, 1982a, b) is discharged into the Tub Run Bog both chronically via interflow and as a pulsed loading in overland flow following a precipitation event.

In addition to the surface mine in the Tub Run watershed, old underground mines extend into the eastern bank of the slope (Whitehouse, 1980) and dip along with the regional dip (1.6° E–SE; Diehl, 1981) away from the main stream channel of Tub Run. Over 75% of the coal has been subjected to room and pillar underground mining, and in about 50% of the mined areas, pillars of coal have been removed and subsidence of the ceilings has taken place (Fedorko, 1982). As a result of this subsidence, the sandstone overlying the mined coal seam is highly fractured. Precipitation falling on the undermined land east of the surface mine percolates downward into the underground mines and then flows eastward, eventually draining into the North Fork of the Blackwater River about 2.5 km east of Tub Run Bog (Whitehouse, 1980). At Tub Run, the traditional method of determining watershed area by connecting topographic highs upslope from the gaging station provided an estimate of watershed area of 297 ha. Because of the past underground mining and its effect of rerouting water movement away from Tub Run, the undermined area (122 ha) was subtracted from the 297 ha (Figure 1). Water data in this paper are based on a watershed area of 175 ha.

Climatological data for the general study area are available from a national weather station at Canaan Valley, WV, located about 10 km east of the Tub Run Bog at an elevation of 991 m above sea level (NOAA, 1946–1950, 1952–1981). Mean annual temperature is 7.9 °C with a minimum monthly mean of -3.2 °C in January and a maximum monthly mean of 18.3 °C in July. Mean annual precipitation is 133 cm with a minimum monthly mean of 9 cm in October and November and a maximum monthly mean of 13 cm in June. Mean annual potential evapotranspiration (PET), calculated by the Thornthwaite (1948) method, is 58.8 cm, indicating a mean annual water surplus of 74.2 cm. However, one or more months in late summer-early autumn typically show a net water deficit where monthly PET exceeds precipitation (Wieder, 1982). At Canaan Valley, for the 1980–81 and 1981–82 water years (1 October through 30 September) total annual precipitation was 139 and 145 cm. For both years the calculated annual PET value was 57 cm.

The chemistry of precipitation falling on the general study area is typical of the phenomenon of acid precipitation. For the 1980–81 water year, volume weighted mean pH of wetfall was 4.16 and mean concentrations of NO_3^- and $SO_4^=$ were 1.82 and 3.51 mg L^{-1}, respectively, at Parsons, WV, about 10 km southwest of Big Run Bog (NADP, 1980, 1981).

3. Methods

Precipitation volume recorders and stream stage height recorders were installed at each of the three watersheds (Figure 1). Data were recorded at 15 min intervals. Rating curves for stream discharge as a function of stage height were established and periodically checked for each of the three streams. Installation, monitoring, and maintenance of all instrumentation, as well as hydrologic data analysis and reduction were carried out by the U.S. Geological Survey, Morgantown, WV. For each watershed, measurements or estimates of mean daily discharge and total daily precipitation were available for every day of the 1980–81 and 1981–82 water years.

Stream water samples were collected at each of the stage height recording stations at one to two week intervals from October 8, 1980 through December 31, 1981, and from May 5, 1982 through September 29, 1982. Immediately upon returning to the laboratory, pH was determined on a 50 mL aliquot and the remaining water was frozen for subsequent cation and anion analysis. Calcium, Mg, and Fe concentrations were determined on a Varian Model AA6 atomic absorption spectrophotometer; to the solutions for Ca and Mg determinations, La was added as a releasing agent. Concentrations of K and Na were determined by flame photometry on a Technicon AutoAnalyzer.

The NH_4^+, NO_3^-, Cl^-, and $SO_4^=$ concentrations were determined colorimetrically on a Technicon AutoAnalyzer (Technicon Industrial Systems, 1977; Cronan, 1979). Suspended solids concentrations of the small clearwater mountain streams within the general study area are typically quite low (Dyer, 1982). Since our stream water samples were not filtered, values for Ca, Mg, Fe, K, and Na represent total elemental concentrations, but are expressed in their ionic forms in this paper.

4. Results and Discussion

4.1. WATER

Monthly and annual precipitation inputs were averaged across the three study watersheds since differences between watersheds were generally small. Using PET values calculated from temperatures recorded at Canaan Valley, monthly balances between precipitation inputs and potential water losses through evapotranspiration were estimated (Figure 2). July and August 1981 exhibited a calculated net water deficit (as did September 1980, Wieder, 1982), whereas for every month of the 1981–82 water year, precipitation exceeded PET.

Monthly per hectare stream discharge values were of comparable magnitude for all three watersheds (Figure 2), indicating that the presence of a wetland or a wetland and a surface mine had no detectable influence on the monthly distribution of streamflow. Similarly, Verry and Boelter (1975, 1979) reported that the fen portion of an otherwise forested watershed had only a minor effect on the seasonal distribution of streamflow. Some studies have suggested that the presence of a wetland within a watershed may result in augmented spring streamflows because of high runoff from saturated peat and diminished summer and autumn streamflows because of high evapotranspiration within the wetland (Carter *et al.*, 1979; Novitsky, 1979; Verry and Boelter, 1975, 1979). However, these patterns are not evident in our data. Results from the Tub Run watershed are consistent with the 10 yr study of Collier *et al.* (1970) which revealed no consistent differences between an unmined watershed (Helton Branch) and a partially mined watershed (Cane Branch), with respect to the percentage of incident precipitation that left each watershed in streamflow (Table I).

Of the 153 and 159 cm of incident precipitation recorded in the two water years, an average of 72% left the three watersheds via streamflow (Table I). Actual evapotranspiration (AET), estimated as the difference between precipitation and streamflow (assuming no other major inputs or outputs of water and no change in basin storage), averaged 44 cm for the three watersheds over the two water years. Although this estimate of AET is considerably lower than the Thornthwaite PET value of 57 cm, the magnitude of the discrepancy is consistent with data for other watersheds in the mountainous regions of West Virginia (Boyer, 1976).

The percentage of precipitation that left each of the three watersheds in streamflow was considerably higher than that reported for other watersheds in the eastern United States (Table I). Relatively high streamflow, and correspondingly low evapotranspir-

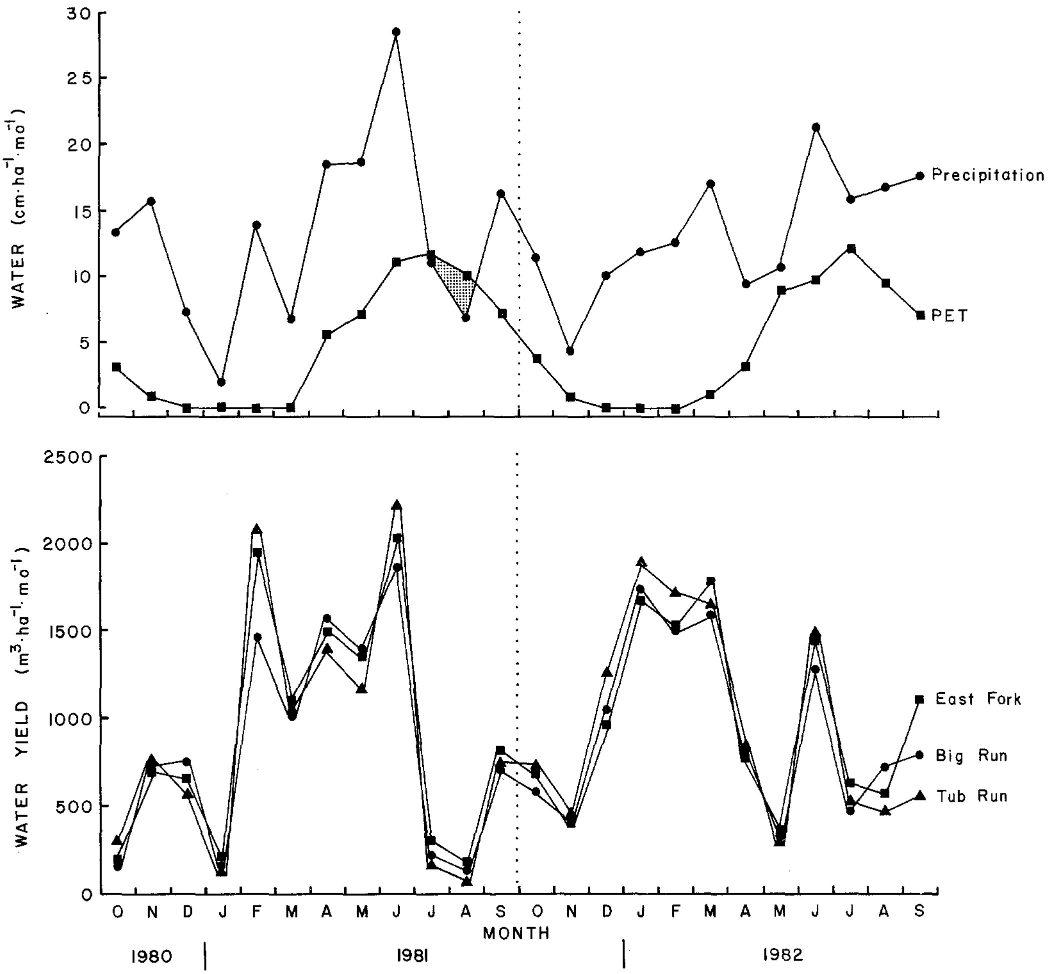

Fig. 2. Hydrologic data for the two water years. The upper panel shows the monthly balance between precipitation and potential evapotranspiration, PET. The stippled region for July and August 1981 indicates a net potential water deficit. The lower panel shows monthly per hectare water yields in streamflow from the three watersheds.

ation, for the East Fork, Big Run, and Tub Run watersheds is attributable to the generally steep slopes of the upland regions, in combination with the rockiness and low water holding capacity of the upland soils (Losche and Beverage, 1967; Boyer, 1976).

4.2. EAST FORK – BIG RUN COMPARISONS

The East Fork and Big Run watersheds are generally similar with respect to underlying geology, upland soils, upland vegetation, and climate, variables which can contribute to the regulation of stream water chemistry. The main distinguishing factor between the entirely forested East Fork watershed and the adjacent Big Run watershed is that 8% of the latter is occupied by a wetland, Big Run Bog. If Big Run Bog does influence stream

TABLE I

Comparison of annual hydrologic budgets for the East Fork, Big Run, and Tub Run watersheds and for other sites in the eastern United States. Evapotranspiration is the difference between precipitation and streamflow.

	Years of record	Precipitation (cm ha^{-1})	Streamflow		Evapotranspiration	
			(cm ha^{-1})	(%)	(cm ha^{-1})	(%)
East Fork, WV	1980–81	153	110	72	43	28
	1981–82	159	120	75	39	25
Big Run, WV	1980–81	153	102	67	51	33
	1981–82	159	114	72	45	28
Tub Run, WV	1980–81	153	107	70	46	30
	1981–82	159	119	75	40	25
Hubbard Brook, NH[a]	19	129	80	62	49	38
Cane Branch, KY[b]	10	120	44	37	76	63
Helton Branch, KY[b]	10	113	43	38	70	62
Walker Branch, TN[c]	6	151	86	57	65	43
Coweeta, NC[d]	30	181	96	53	85	47

[a] Likens *et al.* (1977).
[b] Collier *et al.* (1970).
[c] Henderson *et al.* (1977).
[d] Control watershed 18, Johnson and Swank (1973).

water chemistry, then comparisons between East Fork and Big Run should reflect that influence.

For most ions, differences in mean concentration between East Fork and Big Run stream waters were small in magnitude (Table II). Exceptions are Na^+ and Cl^- whose especially high concentrations in East Fork resulted from road salt application on Route 219 (Wieder, 1982) which passes through the uppermost regions of the East Fork watershed (Figure 1). Patterns of seasonal variation in stream water chemistry were generally similar in East Fork and Big Run, both for ions that exhibited relatively constant concentrations over a water year (Ca^{++}, Mg^{++}, Na^+, Fe^{++}, Cl^-), and ions that exhibited notable seasonal change (H^+, K^+, $NH_4{}^+$, $NO_3{}^-$, $SO_4{}^=$) (Figure 3). Although many of the observed patterns of seasonal variation are typical of watersheds with intermediate aged, successional forest, late autumn pH drops in East Fork and Big

TABLE II

Discharge volume weighted mean ionic concentration (mg L^{-1}) in East Fork, Big Run, and Tub Run stream waters sampled between 1 October 1980 and 30 September 1982 (n = 38)

Stream	pH[a]	Ca^{++}	Mg^{++}	K^+	Na^+	NH_4^+	Fe^{++}	$NO_3{}^-$	Cl^-	$SO_4{}^=$
East Fork	3.85	1.10	0.27	0.25	2.37	0.015	0.24	1.14	4.26	9.46
Big Run	3.91	0.85	0.31	0.35	0.20	0.009	0.31	1.09	0.54	8.02
Tub Run	4.18	1.89	0.42	0.38	0.19	0.019	0.26	0.35	0.41	10.01

[a] Converted from weighted mean H^+ concentration.

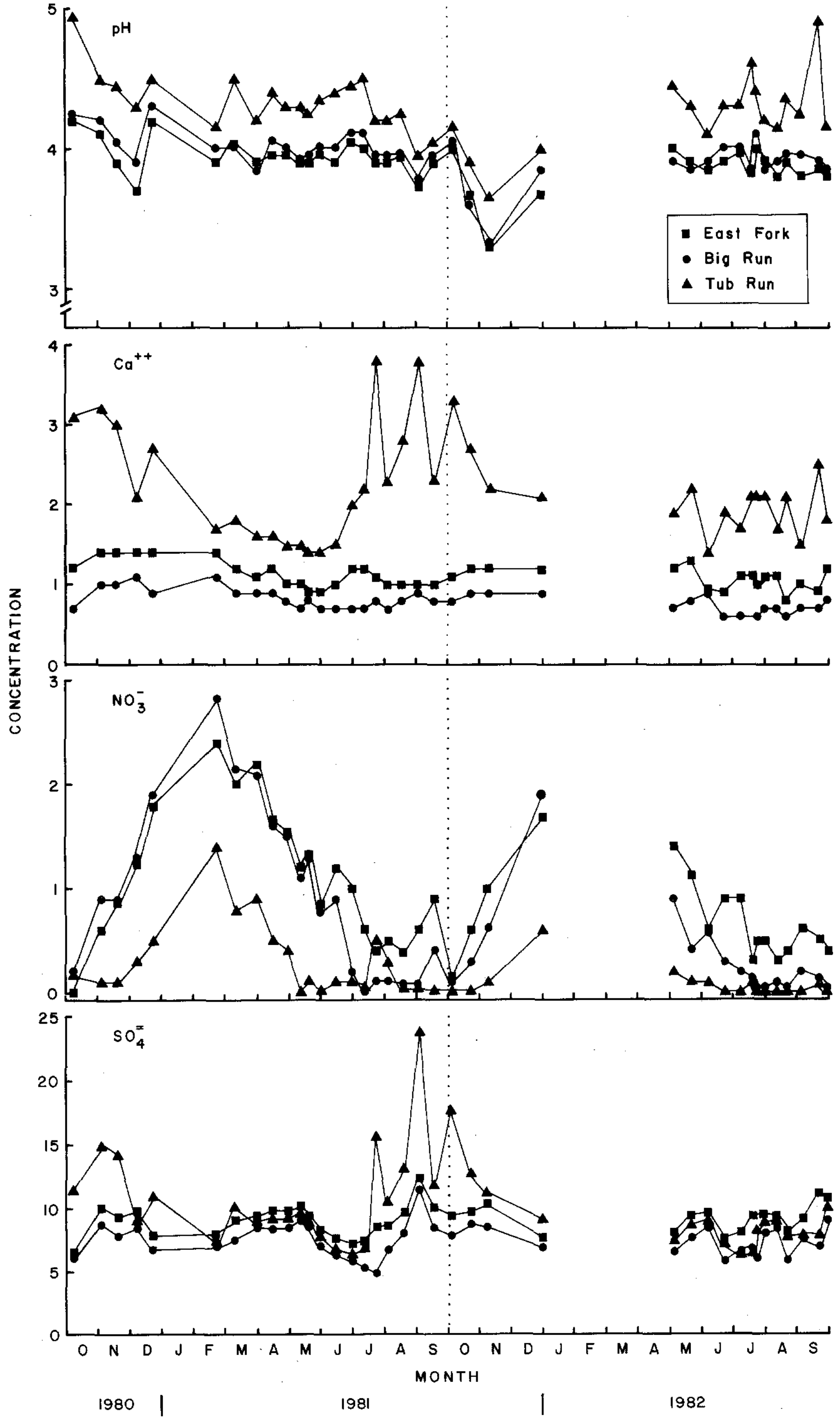

Fig. 3. Seasonal variation in pH and the concentrations of calcium, nitrate, and sulfate in East Fork, Big Run, and Tub Run stream water over the two water years. All data except pH are mg L^{-1}.

Run have not been found in Hubbard Brook (Likens *et al.*, 1977). Concentrations of NO_3^- (Figure 3), and to a lesser extent K^+, were lower during the growing season than in the autumn and winter months, reflecting seasonal uptake and storage (Martin, 1975; Likens *et al.*, 1977; Vitousek, 1977). On 84% of the sampling dates, NH_4^+ concentrations were below the limits of detection, but autumn peaks (up to 0.3 mg L^{-1}) were observed in both East Fork and Big Run, resulting from a pulsed release of mineralized nitrogen derived from senescent and recently dead vegetation (Likens *et al.*, 1977). Both streams exhibited autumn peaks in $SO_4^=$ concentration in 1980 and 1981 (Figure 3), reflecting the flushing of water soluble $SO_4^=$ that had accumulated in upland and/or wetland soils during relatively dry periods (Shriner and Henderson, 1978; Johnson and Henderson, 1979; Christophersen and Wright, 1981). These peaks were absent in the relatively wetter autumn of 1982 (cf. Braekke, 1981). The overall similarity between East Fork and Big Run stream waters regarding patterns of seasonal variation provides little insight into the question of whether Big Run Bog influences Big Run stream water chemistry. To more directly address this question, the following analysis was undertaken.

Hydrologic studies in two other West Virginia watersheds containing wetlands which are physiographically similar to Big Run Bog and Tub Run Bog have concluded that at low flow less than 1% of stream discharge is contributed by wetland-derived water. Moreover, as stream discharge increases, so does the magnitude of wetland water contribution (Evans and Rauch, 1983). Detailed hydrologic investigations are being initiated in the East Fork, Big Run, and Tub Run watersheds. However, for the present analysis, by assuming that the findings of Evans and Rauch (1983) are also qualitatively true for Big Run Bog's contribution to Big Run discharge, we were able to statistically assess the impact of Big Run Bog on stream water chemistry. For each ion, we calculated the ratio of its concentration in Big Run to its concentration in East Fork on each sampling date. If Big Run Bog had no impact on the concentration of a particular ion, this ratio should exhibit no directional change with increasing Big Run discharge. Conversely, a directional change in the ratio with increasing Big Run discharge indicates that the wetland does influence the concentration of a particular ion in stream water. Because there was no *a priori* reason to expect a linear change in the ratio as a function of discharge, the nonparametric Daniel's Test for Trend (Conover, 1980) was adopted.

Results of this test (Table III) indicate that Big Run Bog has no apparent influence on H^+ and Cl^- concentrations in stream water but has a significant effect on all other ions. A positive value of ρ could result from a variety of circumstances, e.g., as discharge increases, concentration in Big Run increases and/or concentration in East Fork decreases; or as discharge increases, concentration in Big Run increases more than in East Fork. Comparable arguments apply to negative values of ρ. Thus, to more closely assess the nature of the significant effects of Big Run Bog on stream water chemistry, Daniel's Test was used to evaluate changes in concentration of individual ions as a function of increasing discharge in each stream (Table III). In this analysis, significantly negative values of ρ in either stream reflect dilution (increasing discharge is associated

TABLE III

Evaluation of changes in ionic concentrations in stream water as a function of discharge using Daniel's Test for Trend (see text for further details). Significant trends (p = 0.05) are indicated with an asterisk. NH_4^+ is excluded because concentrations were usually below limits of detection.

	Dependent variable					
	Big Run[a]/East Fork		Big Run[a]		East Fork[b]	
	ρ[c]	$p > \lvert\rho\rvert$[d]	ρ	$p > \lvert\rho\rvert$	ρ	$p > \lvert\rho\rvert$
H^+	-0.140	0.4027	0.359	0.0269*	0.502	0.0013*
Ca^{++}	0.664	0.0001*	0.336	0.0393*	-0.289	0.0780
Mg^{++}	0.554	0.0003*	-0.016	0.9220	-0.584	0.0001*
K^+	0.397	0.0135*	0.120	0.4713	-0.354	0.0293*
Na^+	0.491	0.0018*	-0.276	0.0936	-0.680	0.0001*
Fe^{++}	-0.723	0.0001*	-0.382	0.0178*	0.413	0.0100*
NO_3^-	0.425	0.0078*	0.426	0.0077*	0.324	0.0470*
Cl^-	0.181	0.2763	-0.454	0.0042*	-0.715	0.0001*
$SO_4^=$	0.489	0.0019*	0.542	0.0004*	-0.383	0.0176*

[a] Independent variable = Big Run mean daily discharge.

[b] Independent variable = East Fork mean daily discharge.

[c] Test statistic is Spearman's ρ; n = 38 for each test.

[d] Probability of obtaining a greater absolute value of ρ.

with decreasing ion concentration), significantly positive values of ρ reflect enrichment (increasing discharge is associated with increasing ion concentration), and nonsignificant values of ρ, whether positive or negative, reflect no directional trend with increasing discharge.

East Fork and Big Run exhibit similar behavior with respect to H^+ (both streams showing enrichment) and Cl^- (both streams showing dilution). Significant dilution of Mg^{++}, K^+, and Na^+ was observed in East Fork, whereas concentrations of these ions showed no significant changes with increasing Big Run discharge. Significant Ca^{++} enrichment was observed in Big Run but not East Fork (Table III). Thus, relative to East Fork, the effect of Big Run Bog on Ca^{++}, Mg^{++}, K^+, and Na^+ concentrations in stream water is to add additional cations with increasing discharge. This result may be counter-intuitive given the renowned ability of *Sphagnum* to adsorb cations from dilute solutions (Bell, 1959; Clymo, 1963). However, cation exchange is an equilibrium-regulated process and it is not necessarily contradictory that *Sphagnum* within Big Run Bog could both remove cations from dilute solutions and still contribute cations to Big Run stream water during periods of high discharge.

Contrasting trends were obtained for Fe^{++}, with enrichment in East Fork and dilution in Big Run. Removal of Fe^{++} from solution within Big Run Bog could be accomplished by adsorption or by the precipitation of iron oxides. Big Run Bog peat has considerable Fe^{++} adsorption capacities (Wieder and Lang, 1984), and oily films, presumably iron oxides, are often seen on surface pools within the wetland. Amorphous iron oxides make up an average of 15% of the total Fe in Big Run Bog surface peat (Wieder and Lang, 1984).

Nitrate and $SO_4^=$ behaved similarly, showing enrichment in East Fork and relatively stronger enrichment (higher values of ρ) in Big Run (Table III). In aerobic surface peat, nitrification (Patrick and Tusneem, 1972; Reddy and Patrick, 1975) and sulfide oxidation (Braekke, 1981; Christophersen and Wright, 1981) can lead to short-term increases in soluble NO_3^- and $SO_4^=$ which can be flushed into the stream following precipitation events, attendant water level rises, and an increased contribution of wetland water to streamflow. Also, adsorption of NO_3^- and $SO_4^=$ may be important processes involved in anion retention in iron-rich mineral soils (Johnson and Cole, 1977; Johnson *et al.*, 1980). However, in highly organic soils anion exchange and anion adsorption are relatively insignificant (Clymo, 1963; Johnson *et al.*, 1980). Both the production of NO_3^- and $SO_4^=$ in aerobic surface peat and the low anion adsorption capacity of organic soils may contribute to the relatively higher enrichment in Big Run than in East Fork.

4.3. TUB RUN STREAM WATER CHEMISTRY

Upland soils, upland vegetation, and climate are similar in the Tub Run, East Fork, and Big Run watersheds. However, because of the regional geologic dip, the rock strata underlying the Tub Run watershed distinguish it from the other two watersheds. Relevant consequences of the geologic shift include the outcrop of the mined Upper Freeport coal and its associated acid mine drainage, and the exposure of the Upper Freeport limestone, which crops out stratigraphically below the coal seam.

Daniel's Test was not applied to the Tub Run stream water chemistry data. The test was useful in making Big Run : East Fork comparisons because only one major factor, the presence of Big Run Bog, distinguished the two watersheds, and the previous work of Evans and Rauch (1983) indicated that the contribution of wetland-derived water to streamflow should progressively increase as stream discharge increases. In contrast, three major features in the Tub Run watershed, the wetland, the surface mine, and the limestone, may each have had effects on stream water chemistry. We have no foundation upon which to make assumptions about how the relative impact of these three features might change as a function of increasing Tub Run discharge. Although Daniel's Test could be easily calculated for the Tub Run data, unambiguous interpretations could not reasonably be made.

For certain elements (K^+, Na^+, NH_4^+, NO_3^-, Cl^-) no direct effects of either the surface mine or the limestone on stream water concentrations were expected (cf. Barton, 1978). Although NO_3^- concentration in Tub Run was considerably lower than in the other two streams, concentrations of the other four ions in Tub Run were generally comparable to concentrations in East Fork and/or Big Run (Table II). Patterns of seasonal variation for these five ions in Tub Run were similar to the patterns exhibited in the other two streams, even for NO_3^- (Figure 3). The consistently lower NO_3^- concentrations in Tub Run relative to East Fork and Big Run was an unexpected result, which conceptually must be related to processes that prevented or delayed either NH_4^+

accumulation, NO_3^- accumulation, or NO_3^- mobility (Vitousek *et al.*, 1979). The relative importance of these processes in influencing Tub Run NO_3^- concentrations remains to be investigated.

Relative to East Fork and Big Run, Tub Run had a somewhat higher mean pH, higher mean Ca^{++}, Mg^{++}, and $SO_4^=$ concentrations, and a similar mean Fe^{++} concentration (Table II). From our data, we cannot quantitatively determine the proportional impact of the wetland, limestone weathering, and acid mine drainage on the concentrations of these five ions in Tub Run stream water. However, by independently examining the chemistry of nearby Finley Run, changes in Tub Run chemistry as the stream flows from above the wetland, through the wetland and below the wetland, trends in anion/cation balances, and seasonal variation in Tub Run stream water chemistry, some qualitative relationships can be developed.

Finley Run is a small stream draining a watershed situated adjacent to the Tub Run watershed and containing a surface mine where the Upper Freeport coal has been removed (Figure 1). Runoff from the surface mine does not flow through a wetland before entering Finley Run, and stream water chemistry (Table IV) reflects the inputs of acid mine drainage, i.e., low pH and high concentrations of Ca^{++}, Mg^{++}, Fe^{++}, and $SO_4^=$ (cf. Barton, 1978). Weathering of the Upper Freeport limestone within the Finley Run watershed may have contributed to the relatively high Ca^{++} and Mg^{++} concentrations in stream water, but the acidifying effect of the mine drainage clearly outweighed any possible rise in pH that would have resulted from limestone weathering. Comparisons of Tub Run and Finley Run stream water chemistry suggest that processes within Tub Run Bog remove H^+, Ca^{++}, Mg^{++}, Fe^{++}, and $SO_4^=$ from solution.

The chemistry of Tub Run exhibits notable changes as the stream flows through and beyond Tub Run Bog (Table IV). Upstream from the wetland, Tub Run is chemically quite similar to East Fork and Big Run (Table II). As the stream flows through the wetland, observed chemical changes (Table IV) do not reflect the influence of acid mine drainage inputs. Increased pH and Ca^{++} and Mg^{++} concentrations may have resulted from limestone weathering. In contrast, below the wetland between the gaging station and the Forest Service Road, Tub Run receives inputs of acid mine drainage that to do

TABLE IV

Mean ionic concentrations (mg L^{-1} except pH) in Finley Run ($n = 4$; samples were collected during the summer of 1983), and in Tub Run above the wetland ($n = 23$), within the wetland ($n = 31$), and below the wetland ($n = 7$; all Tub Run samples were collected on 6/7/82 and on 7/7/82)

	pH	Ca^{++}	Mg^{++}	K^+	Na^+	Fe^{++}	$SO_4^=$
Finley Run	3.06	11.77	5.95	0.70	0.21	1.17	179.6
Tub Run							
Above wetland	3.86	0.47	0.17	0.14	0.17	0.16	8.4
Within wetland	4.11	1.17	0.27	0.15	0.15	0.24	7.7
Below wetland	3.79	1.82	1.13	0.36	0.14	0.43	23.2

not flow through a wetland on its way to the main stream channel. Below Tub Run Bog, a sharp drop in Tub Run pH in association with increases in the concentrations of Ca^{++}, Mg^{++}, K^{+}, Fe^{++}, and $SO_4^{=}$ clearly indicate that inputs of acid mine drainage have impacted stream water chemistry.

For East Fork, Big Run, and Tub Run, anion/cation equivalent ratios calculated from Table II are 1.02, 0.91, and 1.02, respectively, indicating that all major anions and cations were analyzed and that our analytical methods were accurate. Based on the data in Table IV, anion/cation ratios for Tub Run above and within the wetland are 0.90 and 0.91, respectively, whereas for Tub Run below the wetland and for Finley Run anion/cation ratios are 1.28 and 1.85, respectively. Because all ions were not measured, anion/cation balances calculated from the data in Table IV were not expected. Nonetheless, the relatively higher ratios for Tub Run below the wetland and for Finley Run suggest that stream waters influenced by mine drainage that does not flow through a wetland may contain relatively high concentrations of cations that we did not measure, such as Al^{+++}, Cu^{++}, Mn^{++}, and Zn^{++} (cf. Barton, 1978).

Seasonal variation in Tub Run pH and Fe^{++} concentrations paralleled the patterns observed in East Fork and Big Run, whereas Ca^{++}, Mg^{++}, and $SO_4^{=}$ exhibited notably different patterns (Figure 3). Specifically, Ca^{++}, Mg^{++}, and $SO_4^{=}$ concentrations in Tub Run were particularly elevated during the autumn of 1980 and the late summer and early autumn of 1981, often appearing as distinct peaks in concentration. Not coincidentally, elevated concentrations of these three ions followed protracted dry periods during which individual months had calculated net water deficits (September 1980, July and August 1981) (Figure 2). Wieder and Lang (1982a) argued that during these relatively dry periods, acid mine drainage becomes progressively more concentrated within the surface mine. When the dry periods are interrupted by major precipitation events, rapid flushing of this solute-laden drainage from the surface mine through the wetland results in peaks in ion concentrations in Tub Run stream water. The peaks in Ca^{++}, Mg^{++}, and $SO_4^{=}$ concentrations were not accompanied by corresponding distinct drops in pH or distinct peaks in Fe^{++} concentration. The ability of Tub Run to remove Ca^{++}, Mg^{++}, and $SO_4^{=}$ inputs in acid mine drainage appears to be dependent on a sufficiently long residence time of water and/or a sufficiently low ion concentration. Removal of H^{+} and Fe^{++} from solution appears to be less dependent on hydrologic factors.

5. Summary and Conclusions

Despite generally similar mean ionic concentrations in East Fork and Big Run, statistical analyses revealed that Big Run Bog does influence the chemistry of Big Run. Tub Run Bog also influences stream water chemistry, apparently accomplishing a chemical modification of inputs of acid mine drainage, thus minimizing the impact of the mine drainage on stream water quality. The concept that wetland areas contribute to the regulation of stream water chemistry in ways that are different from upland areas has been documented in other relatively undisturbed systems as well (e.g., Braekke, 1981;

Verry and Timmons, 1982). In a more applied context, considerable interest has focused on the potential of using wetlands to remove N and P from added sewage effluent (see reviews of Kadlec and Tilton, 1979; Heliotis, 1982). However, comparatively little is known about the ability of wetlands to ameliorate inputs of acid mine drainage.

Results from the present study point to two general areas for further investigation. First, the concentrations of individual ions, particularly H^+, $SO_4^=$, and Fe^{++}, are clearly influenced by physico-chemical and microbially-mediated transformations, yet our knowledge of the factors controlling these processes in wetland peat is incomplete. Second, a characterization of regional hydrology, including short-term hydrologic and biogeochemical responses to individual storm events within these three watersheds would both complement and expand upon the present study. Such information would contribute considerably to both a general understanding of the biogeochemical role of wetlands on the landscape and to a more specific understanding of the processes involved in the apparent ability of wetlands to modify acid mine drainage.

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