

Peat and water chemistry at Big Run Bog, a peatland in the Appalachian mountains of West Virginia, USA

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Abstract. At Big Run Bog, a *Sphagnum*-dominated peatland in the unglaciated Appalachian Plateau of West Virginia, significant spatial variation in the physical and chemical properties of the peat and in surface and subsurface (30 cm deep) water chemistry was characterized. The top 40 cm of organic peat at Big Run Bog had average values for bulk density of $0.09 \text{ g} \cdot \text{cm}^{-3}$, organic matter concentration of 77%, and volumetric water content of 88%. Changes in physical and chemical properties within the peat column as a function of depth contributed to different patterns of seasonal variation in the chemistry of surface and subsurface waters. Seasonal variation in water chemistry was related to temporal changes in plant uptake, organic matter decomposition and element mineralization, and to varying redox conditions associated with fluctuating water table levels. On the average, total Ca, Mg, and N concentrations in Big Run Bog peat were 33, 15, and $1050 \mu\text{mol} \cdot \text{g}^{-1}$, respectively; exchangeable Ca and Mg concentrations were 45 and $14 \mu\text{eq} \cdot \text{g}^{-1}$, respectively. Surface water pH averaged 4.0 and Ca^{++} concentrations were less than $50 \mu\text{eq} \cdot \text{L}^{-1}$. These chemical variables have all been used to distinguish bogs from fens. Physiographically, Big Run Bog is a minerotrophic fen because it receives inputs of water from the surrounding forested upland areas of its watershed. However, chemically, Big Run Bog is more similar to true ombrotrophic bogs than to minerotrophic fens.

Introduction

Sphagnum-dominated peatland ecosystems are a major feature of the landscape in the northern latitudes of North America, but farther south they become progressively fewer and smaller in a real extent (Cameron, 1968). Often, the more southern peatlands are restricted to mountainous regions where the cool, moist conditions at higher elevations compensate for generally warmer, drier climatic conditions associated with the lower elevations at comparable latitudes. In eastern North America, the distribution of inland *Sphagnum* peatlands coincides with the axis of the Appalachian Mountains, with few individual sites existing south of West Virginia (Cameron, 1968).

Comparisons of the southern *Sphagnum* peatlands with their more widespread northern counterparts have revealed some general similarities with regard to floristics, vegetation structure, and plant community development

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(see references in Wieder et al., 1981; Walbridge and Lang, 1982). However, in comparison to the northern peatlands, both annual net production (Wieder and Lang, 1983) and annual organic matter decomposition (cf. Lang and McDonald, 1982) are higher in the southern peatlands, suggesting generally higher rates of organic matter turnover. With decreasing latitude, decomposition apparently increases at a proportionately greater rate than production (Damman, 1979), leading to progressively thinner peat deposits and ultimately to the disappearance of inland *Sphagnum*-dominated peatland ecosystems from the landscape.

Although there are numerous studies of the biogeochemistry of northern *Sphagnum* peatlands (see Richardson et al., 1978), relatively little is known about the more southern peatlands. This paper describes a biogeochemically oriented investigation of Big Run Bog, a representative example of a southern inland *Sphagnum*-dominated peatland in the unglaciated Appalachian Mountains of West Virginia. The objectives are threefold: to investigate spatial patterns in the physical and chemical properties of peat and in water chemistry both across the surface of the wetland and as a function of depth, to examine seasonal variation in surface and subsurface water chemistry, and to compare the data from Big Run Bog with data obtained from other peatlands in the more northern regions of North America and Europe. Although a detailed characterization of the biogeochemical cycling of individual elements requires the quantification of both pool sizes and flux rates, the information in this paper represents a first step toward comparing and contrasting patterns of biogeochemical cycling in southern versus northern peatland ecosystems.

Site description

Big Run Bog (39°07'N, 79°35'W) is located at an elevation of about 980 m above sea level at the headwaters of Big Run of the Blackwater River. Situated in a topographic frost pocket (Hough, 1945), the wetland occupies 15 ha within a 291 ha forested watershed in the Monogahela National Forest (Figure 1). The Big Run watershed is underlain by sandstones of the Pottsville Group and the Allegheny Formation (Diehl, 1981). Upland soils along the ridge crests and midslopes are Typic Dystrochrepts and Entic Normorthods, and in the footslopes are Aquic Fragiudults or Typic Fragiaqualfs (Losche and Beverage, 1967).

The surface of Big Run Bog slopes gently (1–2%) both from upstream to downstream regions and from the upland borders toward the main stream channel (Figure 2). The topographic relationships depicted in Figures 1 and 2 indicate that Big Run Bog receives inputs of water from the surrounding upland areas of its watershed. Thus, physiographically Big Run Bog is a minerotrophic fen and not a true ombrotrophic bog (Wieder, 1982).

Climatological data for Big Run Bog were taken from 35 years of observation at Canaan Valley, West Virginia, located 15 km east of Big Run Bog

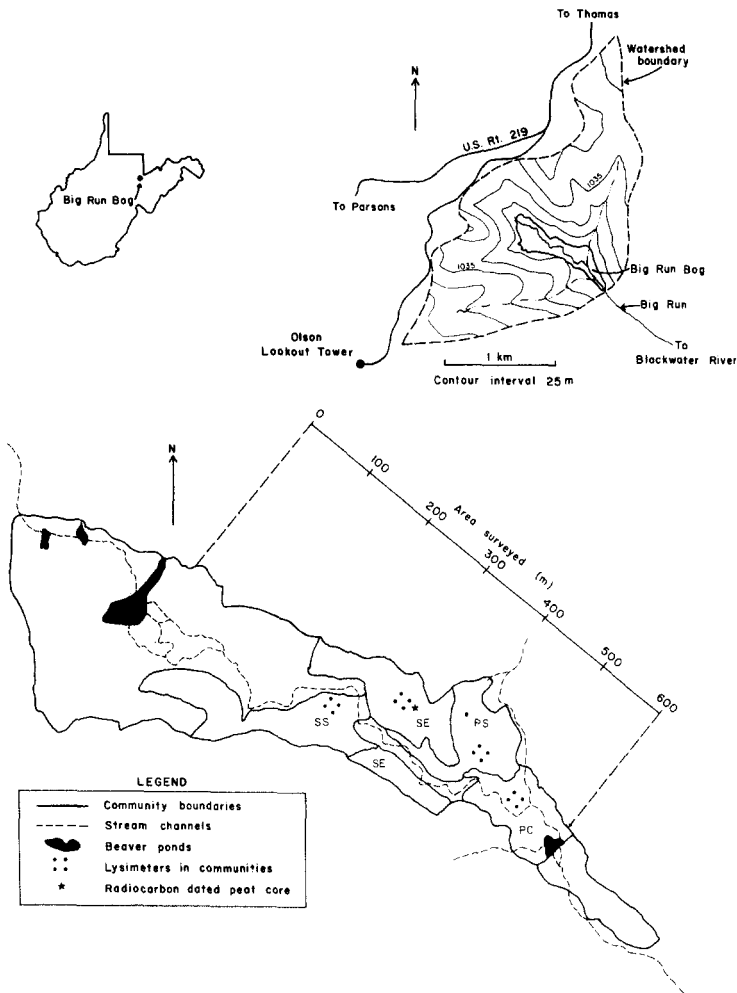


Figure 1. Location of Big Run Bog within West Virginia and a topographic map of the Big Run watershed. The detailed map of the wetland, adapted from Wieder et al. (1981) and Walbridge (1982), delineates the areas occupied by the four major plant communities. Plant community designations are: PC = *Polytrichum-Carex canescens*; PS = *Polytrichum*-shrub; SE = *Sphagnum-Eriophorum virginicum*; SS = *Sphagnum*-shrub.

at an elevation of 991 m above sea level (NOAA 1946–1950, 1952–1981). Mean annual precipitation is 133 cm and is fairly evenly distributed throughout the year (Table 1). Mean annual temperature is 7.9°C. The average frost-free period is 97 days, from 2 June–7 September.

On the average, total annual precipitation (133 cm) exceeds total annual PET (59 cm), indicating an overall annual water surplus. However, every year of record had at least one month between April and October with a calculated

potential water deficit, i.e. PET exceeded precipitation (Table 1). On the average, 1.5 months/year exhibited a calculated potential water deficit (Wieder, 1982).

The chemistry of precipitation falling on Big Run Bog is characteristic of the regional phenomenon of acid deposition. For the 1980 calendar year, volume weighted mean pH of precipitation (wetfall only) was 4.16 and concentrations of SO_4^{2-} and NO_3^- were 73 and $29 \mu\text{eq}\cdot\text{L}^{-1}$, respectively, at Parsons, WV, about 10 km southwest of Big Run Bog (NADP, 1981).

For the most part, 1980 was a typical year climatically (Table 1). Somewhat higher than average precipitation in July and August resulted in greater than average water surplus values. In contrast, relatively high temperatures, coupled with below average precipitation in September produced a potential water deficit. The frost-free season in 1980 lasted 91 days, from 12 June–11 September.

A total of 9 bryophyte and 58 vascular plant species have been reported for Big Run Bog (Wieder et al., 1981; Walbridge, 1982). *Sphagnum* and *Polytrichum* mosses cover 85% of the wetland surface and both are important in the formation of peat. The vascular component of the flora is dominated by sedges, rushes, and other herbaceous species. Although some shrub species are distributed throughout the wetland, trees and upland shrubs are generally restricted to the wetland margins (Wieder et al., 1981; Walbridge, 1982).

The vegetation of Big Run Bog consists of a series of distinct plant communities (Wieder et al., 1981; Walbridge, 1982). The community designations of Wieder et al. (1981) are used in this paper (Figure 1). In the four communities, *Sphagnum* and *Polytrichum* cover 88–100% of the surface, but in two communities *Polytrichum* is more abundant than *Sphagnum*. Two of the communities have relatively few upright shrubs, whereas each of the other two communities has a mean upright shrub cover of over 11%.

Methods

Physical and chemical properties of peat

In September 1980 four 40 cm deep, 10 cm diameter, peat cores were excavated with a hand trowel from hollow areas in each of the four plant communities. Hummocks were avoided. The water table level was within 5 cm of the peat surface in the immediate vicinity of each of the 16 cores. Each core was divided into 10 cm depth intervals. From each core at each depth interval, one subsample was extracted horizontally using a plastic tube of known volume. These subsamples were oven-dried at 70°C for 24 h to determine bulk density and volumetric water content (Boelter, 1965), ground, and analyzed for organic matter by combusting at 200°C for 2 h and then at 400°C for 4 h. The resulting ash was weighed, digested in 6 N HCl, filtered, and the filtered digest solution was analyzed for

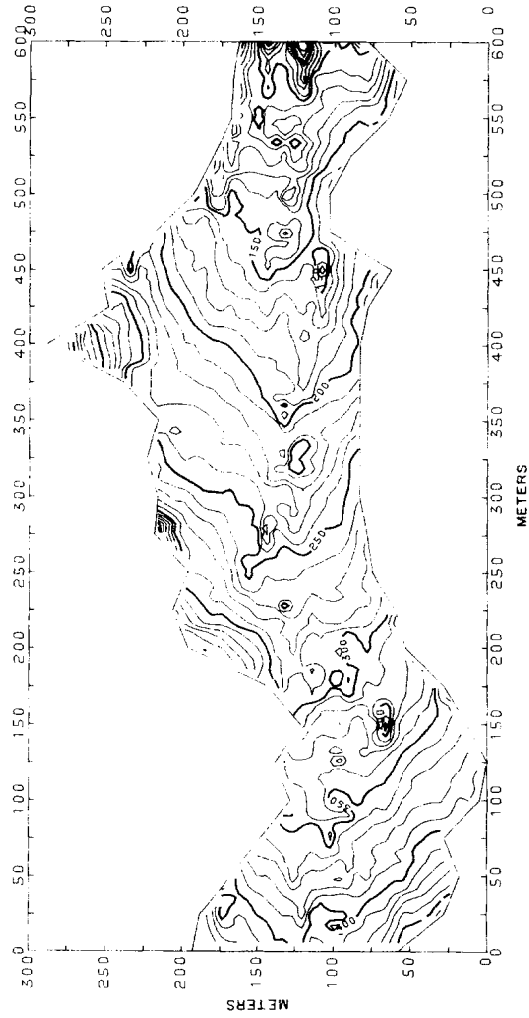


Figure 2. Surface topography of the surveyed region of Big Run Bog indicated in Figure 1. Contour interval is 10 cm. The map is taken from Wieder (1982).

Table 1. Climatological data for Canaan Valley, West Virginia. Mean values are based on 35 years of observation. For each year of record, monthly potential evapotranspiration (PET) was calculated by the Thornthwaite method (Thornthwaite 1948). Water surplus was calculated by subtracting monthly PET from monthly precipitation

	Month											
	J	F	M	A	M	J	J	A	S	O	N	D
Temperature (°C)	Mean	-3.1	-2.6	1.8	8.0	12.8	16.4	18.3	17.8	14.5	8.9	3.4
	1980	-2.9	-5.7	0.8	7.3	13.4	15.4	19.6	19.2	16.1	7.2	2.3
Precipitation (cm)	Mean	11.5	10.7	12.4	10.8	12.3	12.8	12.5	12.4	9.2	9.0	9.1
	1980	9.8	8.4	15.7	14.1	12.5	14.5	15.3	16.7	5.9	6.8	12.4
PET (cm)	Mean	0.1	0.1	1.1	4.2	7.8	10.2	11.6	10.5	7.5	4.2	1.4
	1980	0.0	0.0	0.3	3.9	8.1	9.5	12.4	11.3	8.2	3.3	0.9
Water surplus (cm)	Mean	11.4	10.6	11.3	6.6	4.5	2.6	0.9	1.9	1.7	4.8	7.6
	1980	9.8	8.4	15.4	10.2	4.4	5.0	2.9	5.4	-2.3 ^a	3.5	11.5
Frequency of water deficit in a given month ^b		0	0	0	2.9	28.6	34.3	45.7	40.0	40.0	11.4	0

^aA negative water surplus value indicates a water deficit.

^bFrequency = $\frac{\text{Number of years in which a monthly water deficit occurred}}{35 \text{ years of record}} \times 100.$

concentrations of major cations and metals (Likens and Bormann, 1970). Total N and total P were determined following sulfuric acid (Kjeldahl) digestion.

In addition, at each depth interval in each core, a second subsample was collected, air-dried, and ground. A 2.5 g aliquot was analyzed for exchangeable cations using 1N ammonium acetate adjusted to pH 7.0, and for cation exchange capacity using acidified KCl (USDA, 1972; Finney et al., 1974).

Water chemistry

Four surface and four subsurface water samples were collected in each plant community at approximately monthly intervals from April 1980–December 1980, and in April 1981. Surface water was collected from standing pools, although during dry periods four pools of standing water could not always be located within each community. Subsurface water was collected in porous cup tube lysimeters. Four lysimeters were installed in each community to a depth of 30 cm below the peat surface (Figure 1).

On each sampling date, immediately upon return to the laboratory pH was determined on a 50 mL aliquot from each collected water sample and the remaining water was frozen for subsequent chemical analysis of major cations and anions.

Chemical determinations

Concentrations of Ca, Mg, Fe, Al, Mn, Zn, and Pb in peat extractions and water samples were measured by atomic absorption spectrophotometry. Lanthanum added to solutions used in Ca and Mg determinations as a releasing agent. K and Na in peat extractions and water samples were analyzed by flame photometry using a Technicon AutoAnalyzer. Water samples were analyzed for concentrations of NH_4^+ , NO_3^- , Cl^- , and SO_4^{2-} colorimetrically, on a Technicon AutoAnalyzer (Technicon Industrial Systems, 1977; Cronan, 1979). Generally, surface water was not colored and lysimeter water was occasionally only slightly colored. Since water samples were not subjected to a decolorization treatment prior to SO_4^{2-} determination, the values reported here may be slight overestimates (Cronan, 1979). The accuracy of the HCl digestions done on dry-ashed peat samples was verified by simultaneously analyzing standard plant tissue (orchard leaves) obtained from the National Bureau of Standards.

Statistical analyses

For the data on the physical and chemical properties of peat, community and depth effects were assessed using a two-way analysis of variance. When there was no significant interaction, pairwise comparisons between either community means (averaged across depth) or depth means (averaged across the four communities) were made using the least significant difference, LSD, procedure (Snedecor and Cochran, 1978).

To assess community differences in either surface or subsurface water chemistry, an analysis of variance, randomized complete block design (Snedecor and Cochran, 1978) was used with sampling date as the blocked effect. By using a blocked design, seasonal variation in water chemistry was removed from consideration in assessing differences among the four communities. All statistical tests were evaluated at a significance level of 0.05.

Results

Physical and chemical properties of peat

The low bulk densities, high organic matter concentrations, and high volumetric water contents of the peat in the *Polytrichum*-shrub, *Sphagnum-E. virginicum*, and *Sphagnum*-shrub communities (Table 2) are typical of organic soils or histosols (Boelter and Blake, 1964; Boelter, 1968; USDA, 1972). In contrast, the soil in the *Polytrichum-C. canescens* community had markedly higher bulk densities, lower organic matter concentrations, and lower volumetric water contents (Table 2). Because of the low organic matter concentration in the top 40 cm, the substrate in the *Polytrichum-C. canescens* community would not be classified as a histosol (USDA, 1972). High inorganic content of the soil in the *Polytrichum-C. canescens* community is related to the position of the community near the confluences of the main stream channel and the two intermittent streams draining small upland side valleys (Figure 1). Over the course of wetland development, periods of considerable erosion of the upland mineral soils associated with either long-term climatic changes or episodic local disturbances such as forest fire or relatively recent logging activity resulted the deposition of alluvial material in the region of the wetland now occupied by the *Polytrichum-C. canescens* community. Random coring within this community using a Hiller peat corer revealed areas where layers of inorganic material were interspersed with layers of relatively undecomposed organic peat, suggesting an interrupted pattern of peat development.

The peat deposit at Big Run Bog reaches a maximum depth of 225 cm, with an average depth across the entire wetland of less than 60 cm (Table 2). The shallow peat at Big Run Bog is in contrast to the more northern peatlands where accumulations are typically deeper, sometimes exceeding 9 m (Farnham and Grubich, 1970).

Spatial variation in peat chemistry across the surface of Big Run Bog is reflected in differences among the four communities. Five of the 17 chemical characteristics in Tables 3 and 4 (Mg, N, P, Al, and exchangeable Mg) had significant interaction terms in the analyses of variance, indicating that community differences were not consistent at all depths and/or that depth differences were not consistent in all four communities. Because of the significant interaction, overall generalizations about spatial variation cannot be made for these five characteristics.

Table 2. Physical characteristics of the peat at Big Run Bog. Values for bulk density (g cm^{-3}), organic matter concentration (% of dry mass), and water content (% v/v) represent the means of four determinations of each depth in each community. For each of these three characteristics, an LSD value calculated from a two-way analysis of variance (given in parentheses) can be used to make pairwise comparisons between any two means. For characteristics that had no significant interaction in the analysis of variance, communities (means averaged across all depths) with the same letter superscript do not differ significantly and depths (averaged across all communities) with the same number superscript do not differ significantly.

Characteristic	Depth (cm)	Community			
		<i>Polytrichum-C. canescens</i>	<i>Polytrichum-shrub</i>	<i>Sphagnum-E. virginicum</i>	<i>Sphagnum-shrub</i>
Bulk density (0.06)	0-10	0.10			
	10-20	0.21	0.06	0.04	0.05
	20-30	0.32	0.08	0.05	0.06
	30-40	0.54	0.11	0.07	0.08
Organic matter (16)			0.23	0.09	0.12
	0-10 ¹	68 ^c	83 ^b	92 ^a	93 ^{a, b}
	10-20 ¹	48	79	92	86
	20-30 ²	28	73	83	74
Water content (5)	30-40 ³	14	47	71	57
	0-12 ²	61 ^c	77 ^b	88 ^a	80 ^a
	10-20 ¹	65	84	92	86
	20-30 ¹	64	84	94	91
Mean peat depth (cm)*	30-40 ^{1, 2}	53	80	90	89
Maximum peat depth (cm)		38	46	79	39
		73	80	225	64

* n = 31 except in the *Sphagnum-E. virginicum* community where n = 73.

Table 3. Elemental concentrations ($\mu\text{mol}\cdot\text{g}^{-1}$) in Big Run Bog peat. Format is the same as that in Table 2.

Characteristic	Depth (cm)	Community			
		<i>Polytrichum-C. canescens</i>	<i>Polytrichum-shrub</i>	<i>Sphagnum-E. virginicum</i>	<i>Sphagnum-shrub</i>
Ca (6)	0-10 ¹	10 ^d	24 ^c	37 ^b	55 ^a
	10-20 ¹	8	31	45	63
	20-30 ¹	8	34	47	51
	30-40 ¹	6	24	43	39
Mg (2)	0-10	12	11	12	14
	10-20	12	13	14	19
	20-30	19	14	16	16
	30-40	17	13	17	14
K (4)	0-10 ³	24 ^a	16 ^b	10 ^{b,c}	7 ^c
	10-20 ^{2,3}	25	16	9	12
	20-30 ^{1,2}	29	16	19	13
	30-40 ¹	25	21	25	18
Na (0.9)	0-10 ³	3.5 ^a	3.0 ^b	1.7 ^{b,c}	1.7 ^c
	10-20 ^{2,3}	5.2	3.0	1.7	1.7
	20-30 ^{1,2}	6.5	3.0	2.6	2.2
	30-40 ¹	6.1	3.9	4.3	3.5
N (151)	0-10	1009	1146	957	957
	10-20	984	1255	1158	1292
	20-30	693	1049	1341	1362
	30-40	350	855	1391	991
P (5)	0-10	40	32	22	23
	10-20	37	38	26	32
	20-30	29	36	30	35
	30-40	22	29	32	25

Fe (102)	0-10 ¹	365 ^a	376 ^a	208 ^a	171 ^a
	10-20 ²	103	260	174	110
	20-30 ²	82	170	119	82
	30-40 ²	308	119	102	70
Al (50)	0-10	233	236	129	122
	10-20	386	319	153	151
	20-30	381	321	258	200
	30-40	297	299	359	258
Mn (0.29)	0-10 ^{2,3}	0.66 ^c	1.36 ^b	2.35 ^a	2.18 ^a
	10-20 ¹	0.51	1.80	2.91	2.89
	20-30 ^{1,2}	0.60	2.09	2.69	2.28
	30-40 ³	0.47	1.47	2.20	1.91
Zn (0.43)	0-10 ³	0.64 ^b	0.66 ^a	0.54 ^a	0.69 ^a
	10-20 ¹	0.52	1.76	1.94	1.47
	20-30 ^{1,2}	0.63	1.59	1.61	1.35
	30-40 ^{2,3}	0.23	0.87	1.59	0.87
Pb (0.010)	0-10 ²	0.053 ^c	0.058 ^b	0.063 ^a	0.063 ^a
	10-20 ¹	0.048	0.068	0.083	0.082
	20-30 ²	0.029	0.058	0.077	0.072
	30-40 ³	0.024	0.034	0.058	0.043

Table 4. Exchange characteristics of the peat at Big Run Bog. Values are $\mu\text{eq g}^{-1}$ except for base saturation which is %. Format is the same as that in Table 2.

Characteristic	Depth (cm)	Community			
		<i>Polytrichum-C. canescens</i>	<i>Polytrichum-shrub</i>	<i>Sphagnum-E. virginicum</i>	<i>Sphagnum-shrub</i>
Ca (8.7)	0-10 ³	7.6 ^d	31.6 ^c	48.2 ^b	61.5 ^a
	10-20 ^{1,2}	7.9	45.2	67.2	76.5
	20-30 ¹	10.4	45.0	69.0	84.7
	30-40 ^{2,3}	10.5	35.9	61.0	63.1
Mg (2.4)	0-10	8.8	9.3	15.6	20.4
	10-20	4.7	13.6	20.2	21.8
	20-30	3.7	13.2	19.7	24.7
	30-40	3.7	10.9	18.3	16.2
K (2.9)	0-10 ¹	16.6 ^a	11.4 ^a	8.6 ^a	7.3 ^a
	10-20 ²	3.5	2.7	6.8	3.6
	20-30 ²	1.3	2.3	3.3	2.5
	30-40 ²	1.3	1.7	3.0	1.5
Na (0.4)	0-10 ¹	1.6 ^b	1.5 ^b	2.2 ^a	1.0 ^b
	10-20 ²	0.4	0.6	2.3	0.3
	20-30 ²	0.3	0.6	1.3	0.6
	30-40 ²	0.5	0.4	1.3	0.2
Cation exchange capacity (180)	0-10 ¹	940 ^b	1500 ^a	1260 ^a	1390 ^a
	10-20 ¹	720	1380	1480	1380
	20-30 ²	470	1210	1320	1120
	30-40 ³	430	800	1000	780
Base saturation (1.1)	0-10 ²	3.6 ^d	3.6 ^c	6.1 ^b	6.7 ^a
	10-20 ²	2.5	4.6	6.8	7.6
	20-30 ¹	3.7	5.0	7.2	10.2
	30-40 ¹	3.9	6.5	8.3	10.6

For 9 of those 12 characteristics with no significant interaction, the *Polytrichum-C. canescens* community was significantly different from the other three communities, having higher mean concentrations of K and Na, lower mean concentrations of Ca, Mn, Zn, Pb, and exchangeable Ca, and lower mean cation exchange capacity and base saturation. Thus, associated with the anomalous physical properties of the substrate in the *Polytrichum-C. canescens* community are numerous distinguishing chemical characteristics. For most of the chemical characteristics in Tables 3 and 4, mean values in the *Polytrichum*-shrub, *Sphagnum-E. virginicum*, and *Sphagnum*-shrub communities were similar, generally differing by less than a factor of two.

The only chemical characteristics of the peat that separated all four communities were total Ca, exchangeable Ca, and base saturation. Highest values for these characteristics were obtained in the *Sphagnum*-shrub community which is located upslope from the other three communities (Figure 1). Downslope, through the *Sphagnum-E. virginicum*, *Polytrichum*-shrub, and *Polytrichum-C. canescens* communities, the values for total Ca, exchangeable Ca, and base saturation progressively declined. This pattern could result either from spatial variation in the chemistry of minerotrophic drainage entering the wetland, or from the preferential removal of Ca from solution by cation exchange as water flows through the wetland (cf. Vitt et al., 1975).

Four distinct patterns of change in chemical characteristics with depth were seen consistently in all four communities. Total Ca showed no depth effect, K, Na, and base saturation increased with depth, Fe, exchangeable K, exchangeable Na, and cation exchange capacity decreased with depth, and Mn, Zn, Pb, and exchangeable Ca had maximum concentrations at the intermediate (10–20 and 20–30 cm) depths (Tables 3 and 4). In ombrotrophic bog peat, Damman (1978) also found no marked trend with depth for Ca and an accumulation of Zn and Pb in the zone of water table fluctuation.

Concentrations of exchangeable base cations in Big Run Bog peat (Table 4) were lower than totals (Table 3), indicating that some Ca, Mg, K and Na was present in a nonexchangeable form (cf. Gore and Allen, 1956; Sonesson, 1970). Ratios of exchangeable to total cation concentrations for Ca and Mg were significantly lower in the *Polytrichum-C. canescens* community than in the other three communities (Table 5), reflecting the relatively high inorganic matter concentration in the *Polytrichum-C. canescens* community (Table 2). In contrast, ratios of exchangeable to total K did not differ significantly among the four communities. For Na, 87% of the cations were in an exchangeable form in the *Sphagnum-E. virginicum* community, compared to only 22–33% in the other three communities.

Exchange properties of Big Run Bog peat varied as a function of the organic matter concentration of the peat. With increasing organic matter concentration, both cation exchange capacity and the sum of the base cations increased (Figure 3). However, over the entire range of organic matter

Table 5. Percentages of total base cations present in an exchangeable form in Big Run Bog peat. Each value is the mean of all depths in all four cores from each community. For each characteristic, mean values with the same letter superscript do not differ significantly

Characteristic	Community			
	<i>Polytrichum-C. canescens</i>	<i>Polytrichum-shrub</i>	<i>Sphagnum-E. virginicum</i>	<i>Sphagnum-shrub</i>
Exchangeable Ca: total Ca	60 ^a	71 ^b	71 ^b	71 ^b
Exchangeable Mg: total Mg	20 ^a	48 ^b	62 ^c	68 ^c
Exchangeable K: total K	28 ^a	30 ^a	51 ^a	42 ^a
Exchangeable Na: total Na	22 ^a	27 ^a	87 ^b	33 ^a

concentration values, base saturation of the exchange sites remained quite low, generally less than 10% (see Table 4).

Water Chemistry

Spatial variation. Although the physical and chemical properties of peat often statistically separated the *Polytrichum-C. canescens* community from the other three communities, such a distinction was not generally evident in the surface and subsurface water chemical data (Table 6). For certain ions, however, there was a suggestion that spatial variation was associated with either *Polytrichum* versus *Sphagnum* dominance or high versus low shrub cover. Specifically, the two *Polytrichum*-dominated communities had somewhat lower surface K^+ concentrations and higher surface SO_4^{2-} and subsurface Fe^{2+} , Cl^- , and SO_4^{2-} concentrations than the two *Sphagnum*-dominated communities. Compared to the two communities with relatively low shrub abundance, the communities with high shrub abundance had higher subsurface Ca^{2+} and NH_4^+ concentrations, which may have been associated with either decomposition of root tissue or root exudation (Smith, 1976).

Mean surface concentrations of many ions were markedly different from mean subsurface concentrations (Table 6). Relative to subsurface water, surface water had higher mean concentrations of H^+ , NO_3^- , and SO_4^{2-} , and lower mean concentrations of NH_4^+ , especially in the two communities with higher shrub abundance. At Big Run Bog, increases in peat bulk density with depth (Table 2) suggest that water flows much more rapidly through shallow surface peat than through 30 cm deep subsurface peat (cf. Boelter, 1965; Chapman, 1965; Korpijaakko and Radforth, 1972). Thus, surface water is more strongly influenced by inputs of precipitation and minerotrophic drainage than subsurface water.

Hydrogen ion concentration in subsurface water, besides being lower than in surface water, was also lower than that of either precipitation or forest soil water in the upland areas of the Big Run watershed (pH = 3.9) (Wieder, 1982). Some neutralization capacity in subsurface peat could be contributed by anaerobic dissimilatory sulfate reduction (Wright and Johannessen, 1980). Hydrogen sulfide is present in the interstitial water of Big Run Bog, but on an equivalent basis, SO_4^{2-} is much more abundant than hydrogen sulfide in both

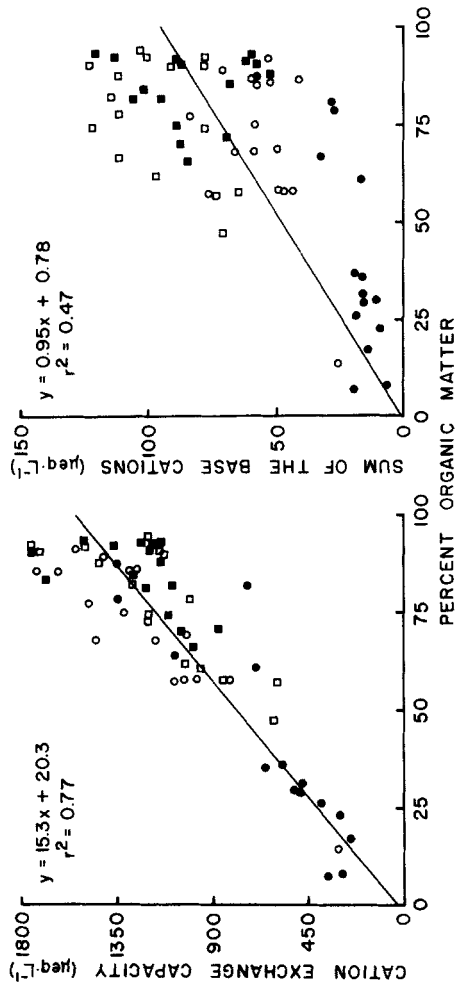


Figure 3. Change in cation exchange properties as a function of organic matter concentration in Big Run Bog peat. Symbols denote the four plant communities: ● = *Polytrichum-C. canescens*; ○ = *Polytrichum-shrub*; ■ = *Sphagnum-E. virginicum*; □ = *Sphagnum-shrub*.

Table 6. Water chemistry ($\mu\text{eq} \cdot \text{L}^{-1}$) in the four major plant communities at Big Run Bog. Values are means averaged over nine sampling dates throughout a year. For either surface water or subsurface water, values for each ion with the same lower case letter do not differ significantly ($p = 0.05$), based on an analysis of variance, randomized complete block design, where sampling date is the blocked effect.

	Community			
	<i>Polytrichum-C. canescens</i>	<i>Polytrichum-shrub</i>	<i>Sphagnum-E. virginicum</i>	<i>Sphagnum-shrub</i>
Surface water				
H ⁺	127.0 ^a	90.2 ^b	120.1 ^a	48.2 ^c
Ca ²⁺	45.6 ^a	26.9 ^b	43.7 ^a	40.4 ^a
Mg ²⁺	19.1 ^a	13.7 ^b	15.8 ^b	21.9 ^a
K ⁺	6.8 ^b	6.2 ^b	12.1 ^a	15.0 ^a
Na ⁺	8.2 ^a	6.8 ^b	8.6 ^a	8.0 ^a
Fe ²⁺	37.0 ^a	24.5 ^b	17.6 ^c	10.4 ^d
NH ₄ ⁺	8.6 ^a	9.5 ^a	8.8 ^a	9.9 ^a
NO ₃ ^{-*}	1.5 ^b	0.2 ^b	1.1 ^b	6.2 ^a
Cl ⁻	19.4 ^a	24.4 ^a	27.1 ^a	25.5 ^a
SO ₄ ²⁻	236.7 ^a	124.9 ^b	110.3 ^{b,c}	83.3 ^c
Subsurface water (30 cm below surface)				
H ⁺	21.8 ^a	18.0 ^a	18.3 ^a	6.4 ^b
Ca ²⁺	33.8 ^b	40.9 ^{a,b}	36.3 ^b	49.7 ^a
Mg ²⁺	23.7 ^b	23.5 ^b	18.7 ^b	32.4 ^a
K ⁺	6.4 ^c	21.7 ^a	13.3 ^b	15.1 ^b
Na ⁺	16.9 ^b	12.1 ^{b,c}	9.7 ^c	29.6 ^a
Fe ²⁺	49.6 ^a	44.2 ^a	20.6 ^b	21.9 ^b
NH ₄ ⁺	33.4 ^c	110.2 ^a	51.2 ^{b,c}	65.3 ^b
NO ₃ ^{-*}	0.3 ^a	0.0 ^a	0.2 ^a	0.1 ^a
Cl ⁻	65.6 ^a	65.1 ^a	40.0 ^b	45.9 ^b
SO ₄ ²⁻	102.4 ^a	115.7 ^a	62.3 ^b	63.8 ^b

* (NO₃⁻ + NO₂⁻)

surface and subsurface water (Wieder, 1982). Aerobic surface water versus anaerobic subsurface water also affected the ionic forms of inorganic N. Although NH₄⁺ was the dominant form of inorganic N in both surface and subsurface water, this dominance was particularly evident in subsurface water where NO₃⁻ was virtually absent (Table 6).

Seasonal variation. Since most ions had qualitatively similar patterns of seasonal variation in the surface or subsurface waters of all four communities, seasonal variation in water chemistry at Big Run Bog as a whole was assessed by averaging ionic concentrations across the four communities for each sampling date (Figure 4). However, subsurface K⁺ and NH₄⁺ concentrations and surface H⁺, SO₄²⁻, and Fe²⁺ concentrations had very different temporal patterns in the *Polytrichum-C. canescens* community compared to the other three communities (Figure 5).

In all four communities, surface water concentrations of Ca²⁺, Mg²⁺, K⁺, and Na⁺ were fairly constant throughout the growing season, but showed sharp peaks in early November (Figure 4). This same pattern was observed for SO₄²⁻ in the *Polytrichum-shrub*, *Sphagnum-E. virginicum*, *Sphagnum-shrub*

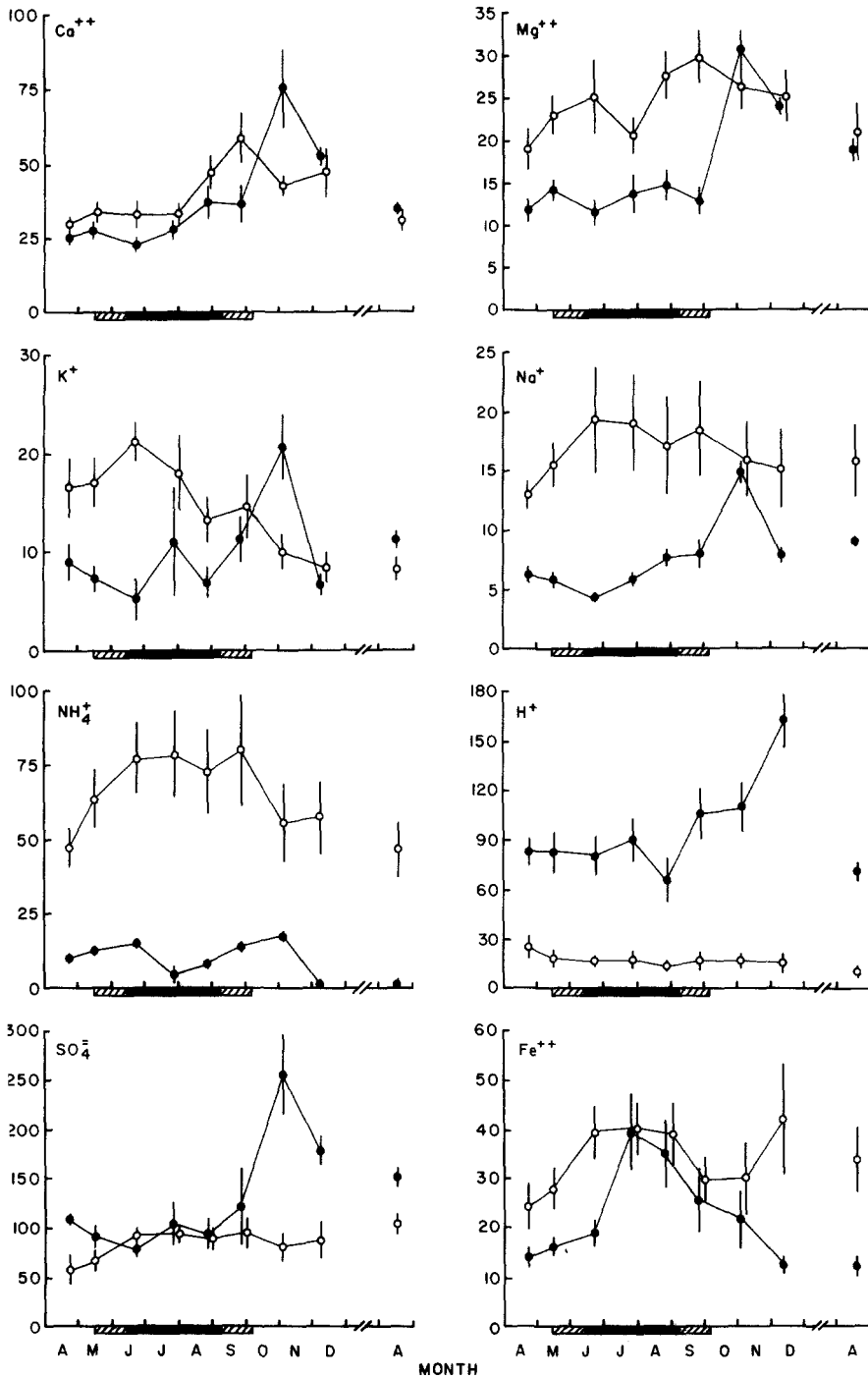


Figure 4. Seasonal patterns in ionic concentrations ($\mu\text{eq} \cdot \text{L}^{-1}$) of surface (●—●) and subsurface (○—○) water. Values are mean \pm one standard error, averaged over the four communities. Below the ordinate axis, the solid and hatched areas represent the portion of 1980 when minimum daily temperatures exceeded 0°C and -2.2°C , respectively.

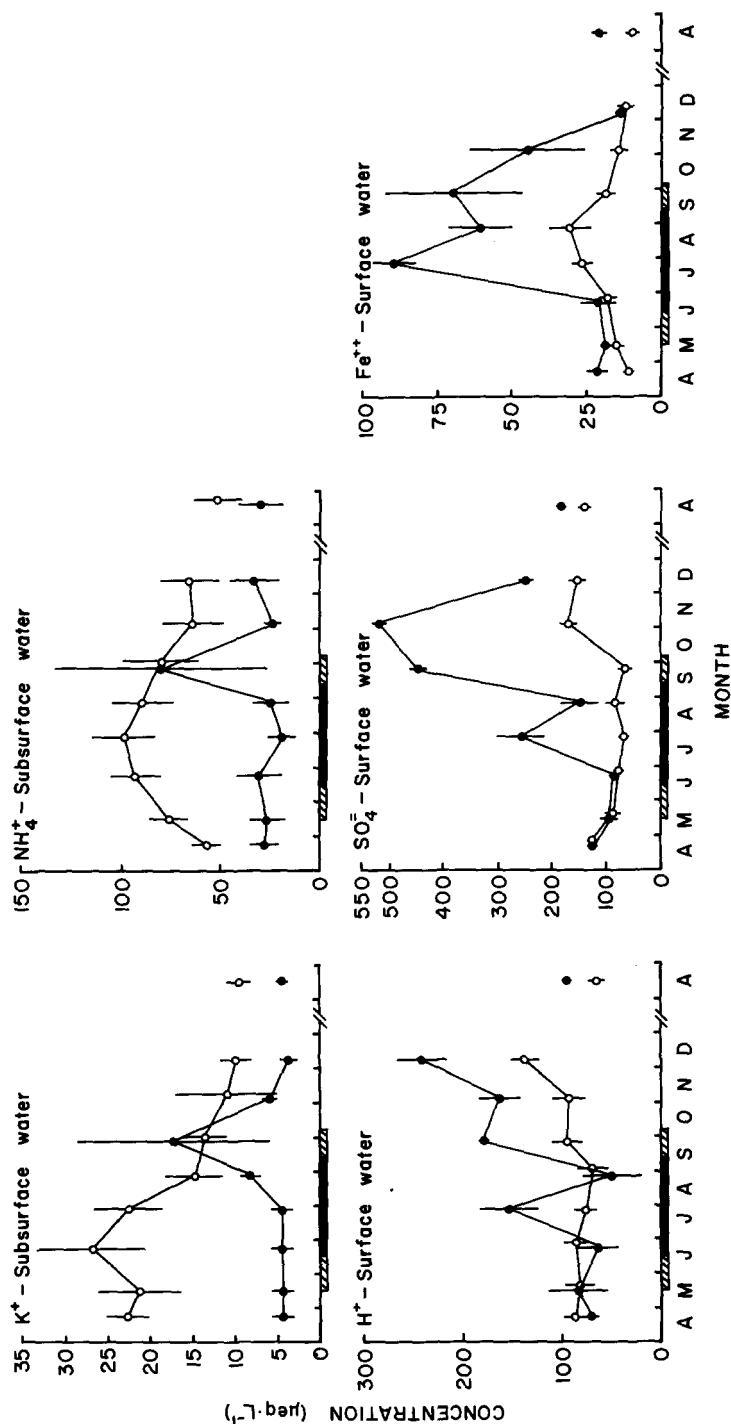


Figure 5. Differences between the inorganic substrate in the *Polytrichum-C. canescens* community (○—○) and the organic peats in the other three communities (●—●) regarding the patterns of seasonal behavior of K^+ and NH_4^+ in subsurface water and of H^+ , SO_4^{2-} , and Fe^{++} in surface water. Values are means \pm one standard error. Below the ordinate axis, the solid and hatched areas represent the portion of 1980 when minimum daily temperatures exceeded 0°C and -2.2°C , respectively.

communities (Figure 5). The November peaks in ionic concentrations were probably the result of leaching from the aboveground vegetation killed by autumn frost. Compared to surface water, concentrations of Ca^{2+} , Mg^{2+} , Na^+ , and SO_4^{2-} in subsurface water were relatively constant over the sampling period (Figure 4).

Surface water NH_4^+ concentrations declined from mid-June—mid-July, a period of maximum productivity at Big Run Bog (unpublished data). Rates of production declined after late July, thus nitrogen demand diminished and surface water NH_4^+ concentrations increased (cf. Klopatek 1978). Peak surface water NH_4^+ concentration was concurrent with the autumn Ca^{2+} , Mg^{2+} , K^+ , and Na^+ peaks, and some of that NH_4^+ may also have been derived from leaching of aboveground plant tissues. The low surface water NH_4^+ concentrations during winter are related to low temperature inhibition of N mineralization in surface peat (Kaila et al., 1953; Lang and McDonald, 1982).

In the *Polytrichum*-shrub and the two *Sphagnum*-dominated communities, subsurface K^+ concentrations generally declined through the growing season (Figure 5), possibly reflecting uptake by actively growing vegetation. Slightly higher subsurface NH_4^+ concentrations during the growing season (Figure 5), may be related to increased NH_4^+ exudation by growing roots. In contrast, in the *Polytrichum*-*C. canescens* community, subsurface K^+ and NH_4^+ concentrations were fairly constant from April—August but showed distinct peaks in late September. September was the driest month of the study period, exhibiting a net potential water deficit of 2.3 cm (Table 1). Field observations indicated that the relatively inorganic substrate in the *Polytrichum*-*C. canescens* community was more susceptible to long, dry periods than the organic soils of the other three communities, responding with more pronounced drops in water table level. The peaks in subsurface K^+ and NH_4^+ concentrations in the *Polytrichum*-*C. canescens* community associated with dry months probably resulted from an increase in K and N mineralization in soil layers made aerobic by marked drops in water table level.

Surface water concentrations of H^+ , SO_4^{2-} and to a lesser extent Fe^{2+} were somewhat more variable than subsurface water concentrations (Figure 4). However, much of the seasonal variation in surface water was contributed by patterns in the *Polytrichum*-*C. canescens* community that differed from patterns in the other three communities. In the *Polytrichum*-*C. canescens* community, sharp increases in surface H^+ , SO_4^{2-} , Fe^{2+} were observed in late July and late September (Figure 5), the two driest months of the study period. These peaks may have resulted from the oxidation of reduced sulfur compounds during periods of low water table levels (cf. Odelein et al., 1975; Rippon et al., 1980; Braekke, 1981).

Nitrate and Cl^- are not plotted in either Figure 4 or Figure 5. Nitrate concentrations in surface and subsurface water and Cl^- in subsurface water exhibited relatively little seasonal variation. Cl^- concentrations in surface

water were inversely related to evapotranspiration, reflecting seasonal dilution and concentration.

Correlations among ions in solution. In addition to evaluating spatial and temporal patterns in water chemistry at Big Run Bog, relationships between dissolved ions were examined (Table 7). A series of significant correlations among ions in Big Run Bog surface water appears to reflect the influence of minerotrophic inputs to the wetland. Soil water in the upland regions of the Big Run watershed has much higher concentrations of H^+ , Ca^{2+} , Mg^{2+} , K^+ , Fe^{2+} , and SO_4^{2-} than either precipitation or wetland surface water (Wieder 1982). Of the 15 possible pairwise correlations among these six ions in Big Run Bog surface water, nine are significant and indicate a positive association. In contrast, in subsurface water which has a higher residence time and is less influenced by minerotrophic inputs of water, only 5 of the 15 possible correlations are significant.

Rising and falling water table levels within Big Run Bog create conditions that alternately favor sulfate reduction and sulfide oxidation in the zone of water table fluctuation (cf. Odelein et al., 1975; Rippon et al., 1980; Braekke, 1981). Significantly positive correlations between H^+ , Fe^{2+} , and SO_4^{2-} in surface water, and to a lesser extent subsurface water (Table 7), at Big Run Bog may reflect the reduction and oxidation of sulfur compounds.

In both surface and subsurface waters of Big Run Bog, Ca^{2+} and Mg^{2+} , the divalent base cations involved in exchange are significantly positively correlated, as are K^+ and Na^+ , the monovalent base cations involved in exchange. Although Na^+ and Cl^- are significantly positively correlated in Big Run Bog surface water, the equivalent Na^+/Cl^- ratio averages only 0.33. The Na^+/Cl^- ratio in precipitation (calculated from annual volume weighted Na^+ and Cl^- concentrations in wetfall) at nearby Parsons WV is 0.72 (NADP, 1981). The relatively low Na^+/Cl^- ratio in Big Run Bog surface water suggests that processes within the wetland act to remove Na^+ from solution and/or retain Cl^- in solution. Numerous other significant correlations occur in Table 7, but their interpretation in terms of biogeochemical processes within Big Run Bog remains obscure.

Discussion

The physical properties of the organic peats in the *Polytrichum*-shrub and the two *Sphagnum*-dominated communities (Table 2) were generally similar to those reported for northern peatlands in both Europe (e.g., Mornsjo, 1968; Sonesson, 1970; Damman, 1978; Waughman, 1980; Braekke, 1981), and North America (e.g., Boelter and Blake, 1964; Boelter, 1968; Korpijaakko and Radforth, 1972). For example, northern Minnesota peats have bulk densities of $0.06\text{--}0.29\text{ g}\cdot\text{cm}^{-3}$, organic matter concentrations of 88–94%, and volumetric water contents of 80–92% (Farnham and Grubich, 1970). In

contrast to the northern peatlands where these physical properties of peat typically remain relatively constant throughout the top meter or more, at Big Run Bog bulk density increased and organic matter concentration declined within the top 40 cm of organic peat in the *Polytrichum*-shrub and the two *Sphagnum*-dominated communities (Table 2). Generally, more decomposed peat has a higher bulk density and a lower organic matter concentration than less decomposed peat (Boelter, 1968). The observed depth patterns at Big Run Bog are consistent with the concept of relatively higher decomposition in the lower latitude peatlands (Damman, 1979). Also, since bryophyte production at Big Run Bog is higher than in the northern peatlands (Wieder and Lang, 1983) and the deepest basal peat was radiocarbon dated to $13\,080 \pm 420$ yr B.P. (Wieder, 1982), the thinness of the peat deposit is not attributable to low production or young age of the peatland. Again, relatively high decomposition is implicated.

The chemistry of Big Run Bog peat (Tables 3–5) is generally similar to the chemistry of other bog and/or poor fen peats (e.g., Gore and Allen, 1956; Kivekas and Kaila, 1957; Chapman, 1964; Mornsjo, 1968; Sonesson, 1970; Damman, 1978; Braekke, 1981). However, Big Run Bog peat did have relatively low concentrations of Na and Pb and relatively high concentrations of Fe and Al. Low Na concentrations result from the lack of a maritime influence on the precipitation falling on Big Run Bog (Weedfall and Dickerson, 1965). Similarly, low Pb concentrations result from low anthropogenic inputs via atmospheric deposition because of the remoteness and elevation of the wetland (cf. Livett et al., 1979). The upland soils of the Big Run watershed are rich in Fe and Al (Losche and Beverage, 1967). The high Fe and Al concentrations that were especially evident in the *Polytrichum*-dominated communities reflect the chronic minerotrophic drainage coupled with the episodic deposition of alluvially transported mineral soil in the organic peats.

The influence of organic matter concentration of the substrate on exchange properties (Figure 3) has also been examined by considering sites along a lake-fen-bog gradient (Gorham, 1967). This lake-fen-bog gradient represented not only a gradient of increasing organic matter concentration, but also a gradient of decreasing soil pH ranging from about 6.5 in lake sediments with low organic matter concentration (< 10%) to a low of about 3.2 in bog peats with high organic matter concentration (> 95%). As with Big Run Bog peat, cation exchange capacity increased with increasing organic matter concentration along the lake-fen-bog gradient. However, in contrast to Big Run Bog peat, at organic matter concentrations less than 80% (and soil pH values greater than 5.0) the exchange sites were dominated by base cations. At higher organic matter concentrations, i.e. the transition from fens to bogs, soil pH dropped sharply and there was an accompanying shift from base cation dominance to H^+ dominance of exchange sites (Gorham, 1967). At Big Run Bog, the consistently low pH of surface and subsurface waters

(Table 6) maintained H^+ dominance of the exchange sites, i.e. low base saturation, over the entire range of organic matter concentrations (Figure 3).

Both peat and water chemical parameters have been used in wetland classification, and particularly as a means of distinguishing bogs from fens (see Gorham, 1967; Moore and Bellamy, 1974; Horton et al., 1979; Waughman, 1980). Generally, rich fen peats have higher Ca and Mg concentrations and lower N concentrations than poor fen or bog peats. In general, bogs have surface water Ca^{2+} concentrations less than $1\text{ mg}\cdot\text{L}^{-1}$ ($50\text{ }\mu\text{eq}\cdot\text{L}^{-1}$) and H^+ and SO_4^{2-} are the dominant cation and anion, respectively (see Moore and Bellamy, 1974). In contrast, fens usually have higher Ca^{2+} concentrations in surface waters and the dominant cation and anion are Ca^{2+} and HCO_3^- , respectively. Based on total Ca, Mg, or N (Table 3), exchangeable Ca, exchangeable Mg, cation exchange capacity, or base saturation (Table 4), or on surface water chemistry (Table 6), Big Run Bog is chemically more similar to ombrotrophic bogs than to fens, despite its clear physiographic classification as a minerotrophic fen.

While Big Run Bog is chemically similar to more northern peatlands, all that I have measured are elemental concentrations in peat and water. These elemental concentration data can be used to calculate pool sizes, but by themselves provide little insight into flux rates between pools. Some evidence has suggested that organic matter turnover at Big Run Bog is more rapid than in the more northern peatlands, but how this relatively rapid turnover might affect patterns and rates of elemental cycling remains to be evaluated. Additional information, derived from either modeling approaches (e.g., Wildi, 1978) or field investigations, is needed to quantitatively characterize elemental cycles and to make comparisons among peatlands.

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